
聲明

本檔案之內容僅供下載人自學或推廣化學教育之非營利目的使用。並請於使用時註明出處。

[如本頁取材自○○○教授演講內容]。

2013 綠色/永續合成化學工作坊
暨南國際大學

十一月二十三日 16:40-17:30

綠色製程實驗方法與實例

減少化學反應加熱或冷卻的用能也是永續重要課程之一。本課程將介紹以微波、超音波、光、電之應用使反應更有效率來達到省能之目的。節能是永續重要課題之一，跳脫傳統加熱、冷卻的過程來促使反應發生，有哪些值得注意的實驗方法？(微波、超音波、流動式反應器...等)

甘魯生

中央研究院化學研究所

Global population: > 7,000,000,000 2050 may reach 9 billion.

Ecological footprint: a measure of the amount of biologically productive space needed on average to support a human being.

Our growing ecological foot print significantly exceeds the carrying capacity of the earth.

Thus we are drifting toward a catastrophe beyond comparison. We shall require a substantially new manner of thinking if mankind is to survive. -Albert Einstein

Green chemistry: A tool to foster sustainable development.

Design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

Minimize waste, energy use, and resource use.



The 12 Principles of Green Chemistry

Provides a framework for learning about green chemistry and designing or improving materials, products, processes and systems.

1. Prevent waste
2. Atom Economy
3. Less Hazardous Synthesis
4. Design Benign Chemicals
5. Benign Solvents & Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis (vs. Stoichiometric)
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Inherently Benign Chemistry for Accident Prevention

第六條: 為用能效率而設計: 化學過程中能的需求應該被認定為對環境和經濟的衝擊縮為最小. 如果可能, 合成方法應該在常溫和常壓下進行.

耗能指數:

5 (反應溫度低於 -20°C 或高於 280°C)

3 (反應溫度 $0 - -20^{\circ}\text{C}$ 或 $160 - 280^{\circ}\text{C}$)

2 (反應溫度 $0 - 10^{\circ}\text{C}$ 或 $90 - 160^{\circ}\text{C}$)

1 (反應溫度 $10 - 20^{\circ}\text{C}$ 或 $30 - 90^{\circ}\text{C}$)

0 (反應溫度 $20 - 30^{\circ}\text{C}$)

問題是如能將每個化學反應耗能指數儘量縮小(最好是0). 因為我們目前用(尤其是很方便)能皆來自化石燃料. 開源既然不易, 所以要從節流上多下功夫. 節流可分二部份, 首先是化學反應的本身. 也就是說發明或設計新的節能反應來替換掉舊的耗能反應.

Optimizing reaction conditions, minimizing energy usage.

Alternative organic synthetic methods



Microwave



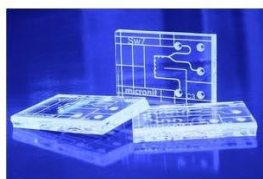
Ultrasound



Reactants



light



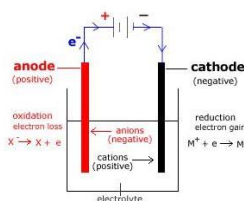
Microflow



Product



mechanochemistry Electrochemistry



Microwave

polar or ionic materials

Microflow

solution

Sonochemistry

solution

Mechanochemistry

solid

Electrochemistry

conductive media

Photochemistry

chromophore

S. K. Sharma, A. Chaudhary, and R. V. Singh, "GRAY CHEMISTRY VERSES GREEN CHEMISTRY: CHALLENGES AND OPPORTUNITIES, RASĀYAN JOURNAL OF CHEMISTRY (RJC), (2008), 1, 68-92.

Microwave heating method

History:

1947 Percy Spencer, heating food

1962 David Compson, lyophilization Microwave heating: in freeze-drying, electronic ovens, and other applications

1973 A.N. Ponomarev and V.A. Tarasenko "Application of Microwave frequency Irradiations for Stimulation of Chemical Processes" (in Russian).

???? Ardalyon N. Ponorev worked in the group of V.L. Tolroze, and they studied different physical methods of stimulations of chemical reactions. In their experiments with microwave irradiation they studied rubber vulcanization and polymerization reactions of methyl methacrylate and styrene in benzene in glass vessels or directly in the space of the metal microwave resonator.

Application of Microwaves in Chemistry <http://www.microwavetec.com/mwchem.php>

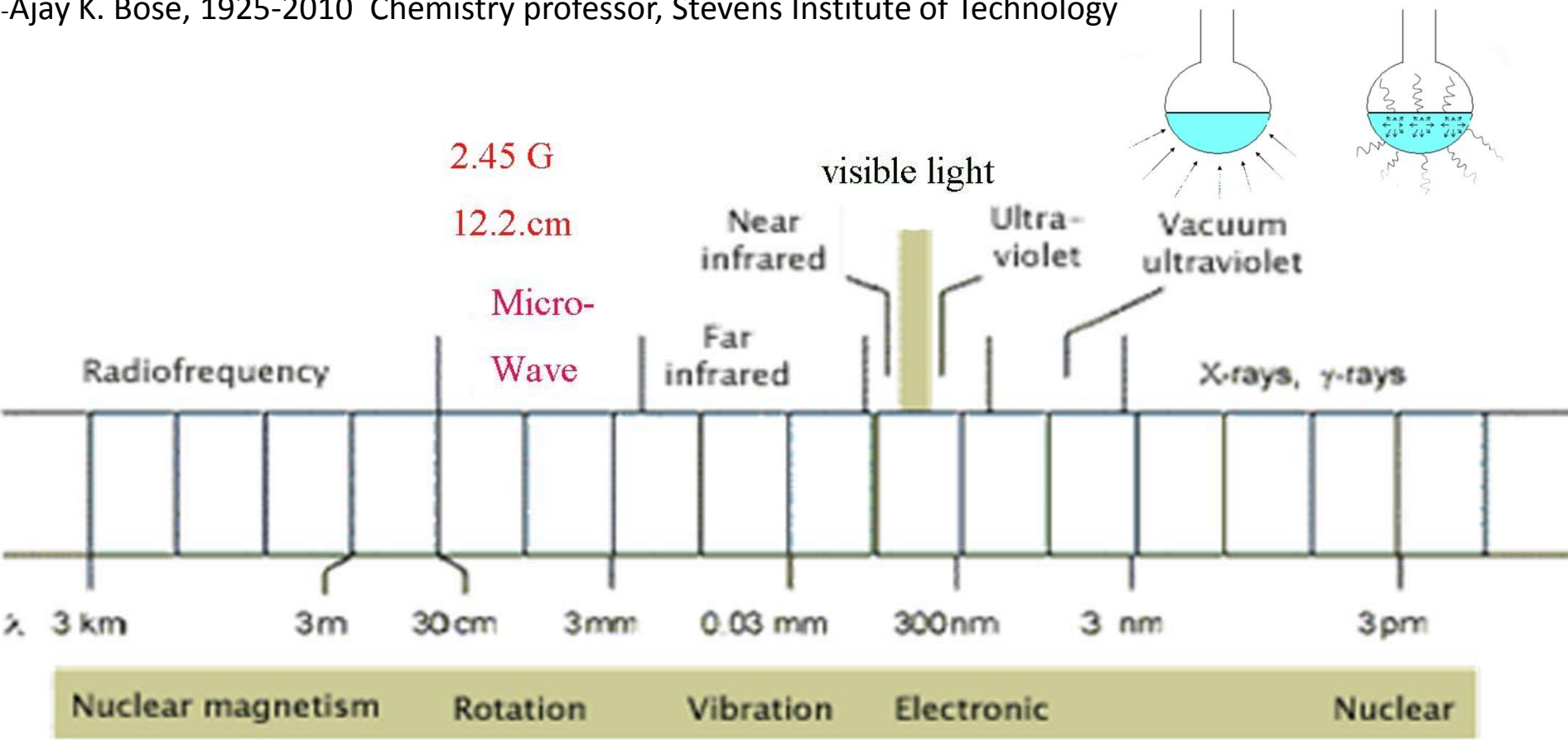
1986 R. Gedye and R.J. Giguere (1986)

Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L. & Rousell, J., The use of microwave ovens for rapid organic synthesis, *Tetrahedron Letters*, (1986) **27**, 279-282.)

Giguere, R. J.; Bray, T. L.; Duncan, S. M. & Majetich, G., Application of Commercial Microwave Ovens to Organic Synthesis. *Tetrahedron Letters*, (1986) **27**, 4945-4948.

“The microwave oven is the Bunsen burner of the 21st century.”

-Ajay K. Bose, 1925-2010 Chemistry professor, Stevens Institute of Technology



Theory:

When irradiated at microwave frequencies, electromagnetic waves pass through the dipoles or ions of the sample and cause the molecules to oscillate. In this process, energy is lost in the form of heat through molecular friction and dielectric loss.

Loss Angle, δ

- Choosing a good solvent for reaction under MW condition
- The capabilities to absorb the MW energy and to convert the absorbed energy into heat must also be taken into consideration. These factors may be considered using the loss angle, δ , which is expressed in the form of tangent

$$\tan \delta = \epsilon'' / \epsilon'$$

ϵ'' = The loss factor, quantifies the efficiency with which the absorbed energy is converted into heat

ϵ' = dielectric constant or relative permittivity, the ability of the material to store electrical potential energy under the influence of an electric field

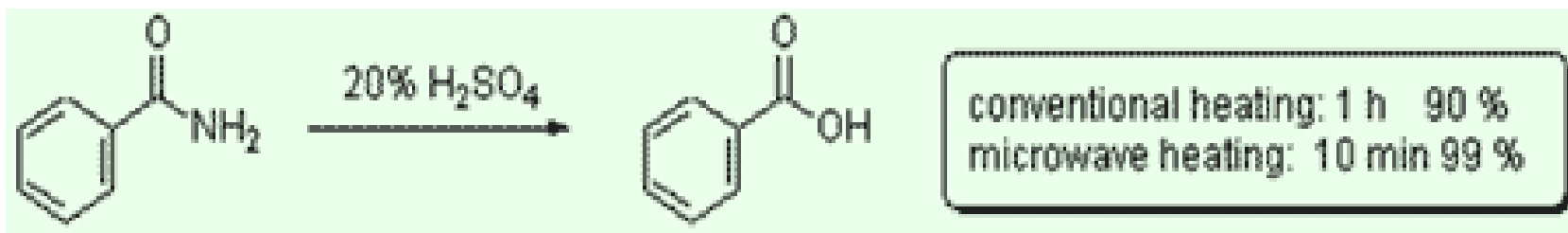
- Higher the $\tan \delta$ value, the better is the solvent at absorbing MW and generating heat

Loss Angle Tangent Data for Common Pure Solvents at Room Temperature

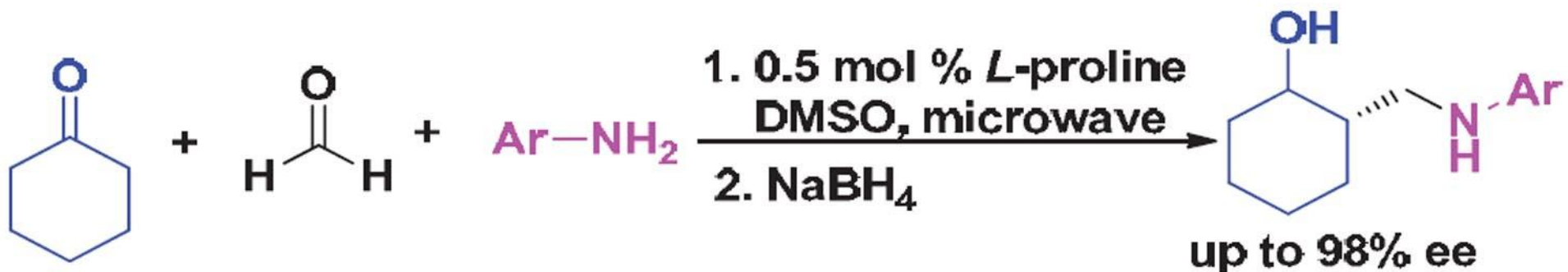
solvent	ϵ'	$\tan \delta$ (2.45 GHz)
dichloromethane	9.1	0.042
tetrahydrofuran	7.6	0.047
acetone	21	0.054
ethyl acetate	6.0	0.059
acetonitrile	38	0.062
chloroform	4.8	0.091
water	80	0.12
dimethylformamide	37	0.16
acetic acid	6.1	0.17
methanol	33	0.66
dimethyl sulfoxide	47	0.82
ethanol	24	0.94
ethylene glycol	38	1.17

Advantages:

- Control of temperature and pressure
- Perform reactions impossible by conventional heating
- Dramatic reduction in reaction time (from days and hours to minutes).



- Increase yields



Mannich reactions: Synthesis of β -amino ketones via three-component condensation

- Reduction of side reactions
- Improve reproducibility

The publications are increased exponentially.

Organic synthesis:

Reviews: (a) C. O. Kappe and D. Dallinger, *Mol. Diversity*, 2009, **13**, 71; (b) S. Caddick and R. Fitzmaurice, *Tetrahedron*, 2009, **65**, 3325. (c) J. D. Moseley and C. O. Kappe, *Green Chem.*, 2011, **13**, 794-806.

Books: (a) *Microwaves in Organic Synthesis*, ed. A. Loupy, Wiley-VCH, Weinheim, 2nd edn, 2006; (b) *Microwave Methods in Organic Synthesis*, ed. M. Larhed and K. Olofsson, Springer, Berlin, 2006; (c) C. O. Kappe, A. Stadler, *Microwaves in Organic and Medicinal Chemistry*, Wiley-VCH, Weinheim, 2005; (d) *Microwave Heating as a Tool for Sustainable Chemistry*, ed. N. E. Leadbeater, CRC Press, Boca Raton, 2011.

Peptide synthesis:

(a) J. M. Collins and N. E. Leadbeater, *Org. Biomol. Chem.*, 2007, **5**, 1141; (b) F. Rizzolo, G. Sabatino, M. Chelli, P. Rovero and A. M. Papini, *Int. J. Pept. Res. Ther.*, 2007, **13**, 203; (c) S. Coantic, G. Subra and J. Martinez, *Int. J. Pept. Res. Ther.*, 2008, **14**, 143; (d) B. Bacsa, S. Bosze and C. O. Kappe, *J. Org. Chem.*, 2010, **75**, 2103; (e) C. U. Hjorringgaard, J. M. Pedersen, T. Vosegaard, N. C. Nielsen and T. Skrydsturp, *J. Org. Chem.*, 2009, **74**, 1329.

Polymer chemistry:

(a) D. Bogdal and A. Prociak, *Microwave-Enhanced Polymer Chemistry and Technology*, Blackwell Publishing, Oxford, 2007; (b) R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2007, **28**, 368; (c) M. Bardts, N. Gonsior and H. Ritter, *Macromol. Chem. Phys.*, 2008, **209**, 25; (d) C. Holtze, M. Antonietti and K. Tauer, *Macromolecules*, 2006, **39**, 5720.

Material sciences:

(a) S. Barlow and S. R. Marder, *Adv. Funct. Mater.*, 2003, **13**, 517; (b) J. Perelaer, B.-J. de Gans and U. S. Schubert, *Adv. Mater.*, 2006, **18**, 2101; (c) W. C. Conner and G. A. Tompsett, *J. Phys. Chem. B*, 2008, **112**, 2110; (d) N. L. Campbell, R. Clowes, L. K. Ritchie and A. I. Cooper, *Chem. Mater.*, 2009, **21**, 204; (e) O. Yoshikawa, T. Sonobe, T. Sagawa and S. Yoshikawa, *Appl. Phys. Lett.*, 2009, **94**, 083301; (f) M. Gharibeh, G. A. Tompsett, K. S. Yngvesson and W. C. Conner, *J. Phys. Chem. B*, 2009, **113**, 8930.

Nanotechnology:

(a) M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa and T. Tsuji, Chem. Eur. J., 2005, **11**, 440; (b) V. Polshettiwar, M. N. Nadagouda and R. S. Varma, Chem. Commun., 2008, 6318; (c) M. D. Roy, A. A. Herzing, A. H. De, Paoli Lacerda and M. L. Becker, Chem. Commun., 2008, 2106; (d) A. L. Washington and G. F. Strouse, J. Am. Chem. Soc., 2008, **130**, 8916; (e) J. G. Duque, M. Pasquali and H. K. Schmidt, J. Am. Chem. Soc., 2008, **130**, 15340; (f) I. Bilecka and M. Niederberger, Nanoscale, 2010, **2**, 1358.

Biochemical processes:

(a) J. R. Lill, Microwave Assisted Proteomics, RSC Publishing, Cambridge, 2009; (b) J. R. Lill, E. S. Ingle, P. S. Liu, V. Pham and W. N. Sandoval, Mass Spectrom. Rev., 2007, **26**, 657; (c) D. D. Young, J. Nichols, R. M. Kelly and A. Deiters, J. Am. Chem. Soc., 2008, **130**, 10048; (d) W. F. Edwards, D. D. Young and A. Deiters, Org. Biomol. Chem., 2009, **7**, 2506; (e) K. M. Rahman and D. E. Thurston, Chem. Commun., 2009, 2875.

Review: R. B. N. Baig and R. S. Varma Chem. Soc. Rev., “Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis”, 2012, **41**, 1559–1584.

Microwave instruments:

J. D. Moseley and E. K. Woodman, “Energy Efficiency of Microwave- and Conventionally Heated Reactors Compared at meso Scale for Organic Reactions”, Energy Fuels, 2009, **23**, 5438.

D. R. Godwin, S. J. Lawton, J. D. Moseley, M. J. Welham and N. P. Weston, “Energy Efficiency of Conventionally-Heated Pilot Plant Reactors Compared with Microwave Reactors”, Energy Fuels, 2010, **24**, 5446.

R. Morschhäuser, M. Krull, C. Kayser, C. Boberski, R. Bierbaum, P. A. Püschner, T. N. Glasnov and C. Oliver Kappe, “Microwave-assisted continuous flow synthesis on industrial scale”, Green Process Synth 1 (2012): 281–290

儀器公司

Anton Paar Microwave Oven

http://www.anton-paar.com/Microwave-Synthesis/59_Corporate_en?productgroup_id=99

CEM MARS (台灣有代理商)

http://www.kohan.com.tw/cem/mars_tubs.html

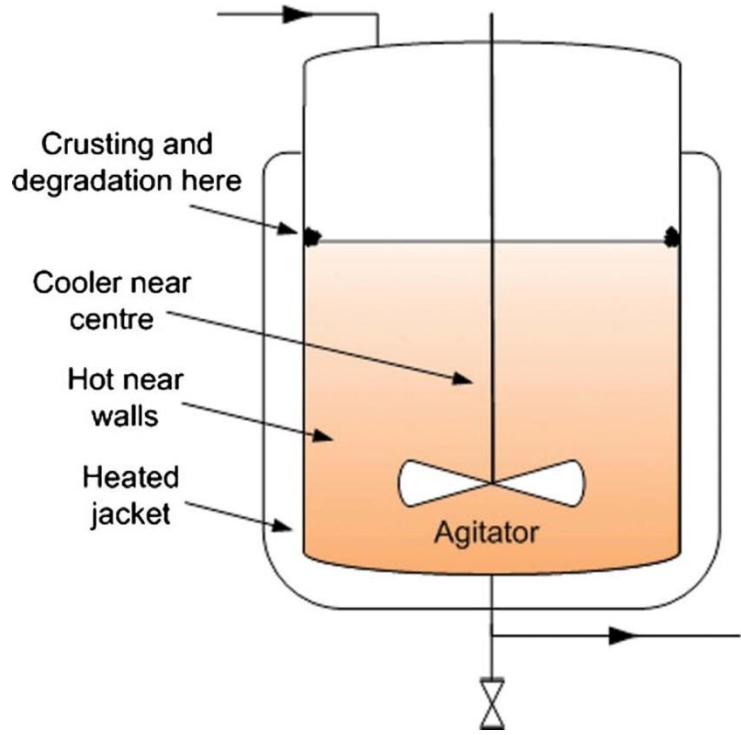
Sineo Microwave

www.sineomicrowave.com

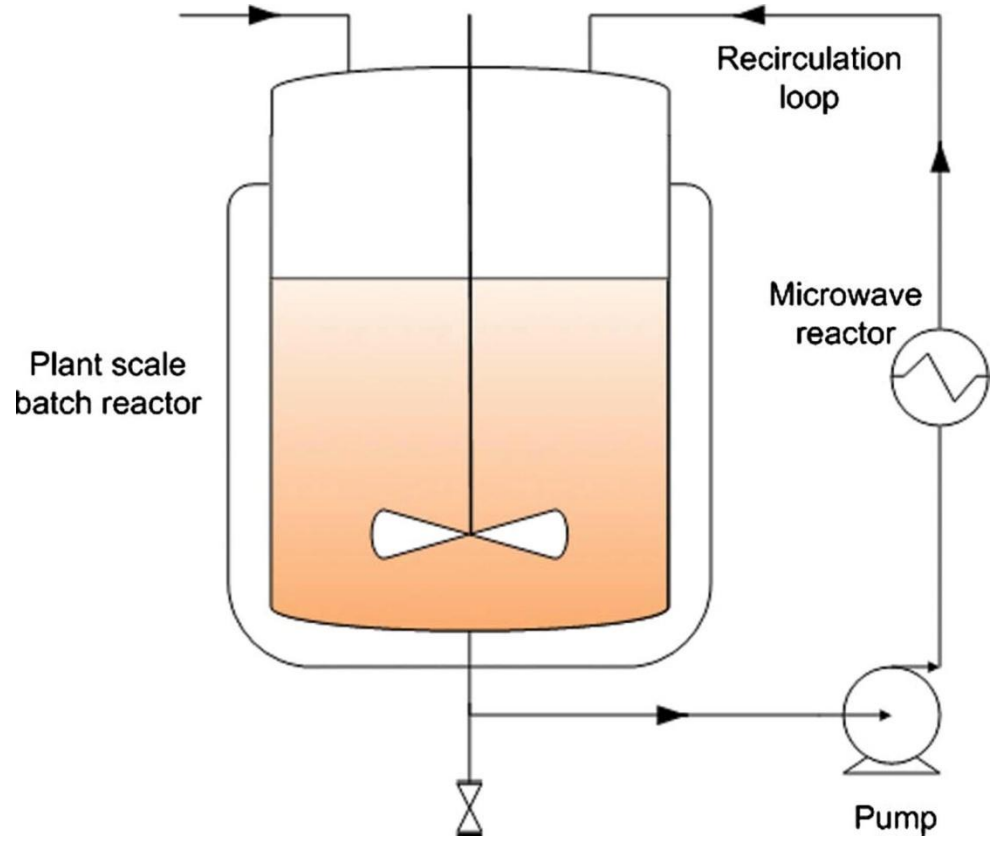
Challenges:

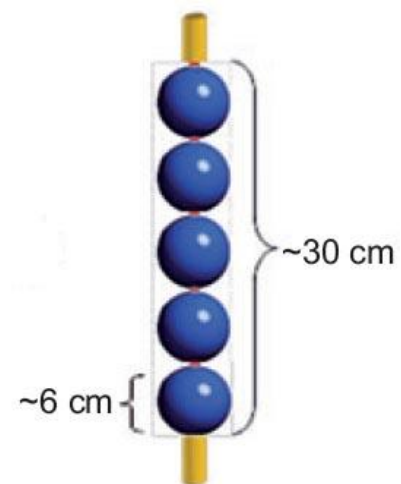
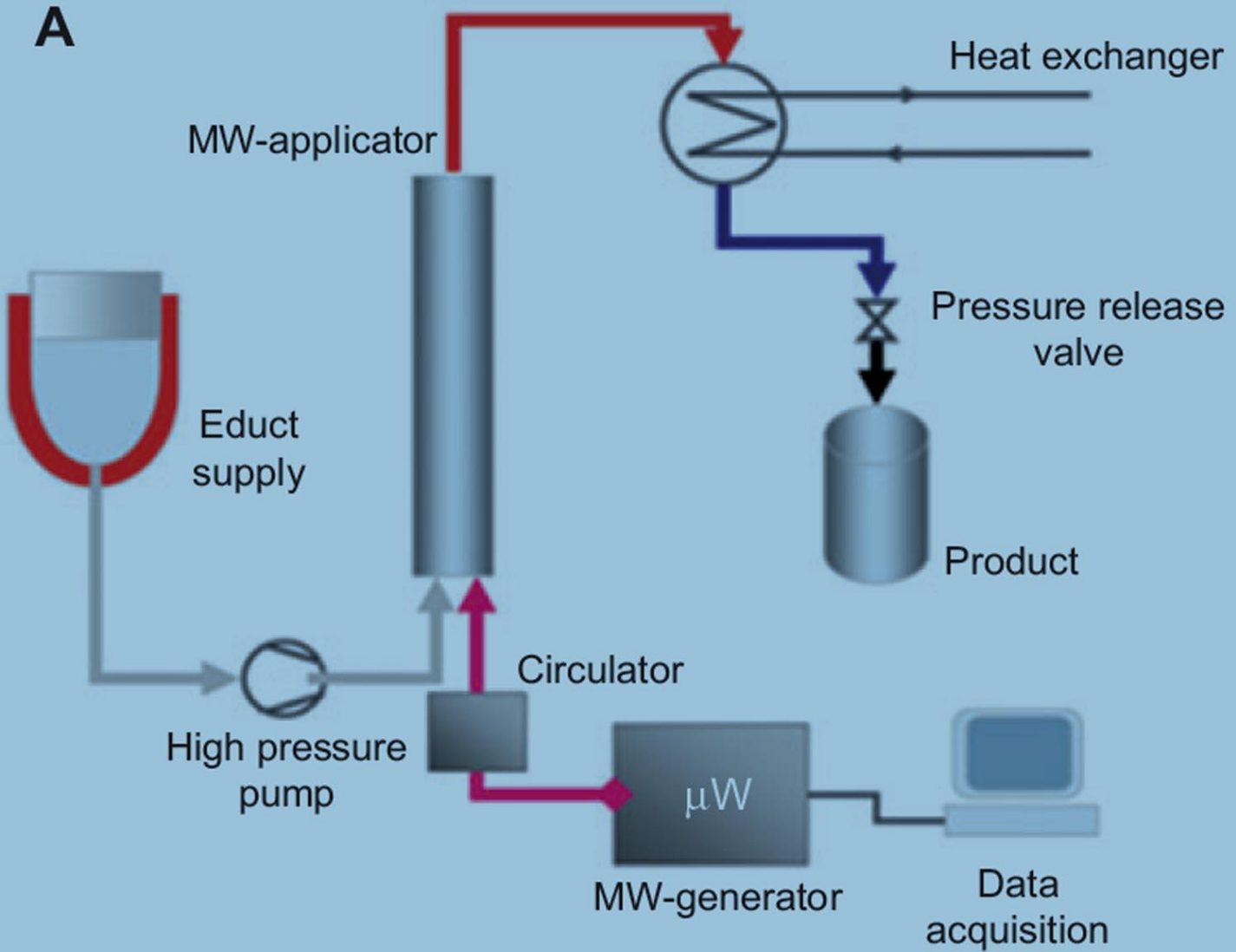
The scalability

Large reactor up to 50 L.



Continuous flow synthesis



A

Flash Chemistry (microflow reactor)

Definition: Micro Flow Reactors contain small internal channel in which chemicals will mix and chemical react under optimal conditions so that more of the desired reaction product can be generated.

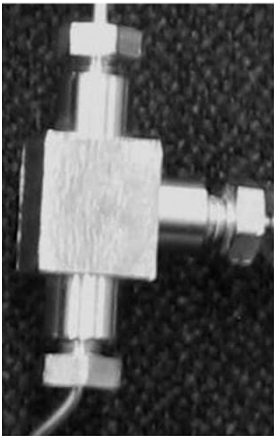
The volume/surface and size relationship



Size	1/100
Surface area	1/10000
Volume	1/1000000
Surface / Volume	100

high surface-to-volume ratio
residence time control
virtue of a short diffusion path

Microflow reactor



highly reactive species

microreactor



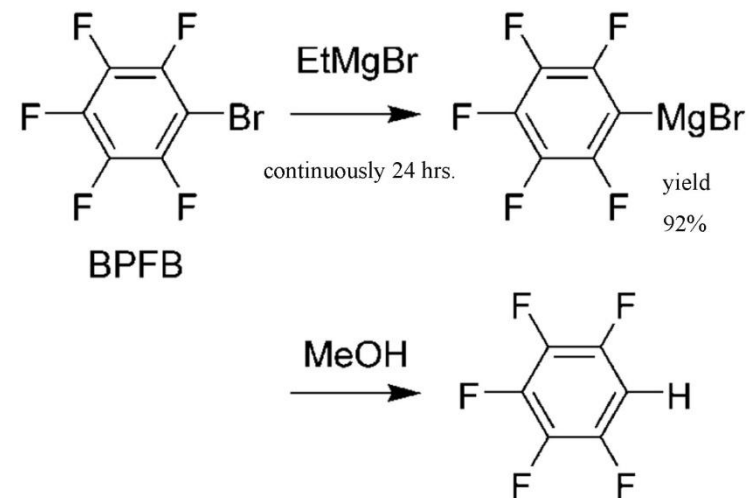
products

substrate

reaction time:
ms - s

Advantages:

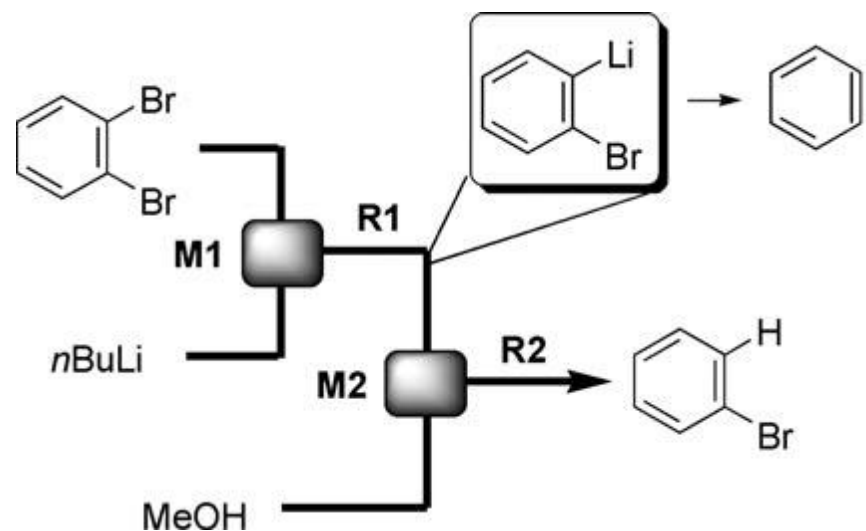
a) highly exothermic reactions that are difficult to control in conventional reactors,



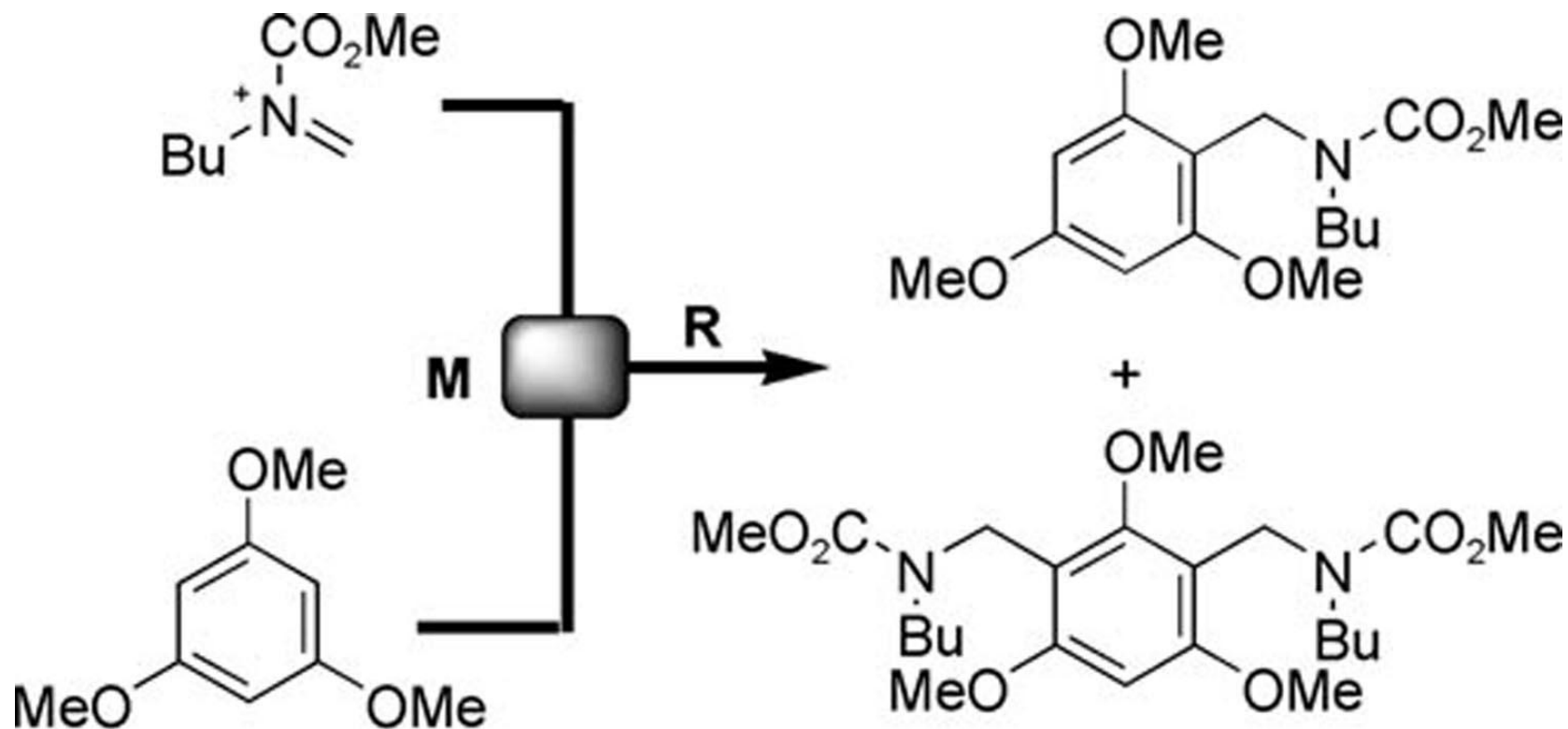
The halogen–magnesium exchange reaction of bromopentafluorobenzene (BPFBr) and EtMgBr reaction.

H. Wakami, J. Yoshida, *Org. Process Res. Dev.* 2005, **9**, 787–791.

b) reactions in which a reactive intermediate easily decomposes in conventional reactors,



c) reactions in which undesired byproducts are produced in the subsequent reactions in conventional reactors, and



	monoalkylation product	dialkylation product
microreactor	92%	4%
flask	37%	32%

Advantages

- 1) Little or no use of auxiliary substances: Flash chemistry avoids the use of auxiliary substances that slow down reactions to obtain better controllability.
- 2) Energy saving: Conventionally, cooling is often used to attain acceptable controllability of fast reactions. The use of microreactor enables reactions to be conducted at higher temperatures, minimizing the energy required for controlling these reactions.
- 3) High selectivity: Better controllability by virtue of the inherent properties of microreactors leads to a high selectivity of the products. Therefore, less waste is produced.
- 4) One-demand and on-site synthesis: Synthesis based on extremely fast reactions using microreactors enables on-demand and on-site synthesis. This leads to less energy for transportation.

ChemSusChem Vol 5, issue 2, pp. 232-439. Special issue on flow chemistry

<http://onlinelibrary.wiley.com/doi/10.1002/cssc.v5.2/issuetoc>

J. Yoshida, Y. Takahashi, and A. Nagaki, Chem. Commun. (2013) **49**, 9896-9904.

Scale-up

Increasing the volume of reactor

1. Convert batch chemistry to flow chemistry on μL -scale;
2. Scaling up the internal dimensions of the reactor to mL-scale;
3. Numbering out mL-scale reactors towards the capacity desired.

Increasing the number of reactors

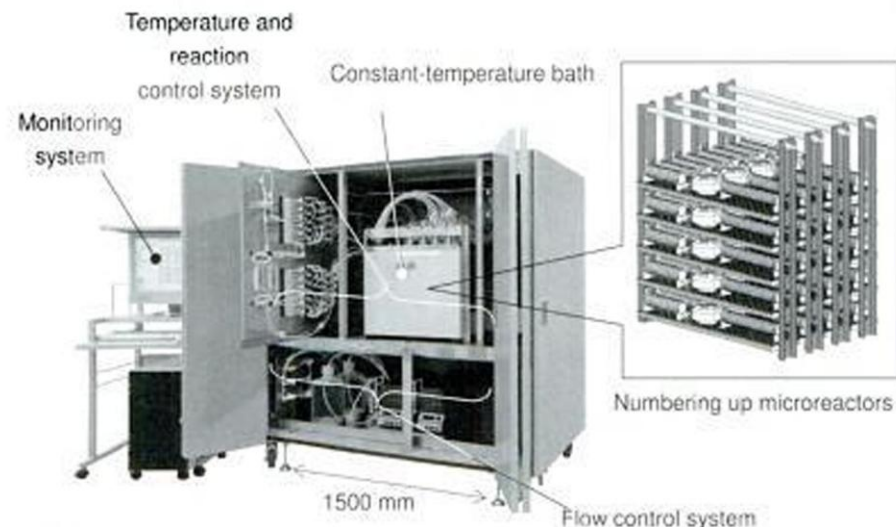
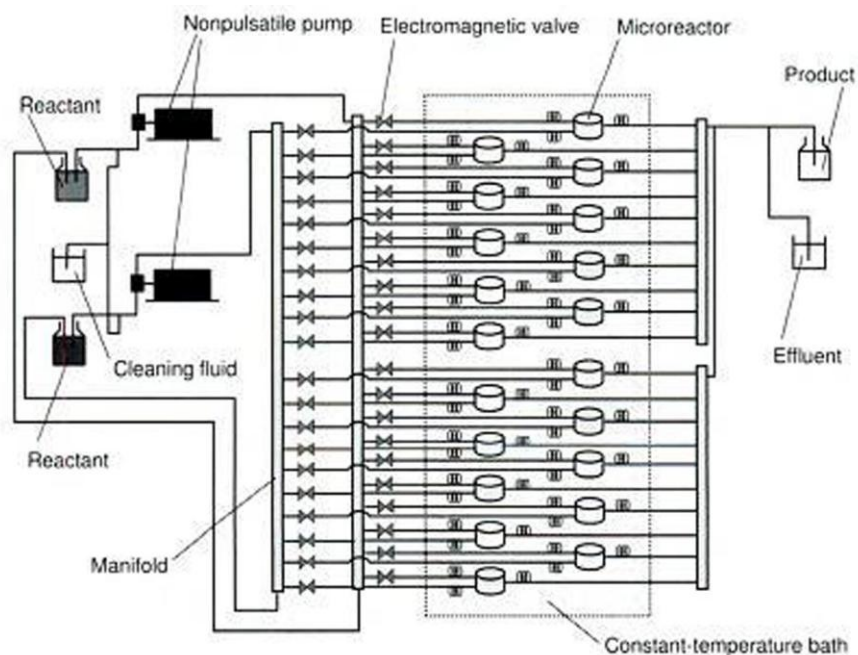


Figure 11.6 Internal structure of pilot plant.

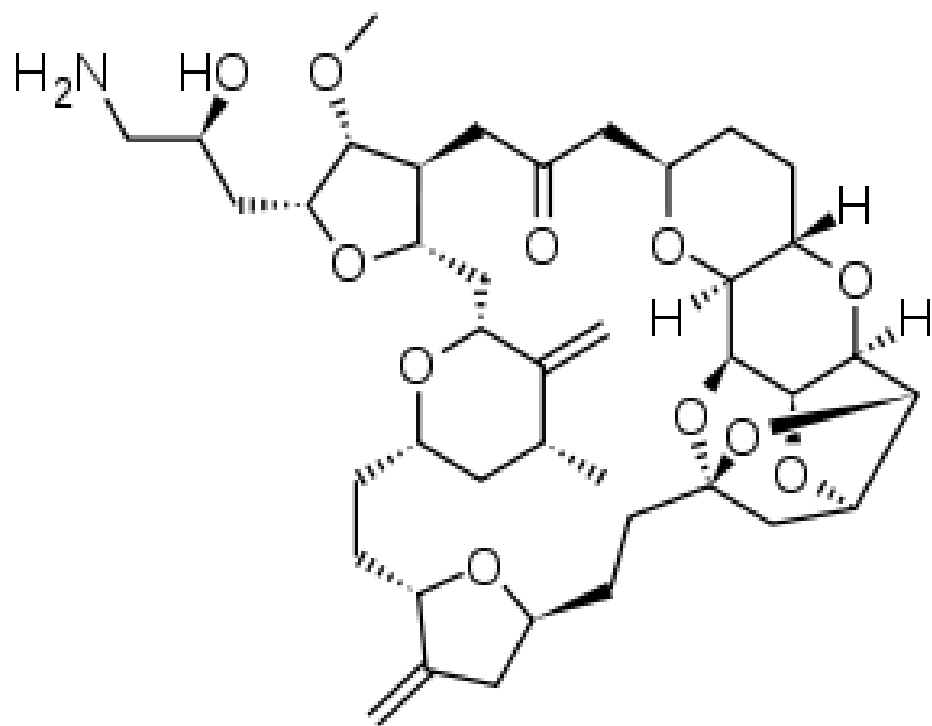
J. Yoshida, A. Nagaki, and T. Yamada, "Flash Chemistry: Fast Chemical Synthesis by Using Microreactors", Chem. Eur. J. 2008, **14**, 7450-7459.

Working continuously.

工業實例 eribulin mesylate (Halaven, Eisai) for the treatment of patients with metastatic breast cancer who have previously received at least two chemotherapeutic regimens for the treatment of metastatic disease

approved by the U.S. Food and Drug Administration on November 15, 2010

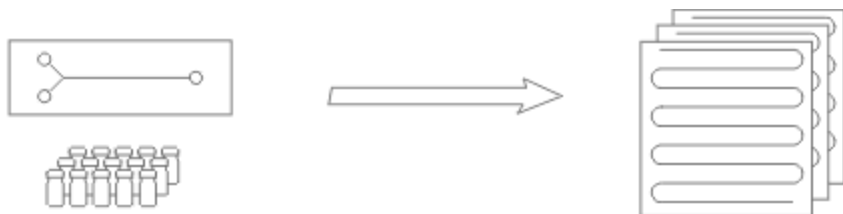
Health Canada on December 14, 2011



Kim DS, Dong CG, Kim JT, Guo H, Huang J, Tiseni PS, Kishi Y (November 2009). "New syntheses of E7389 C14-C35 and halichondrin C14-C38 building blocks: double-inversion approach". *J. Am. Chem. Soc.* **131** (43): 15636–41.

Industrial companies

Access2Flow with its members Flowid B.V., a spin-off company of the Eindhoven University of Technology,

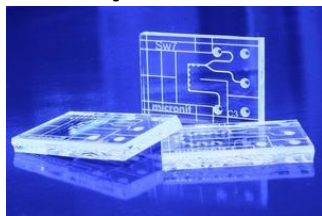


<http://www.access2flow.com/>

Microreactor
complete optimization

Scaled out
parallel manufacturing

FutureChemistry <http://www.futurechemistry.com/>, and **Micronit Microfluidics** has shown the fast scalability and applicability of microreactors in a case study for flow chemistry.



<http://syrris.com/flow-products/asia-flow-chemistry?gclid=CKeCjo-2w7MCFQFKpgodiRAALA>

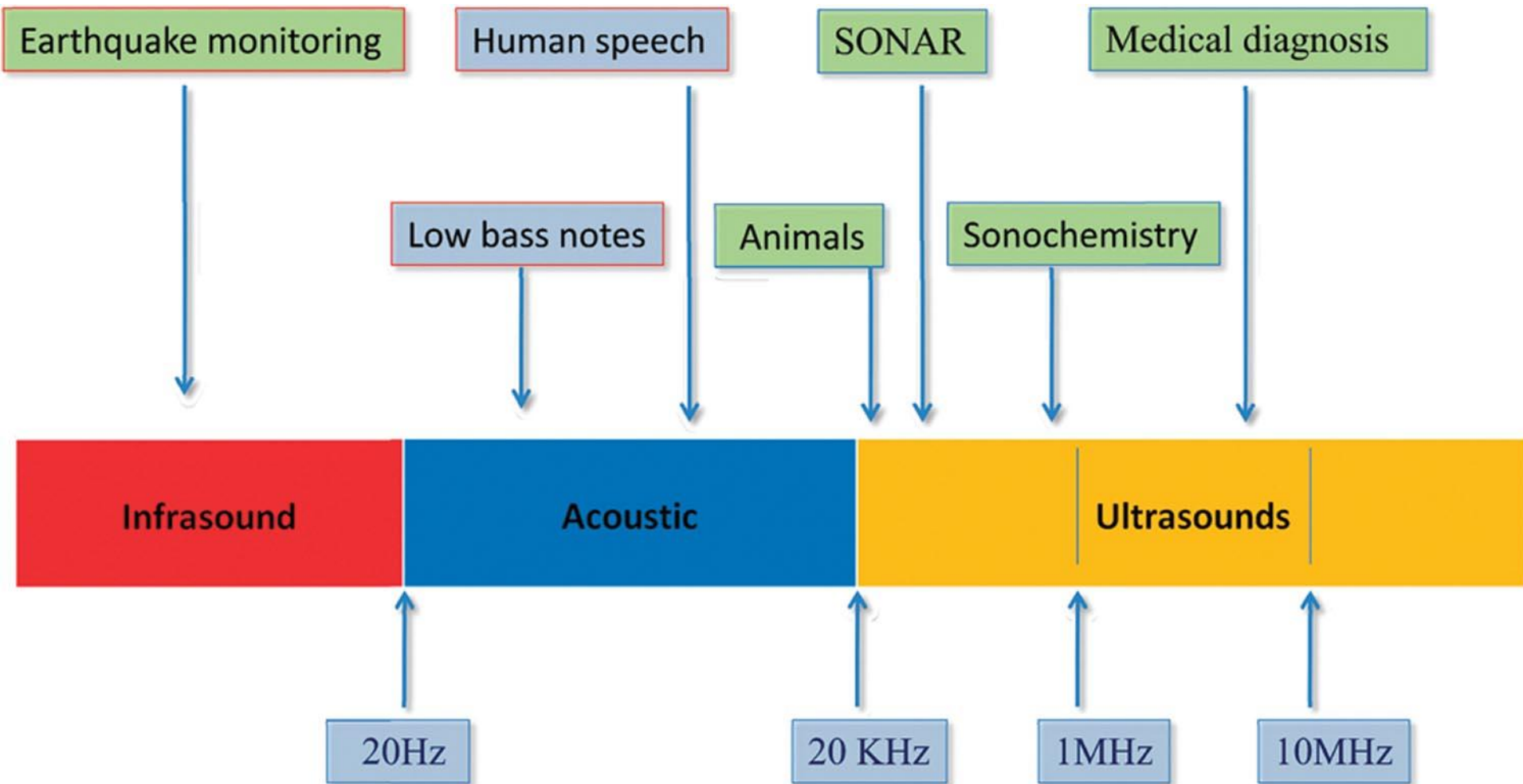
<http://www.micronit.com/assets/Downloads/Fast-Scale-Up-of-Microreactor-Technology.pdf>

J. Yoshida, H. Kim, and A. Nagaki, Green and Sustainable Chemical Synthesis Using Flow Microreactors, *ChemSusChem* (2011) **4**, 331–340. (DOI: 10.1002/cssc.201000271)

Jun-ichi Yoshida, “Flash Chemistry: Fast Organic Synthesis in Microsystems”

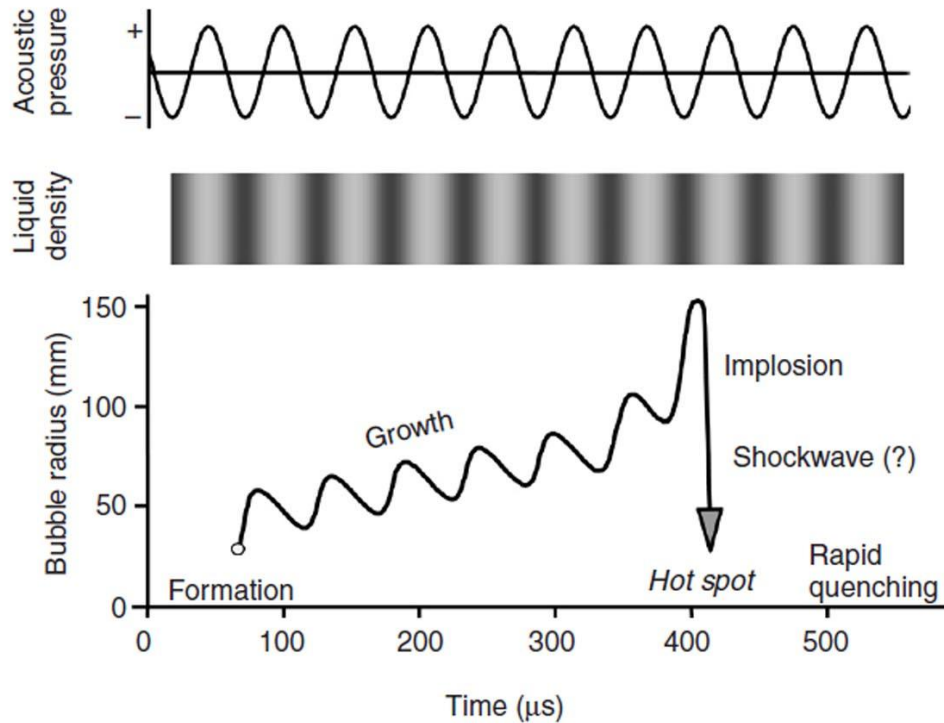
Stoma Care, Edited Jennie Burch, Blackwell Publishing

Sonochemistry



Range: 15 kHz to 1 GHz (10 to 10^{-4} cm).

Theory:



Transient acoustic cavitation: the origin of sonochemistry

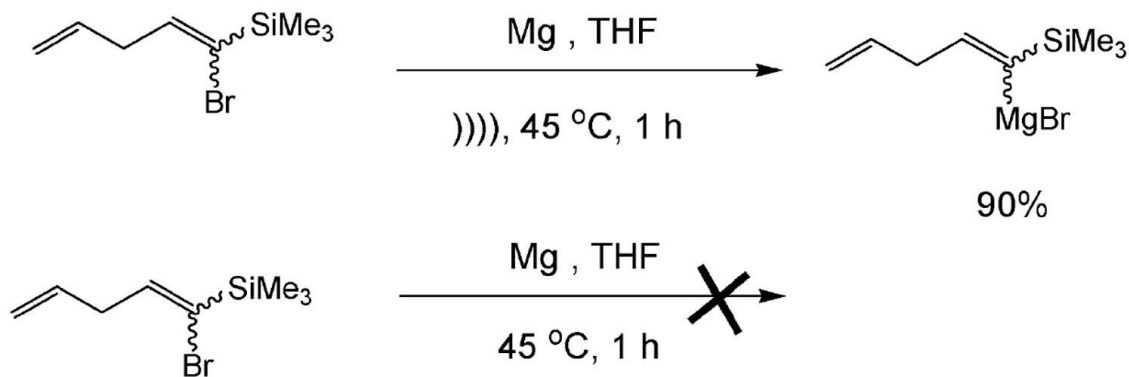
The origin of sonochemistry is acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquids irradiated with high-intensity sound. The collapse of bubbles caused by cavitation produces intense local heating and high pressures, with very short lifetimes (Rayleigh–Plesset equation). In clouds of cavitating bubbles, these hot-spots have equivalent temperatures of roughly 5,000 K, pressures of about 1,000 atm, and heating and cooling rates above 10^{10} Ks^{-1} . In single bubble cavitation, conditions may be even more extreme. Thus, cavitation can create extraordinary physical and chemical conditions in otherwise cold liquids.

Applications:

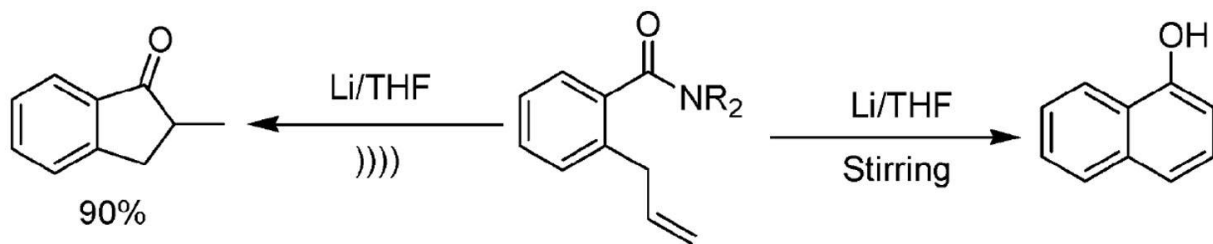
Organic synthesis

Coupling reactions (Heck, Suzuki, Sonograpia, Ullmann, Reformatsky, Michael addition, Baylis–Hillman, Wittig, Diels-Alder, Mannich-type, and Grignard reagent synthesis)

Special cases



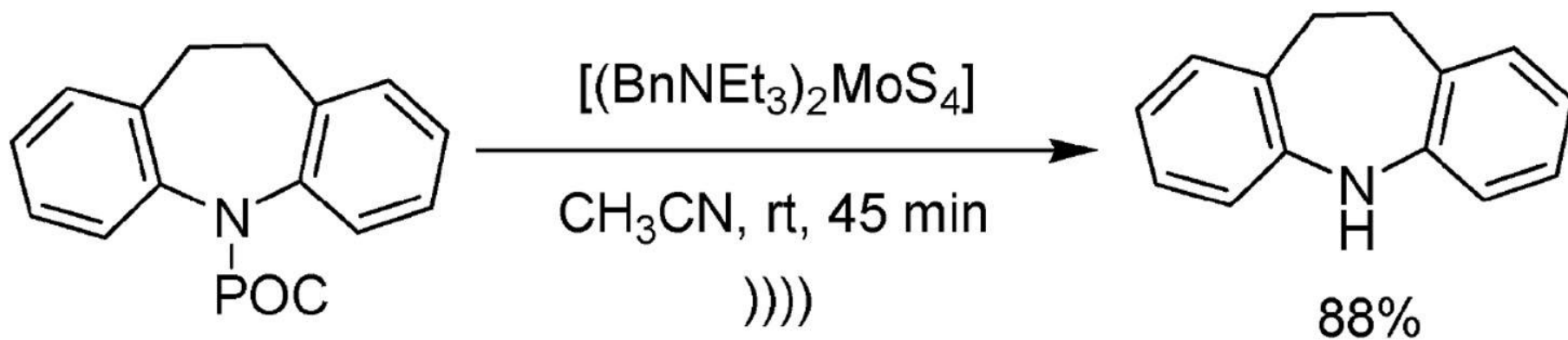
Scheme 55 Ultrasound-assisted synthesis of vinyl GR.



Scheme 70 Synthesis of indanone under sonochemical conditions.

J. Einhorn, C. Einhorn and J.-L. Luche, *Tetrahedron Lett.*, 1988, **29**, 2183.

(b) deprotective group reactions



Scheme 71 Ultrasound assisted deprotection of POC.

(POC: “prop-2-ynyloxy carbonyl”, 45 mins., 88% yield)

S. Sinha, P. Ilankumaran and S. Chandrasekaran, *Tetrahedron Lett.*, 1999, **40**, 771.

(c) oxidation and reduction reactions

(d) carbohydrate chemistry

(e) synthesis of ionic liquid

R. B. Nasir Baig and Rajender S. Varma, “Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis”, *Chem. Soc. Rev.*, 2012, **41**, 1559–1584.

(f) sonochemistry

Ultrasonics Sonochemistry

<http://www.journals.elsevier.com/ultrasonics-sonochemistry/>

Challenges:

wider application
scale-up
energy efficiency.

General References:

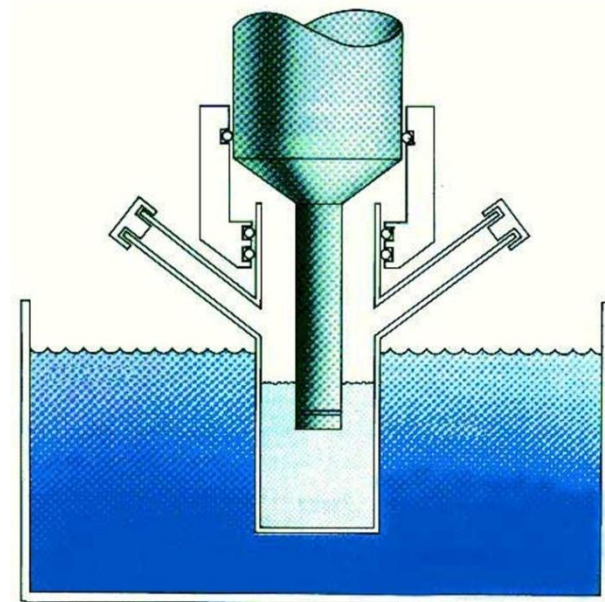
Sonochemistry: Theory, Reactions and Syntheses, and Applications (Chemistry Engineering Methods and Technology), [Filip M. Nowak](#) (Author, Editor)

K. S. SUSLICK, Sonochemistry

<http://www.scs.illinois.edu/suslick/documents/comprehencoordchem.pdf>

Kenneth S. Suslick, THE CHEMISTRY OF ULTRASOUND

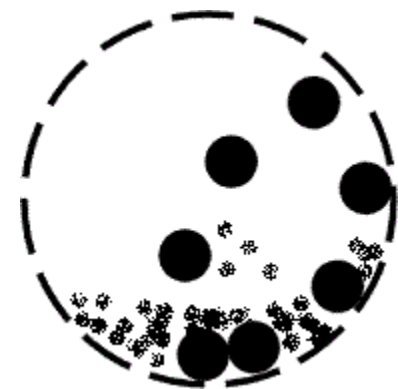
<http://www.scs.illinois.edu/suslick/sonochembritannica.html>



Machnochemistry

Definition: Chemistry in ball mill.

Definition of ball mill: A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints.



優點: 不用溶劑 -最好的溶劑就是沒溶劑

Application in Organic Synthesis

Aldol Condensations

Knoevenagel Condensations

Baylis-Hillman Reaction

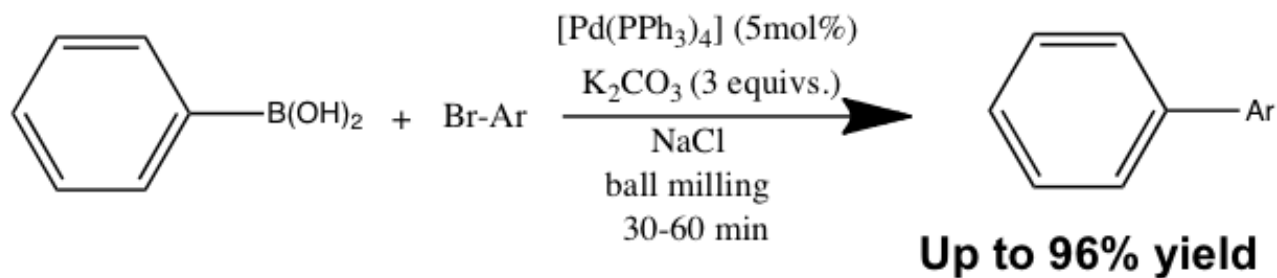
Michael Reaction

Wittig Reaction

Fullerene Cycloadditions

Suzuki Reaction

Heck-Jeffery Reaction, and more



S. F. Nielsen, O. Axelsson, *Synth. Commun.* 2000, 30, 3501.

Sheng-Hsien Chiu: Synthesis of rotaxane *Angew. Chem. Int. Ed.*, 2008, 47, 7475.

注意事項: 反應物性質 溫度 研磨球之性質 數量及大小 旋轉速度等

The reactants:

- The chemistry in ball mills is not restricted to a special type of chemical synthesis, if some requirements are fulfilled.
- At least one of the reactants and the product(s) should have melting points above 70 °C.
- No shock-sensitive materials should be exposed to mechanical stress.
- No gas-evolving reactions should be carried out under closed-vessel conditions, unless not special pressure-save milling beakers are applied.

Type of ball mill:

- There is no fundamental restriction to the type of ball mill used for organic synthesis (planetary ball mill, mixer ball mill, vibration ball mill, ...).
- The scale of reaction determines the size and the type of ball mill.
- Vessels for laboratory vibration ball mills are normally restricted to a volume of 50 cm³.

Types of Ball Mills

Drum ball mill

Bead-mills

Horizontal rotary ball mills

Vibration ball mill

Plantery ball mills

(圖片在附件一)

Milling material:

- The material density determines the energy entry and therefore, the choice of material influence the dissipative heat formation during ball milling. The higher the material density, the higher is the energy entry.
- Milling beakers and milling balls should be of the same material. At least, the material density of the milling beaker should be higher than that of the milling balls.
- The applied material should be chemically inert towards the reaction mixture. For most applications in organic synthesis, including catalysis, ceramic materials (e.g. ZrO₂) are the best choice. They are chemically inert and the material abrasion is comparably low.
- Some materials posses a high porosity (agate, steel) which could lead to memory effects.

Filling degree – Scale of synthesis:

- The scale of the chemical synthesis is related to the type of reaction, the available ball mill(s) and the size of the milling beakers. It is rather recommended to start the reaction at a small scale (≤ 10 mmol) and in case of success perform an up-scaling.
- The filling degree of the milling beakers is essential for the energy entry. Thus, a rule of thumb suggests that one third of the beaker volume should be taken up by the milling balls, one third of the total volume is for the reaction mixture and the remaining third is required for the movement of the milling balls.
- For reason of reproducibility, the procedure for loading of the milling beakers should be maintained throughout a series of experiments: At first the milling balls followed by the reaction mixture **or** the other way round.

Number and size of milling balls:

- The volume of the milling balls should relate to **one third** of the milling beaker volume.
- In contrast to particle refinement, for application in chemical synthesis the size of the milling balls seems not to be crucial. The operator is referred to suggestions provided by the manufacture or to similar examples published in literature.
- It is suggested to work with ≥ 2 milling balls. Otherwise the material abrasion becomes relevant.

Frequency and reaction time:

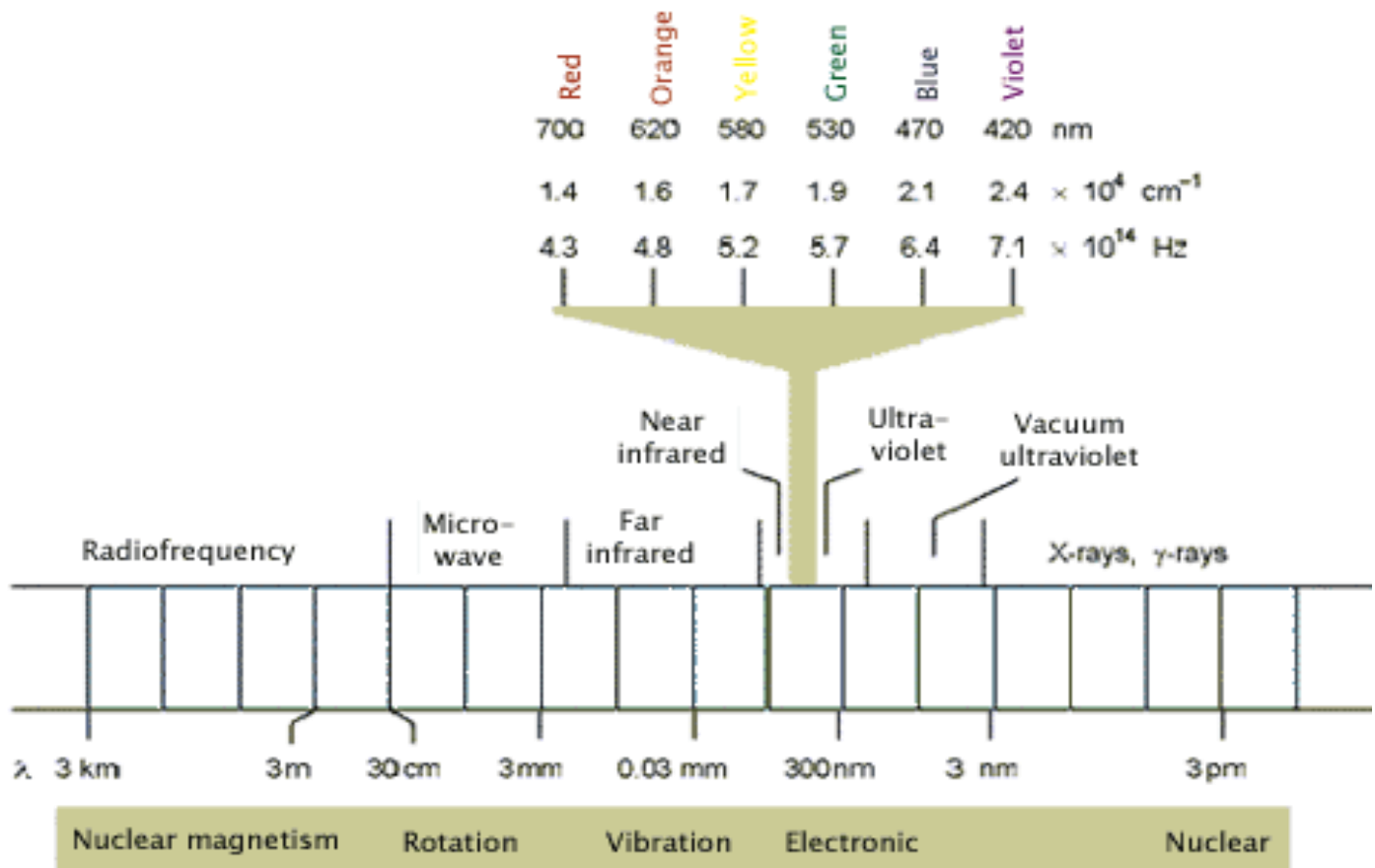
- In case of new reaction procedures, compare to related examples which have eventually been published.
- It is rather recommend changing reaction time than frequency.
- Start with 75-100% of the maximal operation frequency of the ball mill.
- The thermal stress for the reactants could be reduced by using cycled mode: mill for a specific amount of time – 5-10 min pause – start milling again and repeat the procedure for the required amount of time.

Photochemistry

Definition:

Chemical reactions proceed with the absorption of light by atoms or molecules.

Requirement: At least one molecule with chromophore.



Near infrared: 700–2500 nm Visible light: 400–700 nm Ultraviolet: 100–400 nm

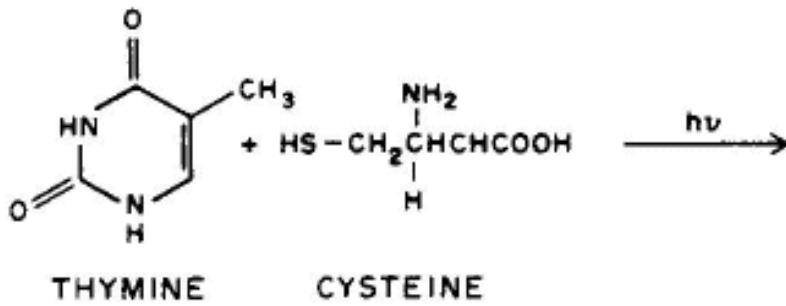
Advantages

Clean

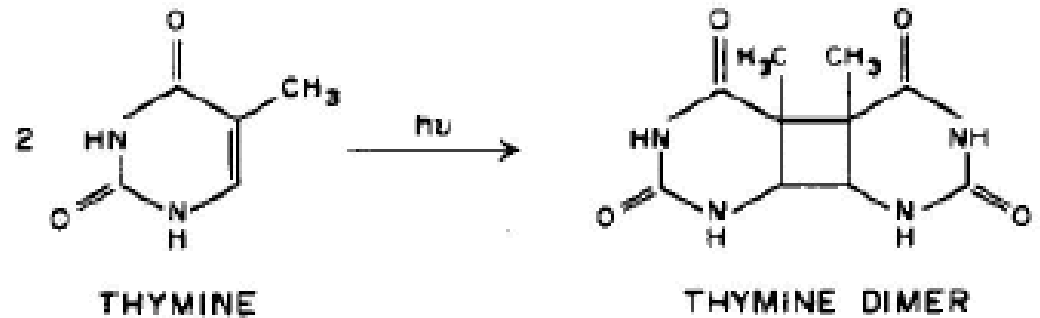
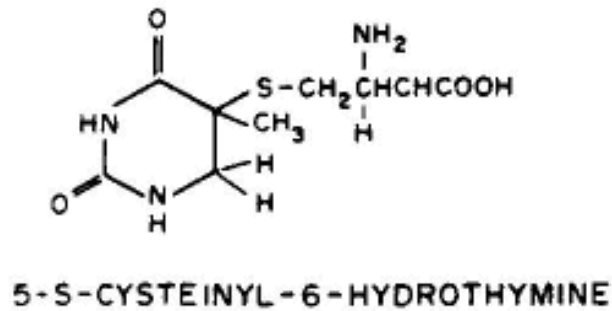
Save energy (sunlight)

Applications:

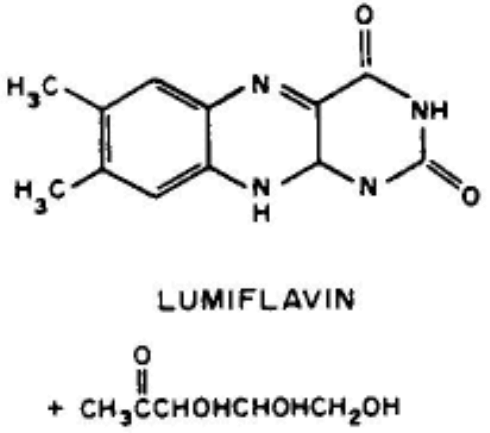
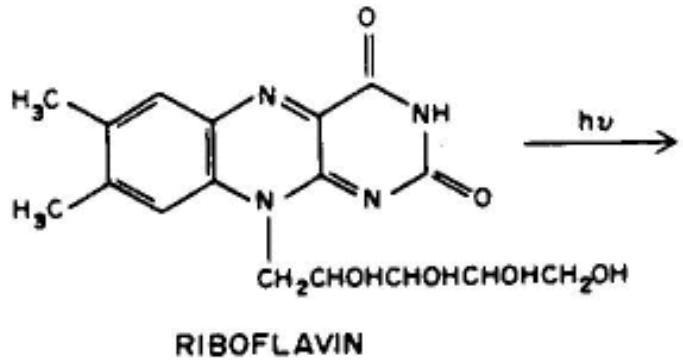
Addition reaction



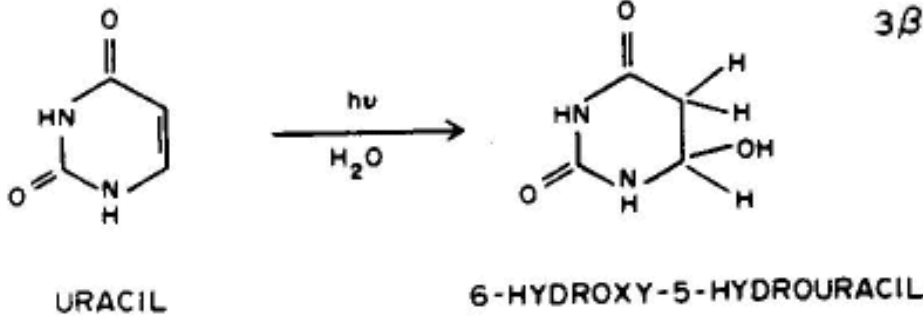
Cycloaddition



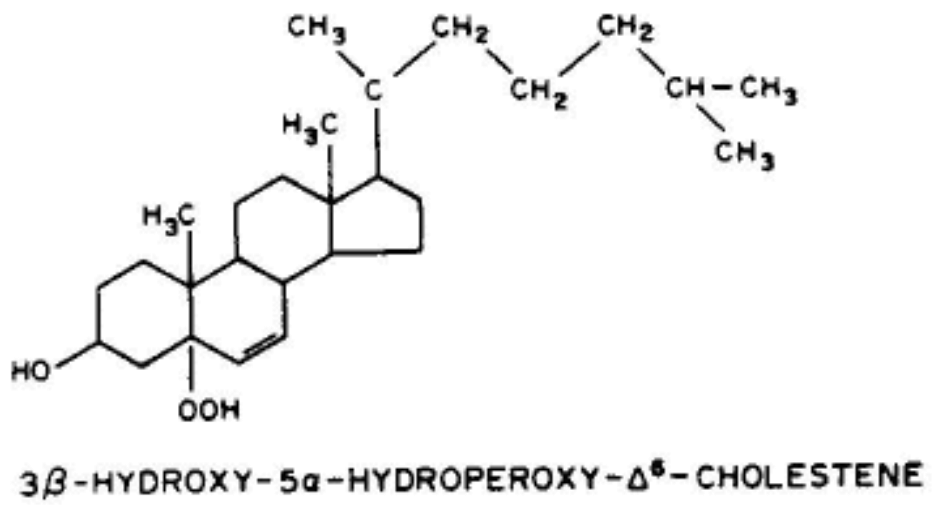
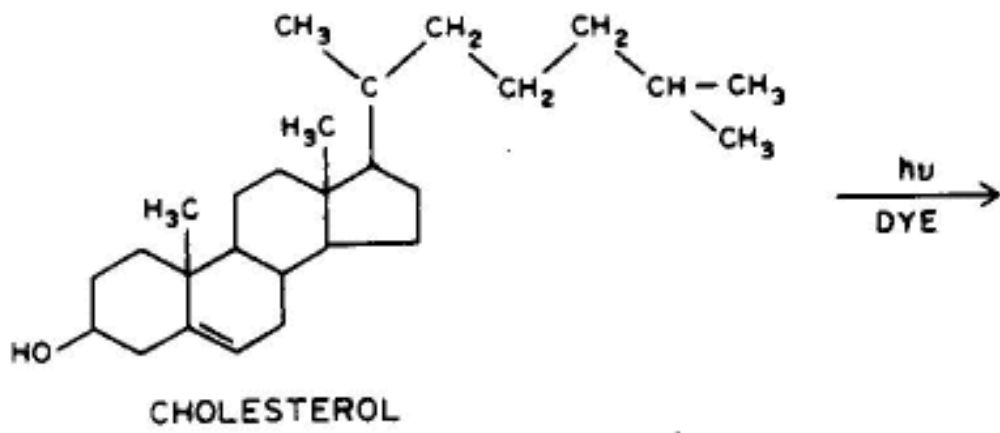
Fragmentation



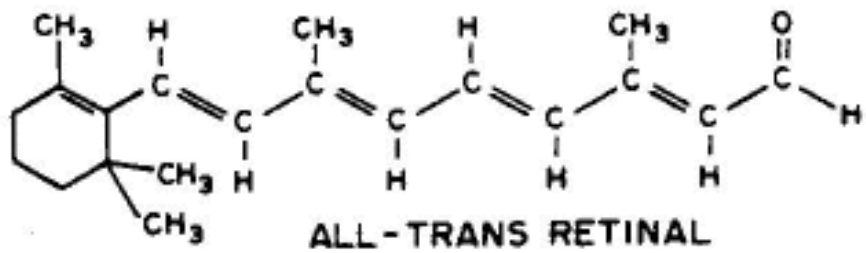
Hydration



Oxidation

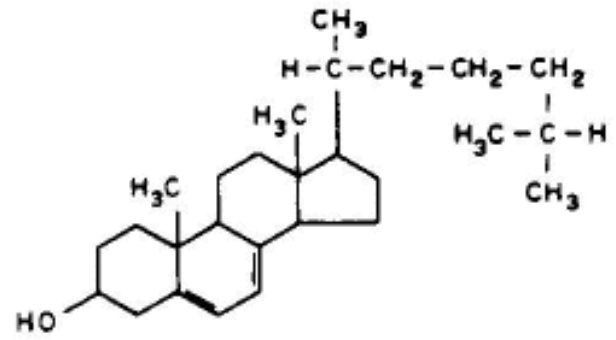
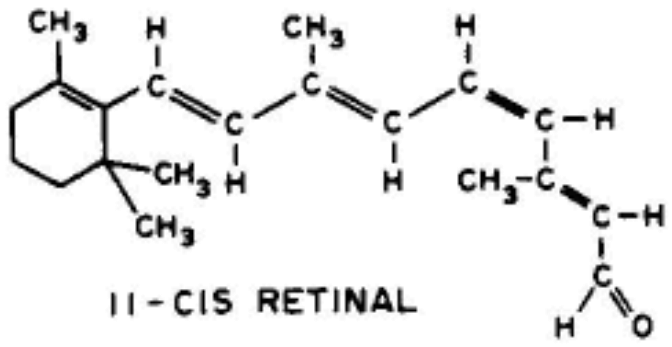


Cis-trans isomerization

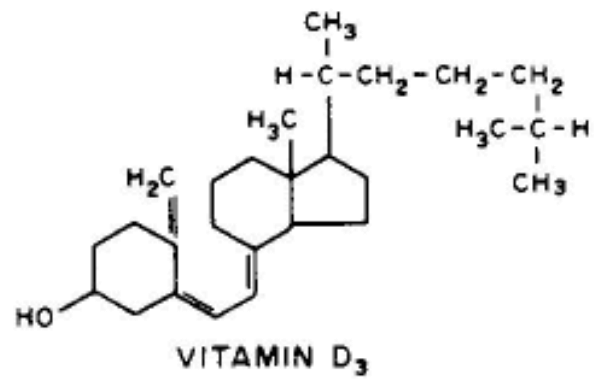


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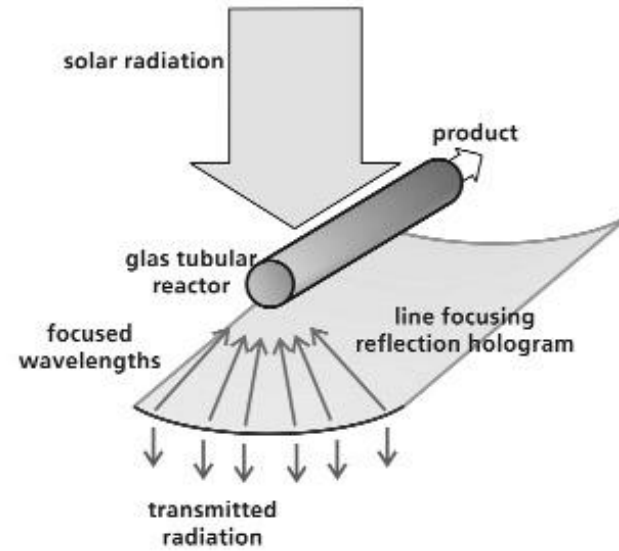
Rearrangement



$h\nu$
SKIN



Scale-up



A parabolic trough reactor



Solar chemical reaction plant (Cologne, Germany)

References

Kendric C. Smith, BASIC PHOTOCHEMISTRY

<http://www.photobiology.info/Photochem.html>

Michael Oelgemoller, Christian Jung, and Jochen Mattay, Green photochemistry: Production of fine chemicals with sunlight, *Pure Appl. Chem.*, (2007) **79**, 1939–1947.

doi:10.1351/pac200779111939c 2007 IUPAC

<http://pac.iupac.org/publications/pac/pdf/2007/pdf/7911x1939.pdf>

Emma Coyle, BSc Ph.D. Thesis (January 2010)

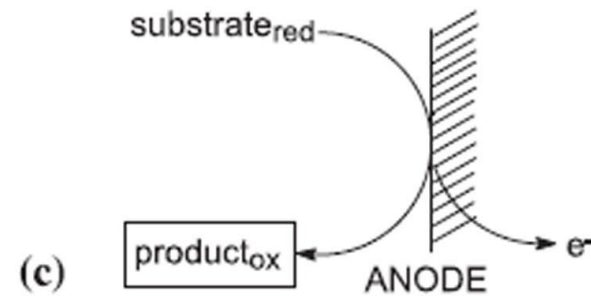
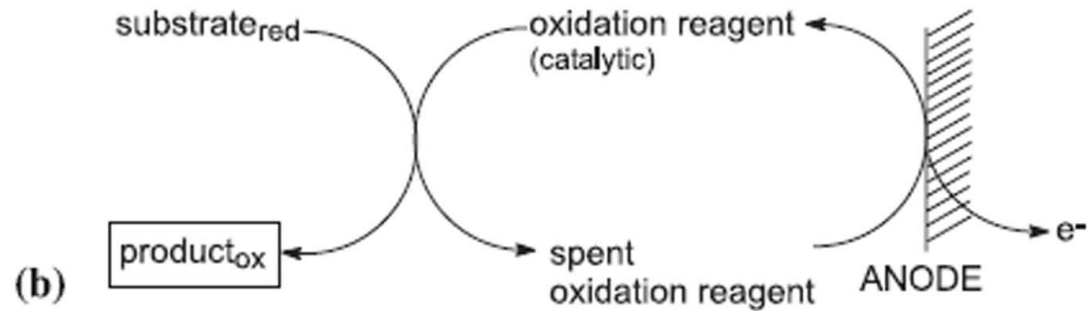
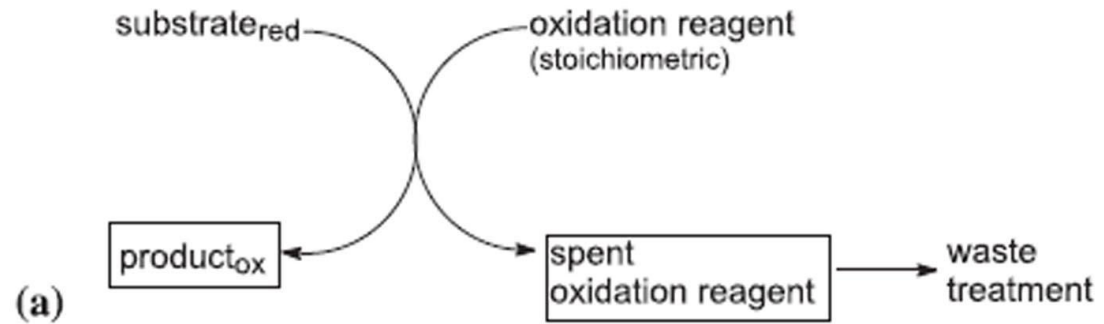
Green Photochemistry the synthesis of fine chemicals with sunlight
Dublin City University, Ireland

http://doras.dcu.ie/15389/1/Emma_Coyle_PhD_thesis.pdf

Electrochemistry

Advantages

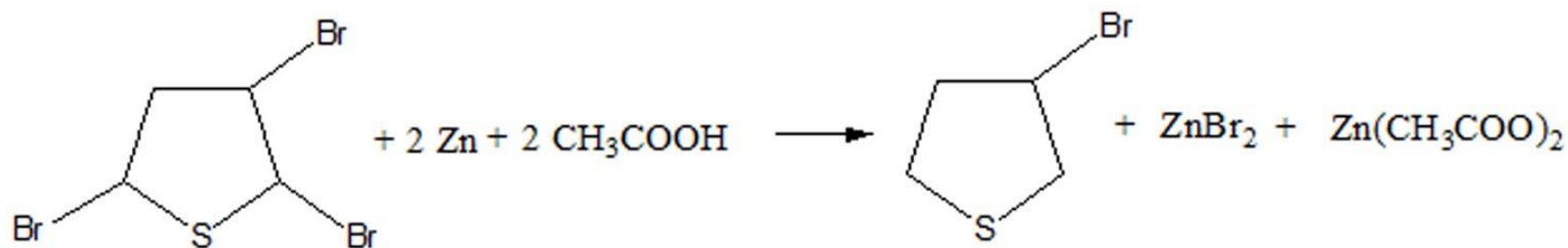
Less wastes Environmentally favorable



Example:

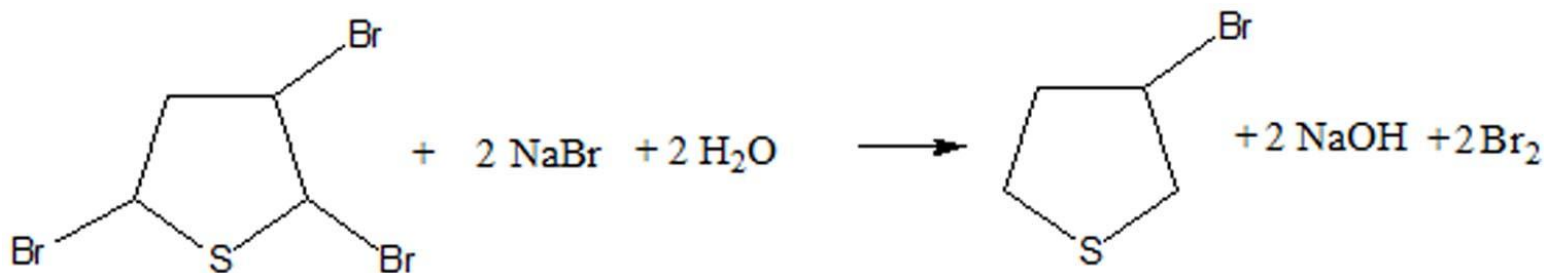
Synthesis of 3-bromothiophene (starting material for pharmaceutical and high polymer products) from 2,3,5-tribromothiophene.

The traditional way is that the 2,3,5-tribromothiophene is reduced by zinc powder in acetic acid.



Excess acetic acid is required to push the reaction to right hand side. Poor E-factor is obtained as a consequence.

Electrochemical method



Bromine molecular is collected at anode and readily being reuse. No excess reagent is needed. Better E-factor is obtained.

Low reaction temperature

The above electrochemical reaction can be carried out at ambient temperature.

Easy products separation

Products are collected on electrodes.

Non-volatile solvent

Water is common used solvent in electrochemical reaction.

Challenges

Difficult to scale-up.

Costly.

References

Electrochemical Reactions, Patricia Ann Mabrouk, Wiley

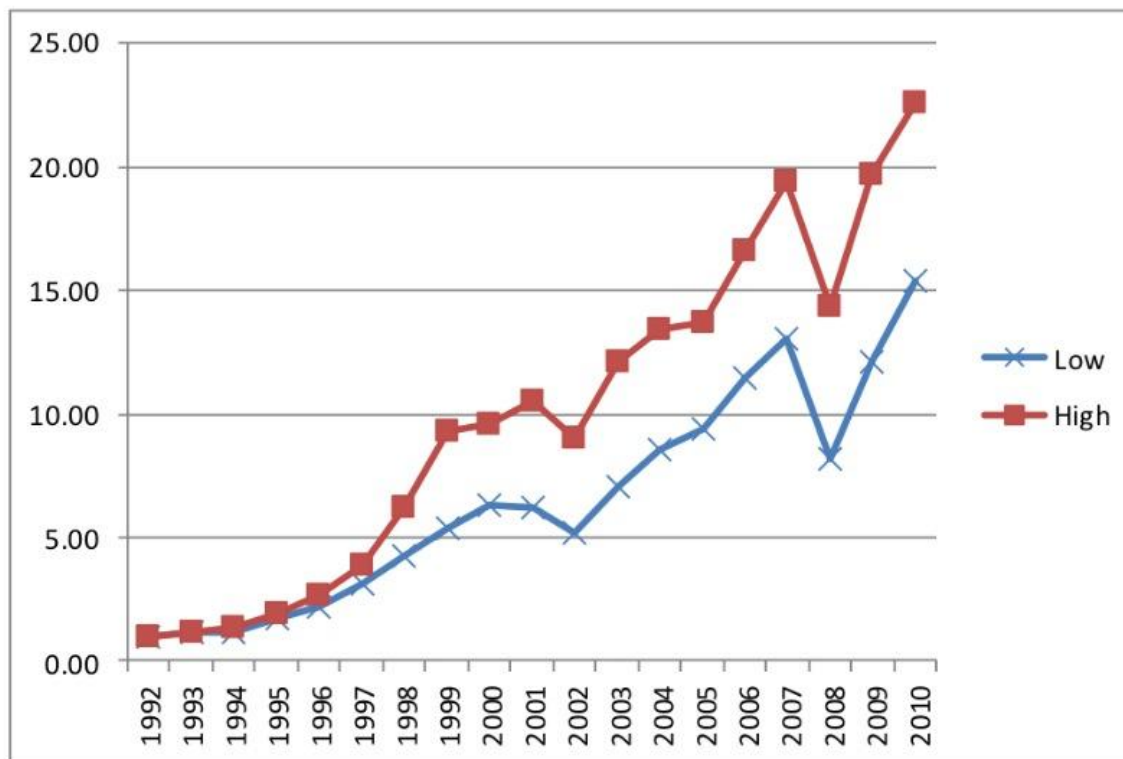
<http://www.iupac.org/publications/pac/2001/pdf/7308x1305.pdf>

Michael A. Matthews, Green electrochemistry. Examples and challenges, Pure Appl. Chem., (2001) **73**, 1305-1308.

E. Steckhan, et al., Environmental protection and economization of resources by electroorganic and electroenzymatic syntheses, Chemosphere, (2001) **43**, 63-73.

A 2012 survey by Independent Chemical Information Services (ICIS) shows 54% of 700+ respondents say their company has a sustainability strategy and /or policy already in place, and a further 17% indicate a policy is currently in development and 17% that initiatives are likely within the next 2-3 years. Only 12% reported that there is little interest. http://img.en25.com/Web/ICIS/FC0126_Chem_201301.pdf

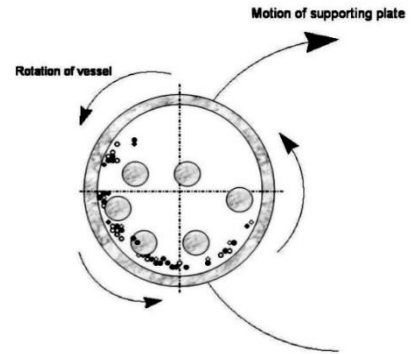
Evolution of \$1 invested in the stock market in value-weighted portfolios



誌謝
綠色/永續合
成化學工作
坊的伙伴們

謝謝大家

Planetary Mills

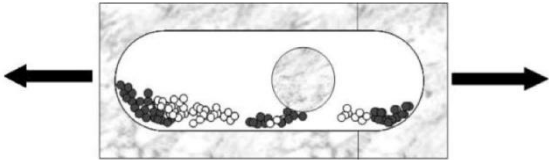


Planetary Ball Mill: The comminution of the material to be ground takes place primarily through the high-energy impact of grinding balls in rotating grinding bowls.

Mixer ball mill:



Vibrating ball mill:



Rotatory Mill

