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Lighting the Way to Sustainable Chemistry: The Power of Flow and Photochemistry

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Photochemistry as a Greener Application

The power of flow and photochemistry.

- We'll explores how the synergy of continuous flow systems and light-driven reactions is transforming chemical synthesis—offering; enhanced safety, process intensification and reduced environmental impact

- Key themes include the benefits of precise reaction control, and improved energy efficiency in photochemical processes.

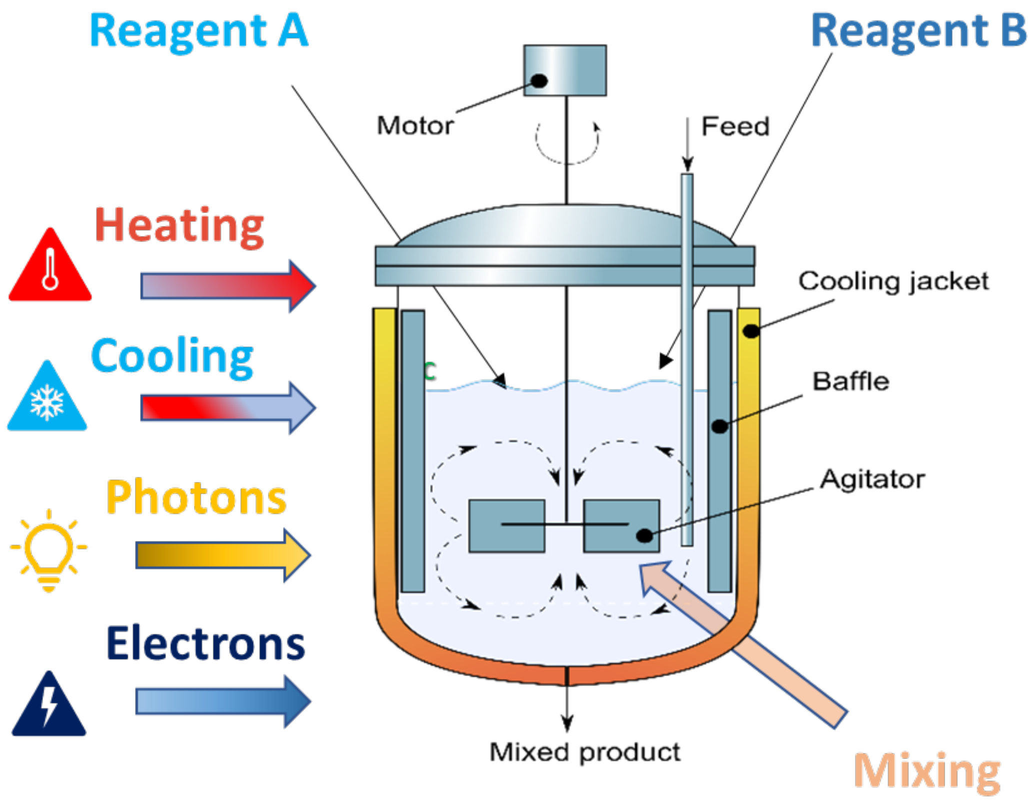
- The session will highlight recent advancements and practical applications, demonstrating how these technologies contribute to a more sustainable future in chemical manufacturing.

How do we Initiate a Chemical Reaction?

Chemical reactions are generally activated by heat or a chemical reagent

- One of the key advantages of modern laboratory equipment is its easier to use some of the lesser used methods:
  - **Electrochemistry** which uses electrons
  - **Photochemistry** which uses light

- An increasing trend in recent years to use both techniques in chemistry, sometimes referred to as reagentless (or traceless) chemistry.



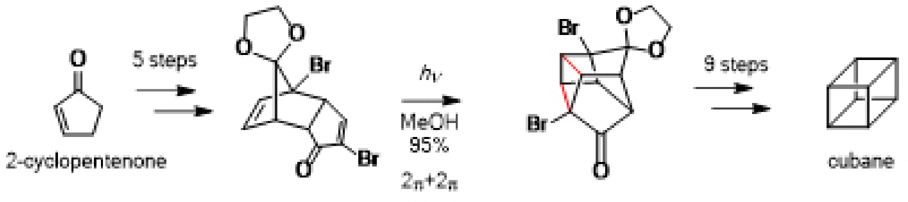
Photochemistry – How It Began

Great masters of Organic Synthesis

The application of photochemistry for the synthesis of organic compounds is not a new concept:

1. Notably **Eaton** 1964 on his cubane synthesis.
2. **Corey** 1964 applied photochemistry and his retrosynthetic approach to carry out the synthesis of caryophyllenes.
3. **Wender**'s synthesis of cedrene, in 1981.

1



P. E. Eaton, T. W. Cole, *J. Am. Chem. Soc.* **1964**, *86*, 962-964.

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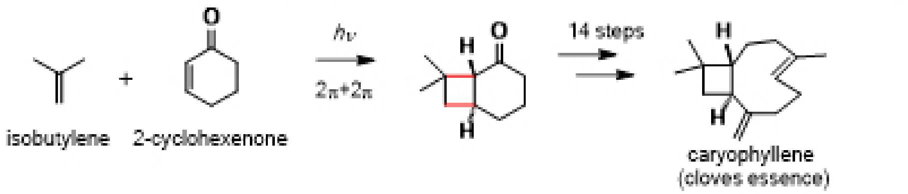

E. J. Corey, R. B. Mitra, H. Uda, *J. Am. Chem. Soc.* **1964**, *86*, 485-492.

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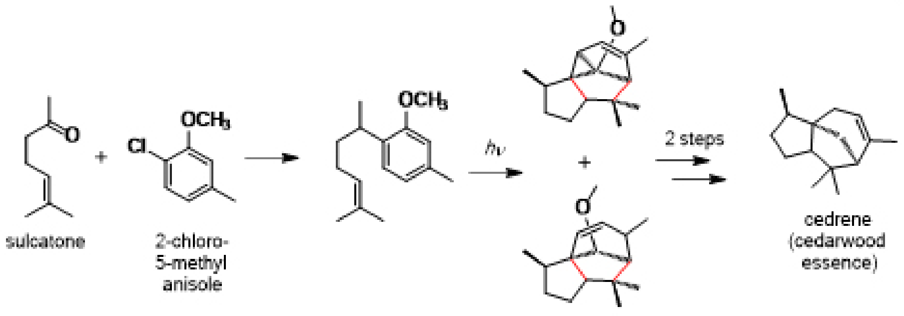


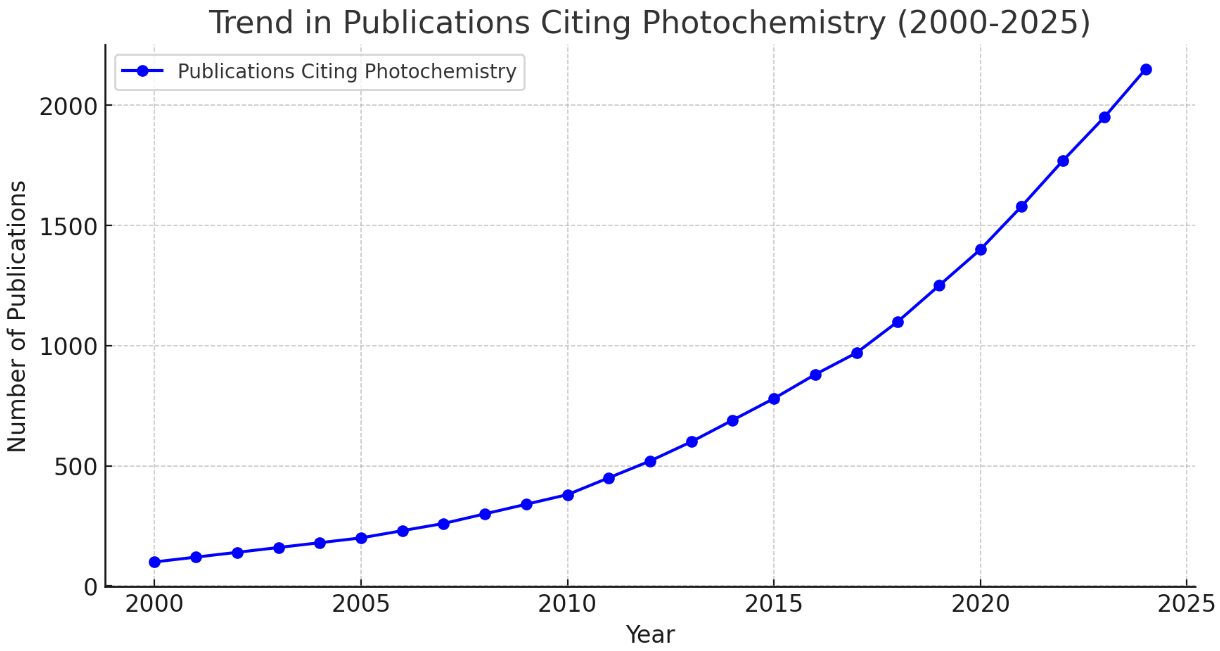
P. A. Wender, J. J. Howbert, *J. Am. Chem. Soc.* **1981**, *103*, 688-690.

Increased use of Photochemistry

Photochemistry Citations

Photochemistry research has seen an increase from researchers in academia and industry for several reasons.

- The development of commercially available photochemistry reactors.
- Novel synthetic routes reducing the number of steps.
- The development of novel photoredox catalysts.
- The awareness of photochemistry as a greener chemistry.



Estimated trend in publications citing "photochemistry" from 2000 - 2025

Recent Advances towards Sustainable Chemistry?

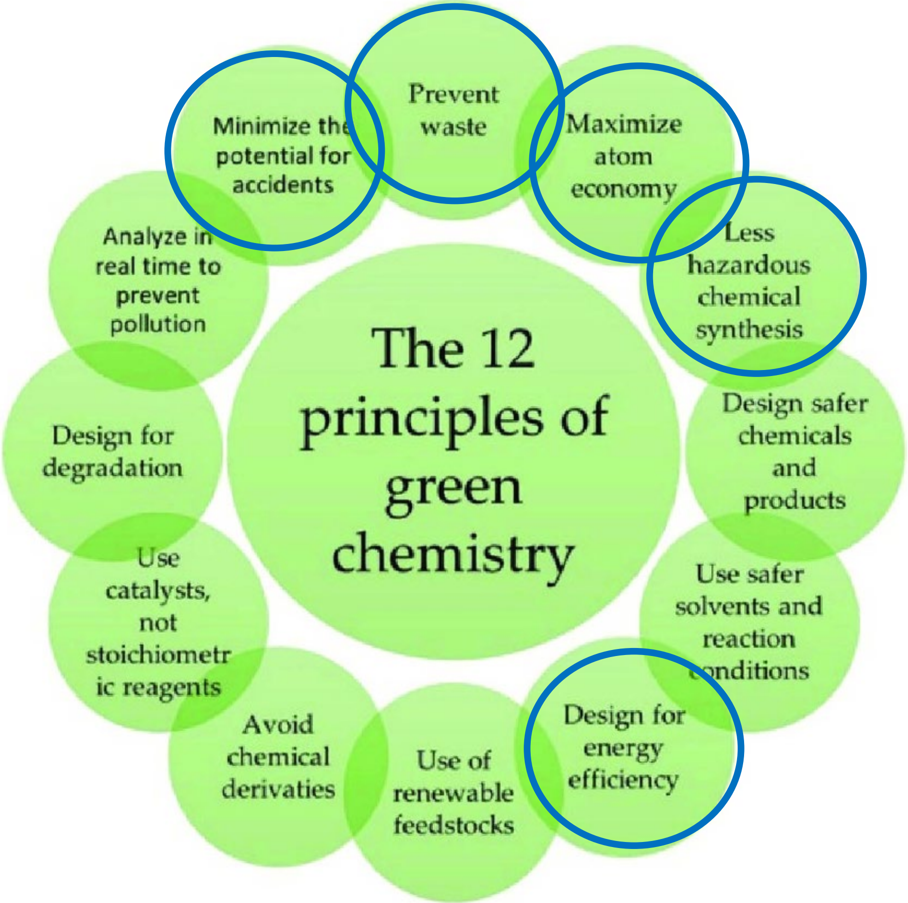
Photochemistry has gained popularity as a “greener” synthetic technique in recent years.

- The impacts in the synthetic photochemistry is already being seen in two main areas:
  - Photons can be used as a traceless reagent to activate otherwise benign starting materials
  - Molecules can be designed in fewer steps enabling savings in resources, time, energy and waste.

- While photochemistry has the potential in the advancement of sustainable processing there are still some hurdles in achieving this:
  - Light source technology.
  - Reactor design.
  - Process understanding.

12 Principles of Green Chemistry

- Photochemistry aligns closely with the 12 Principles of Green Chemistry, offering a sustainable approach to chemical synthesis by utilizing light as an energy source.
- Our focus is on the following factors:
    - The development of new light source technology.
      Better selectivity, improved efficiency, temperature control.
    - The advantages of modern photochemical reactor design.
      Higher photon flux.

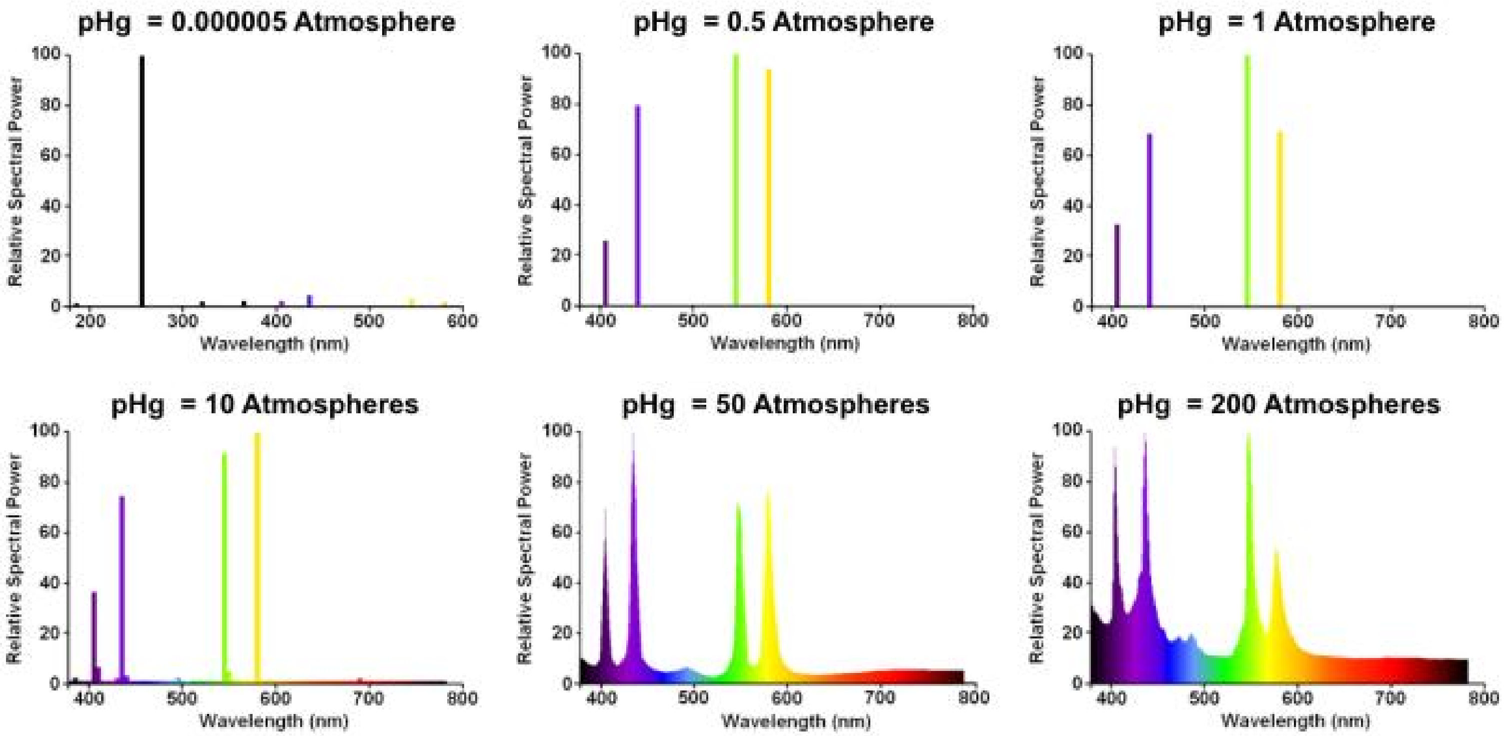


Photochemistry Light Sources

- Photochemistry in the past has utilised high intensity mercury lamps to facilitate photocatalyzed reactions
  - These produce a broad spectrum of wavelengths (200-600 nm).
  - They produce a lot of heat which is transferred to the reaction.
  - They almost always require external cooling to maintain temperature.

- Advances in LED technology have opened-up more targeted photochemistry
  - LEDs have a narrow emission band (normally in 20 nm range). This allows more selective chemistry.
  - LEDs have a small irradiation window which allows them to be directed toward the reactor.
  - LEDs also give off a lot less heat, so external cooling is not always required.

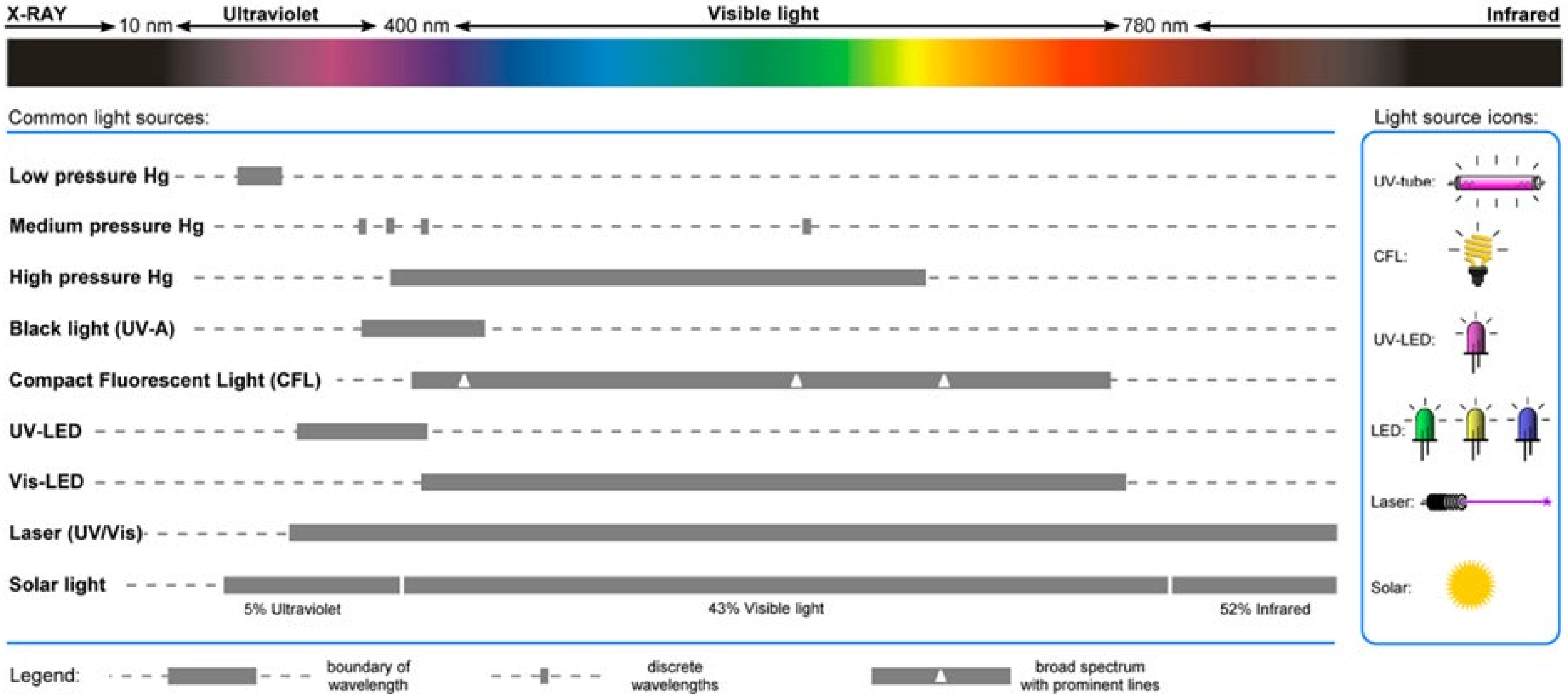
Photochemistry Light Sources



Effects of Mercury Vapour Pressure on the Spectral Power Distribution

[1] Lamptech.co.uk – Mercury Vapour

Photochemistry Light Sources



Emission spectrum of common light sources used for Photochemical Applications[1]

Cambié, D., *et al.*, *Chem. Rev.*, **2016**, *116* (17), 10276–10341

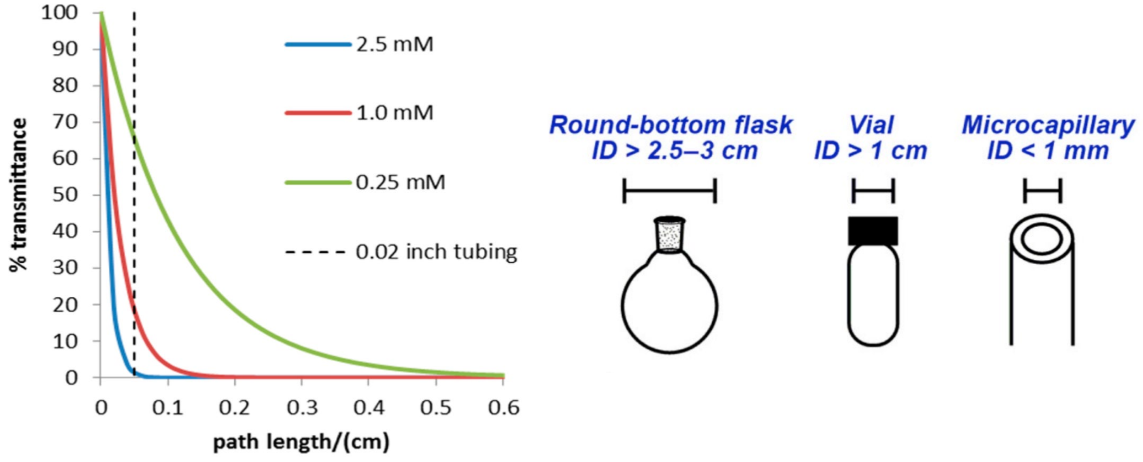
Photochemistry Reactors

The problem with light (photons) is they lose their energy very quickly.
This is described by the ***Bouguer-Lambert-Beer law***, the further the reaction is from the light the less power it sees.

- When using traditional flasks, the reaction is only irradiated near the wall giving non-uniform reaction conditions

When performing photochemical reactions in flow reactors (with i.d. of < 1 mm), full transmission of light is allowed to the reaction solution.

- The result in a more homogeneous irradiation of the reaction giving shorter reaction times and less side-products caused by over-irradiation (often seen in equivalent batch conditions).



Attenuation of light with the distance of irradiation[2,3]

Sambiagio, C.; Noël, T. *Trends Chem.*, **2020**, *2* (2), 92–106
Plutschack, *et al.*, *Chem. Rev.*, **2017**, *117* (18), 11796–11893

Photochemistry Reaction Scalability

Scaling flow photochemistry reactions

- Flow photochemistry strategies can help in the scale up of photocatalytic reactions:
  - We can increase the throughput by running the reactions for longer.
  - We can increase the number of reactors.
  - We can increase the radiant flux into the reaction.

Flow reactors have been shown to deliver a 150-fold increase in absorbed photon flux c.f. batch reactors

- As light (the photon) is the reagent in photochemistry reaction, by increasing the number of photons reaching the reaction mixture, it is possible to increase the reaction rate:
  - We can increase the light intensity into the same photochemistry reactor using the same platform to scale-up our reactions.

$$\text{Moles photons per hour} = \lambda\ (\mathrm{nm}) \times \text{power}\ (\mathrm{W}) \times 3\times10^{-5}$$

Number of moles of photons (einsteins) per hour at a given wavelength (λ)[4]

www.asynt.com
enquiries@asynt.com
+44 (0)1638 781709

Flow Photochemistry?

The benefits of flow chemistry are widely known; these translate to flow photochemistry with further benefits:

- **Improved irradiation of the reaction:**
  - Flow reactors improve light transmission to reaction.
- **Improved reaction scalability:**
  - Increasing light power enables more photons, increasing reaction rates and increasing throughput.
- **Improved reaction selectivity:**
  - Single wavelength LED light sources enable selectivity of reaction pathways.
- **Improved reproducibility:**
  - Controlled reaction exposure times with no over irradiation.
- **Improved mixing and heat exchange:**
  - Flow offers reproducible mixing and precise temperature control.
- **Ability to perform multiphase chemistry:**
  - Small reactor design allows ability to use gases, crucial in photochemical application.
- **Increased safety:**
  - Light proof reactors and power interlocks prevent exposure of user to high intensity light.

Summary and outlook

- Continuous photochemistry has still not reached maturity, especially at a production scale.
- Recent developments have driven interest in the synthetic and process chemistry communities.
- Further development will be reliant on multiple discipline; material scientists for light source technologies and chemical engineering in the design of reactors along with chemists to exploit this technique.
- **The outlook is that Flow photochemistry will become a key technique in the Green Chemists toolbox.**

Asynt Flow Photochemistry

Asynt offers a range of flow photochemistry reactors that cover a wide range of applications, reactor type with efficient temperature control and a range monochromatic LED light sources.

PhotoFLOW

Borealis Flow

PhotoChip

PhotoSyn

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enquiries@asynt.com
+44 (0)1638 781709

Asynt
By chemists, for chemists

Asynt has range of modern flow photochemistry reactors for most scales, & knowledgeable support.

Please come and visit the Asynt booth on stand **H102**.

Contact us for further information. We're happy to talk through your requirements.

www.asynt.com

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