Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

STRIVE

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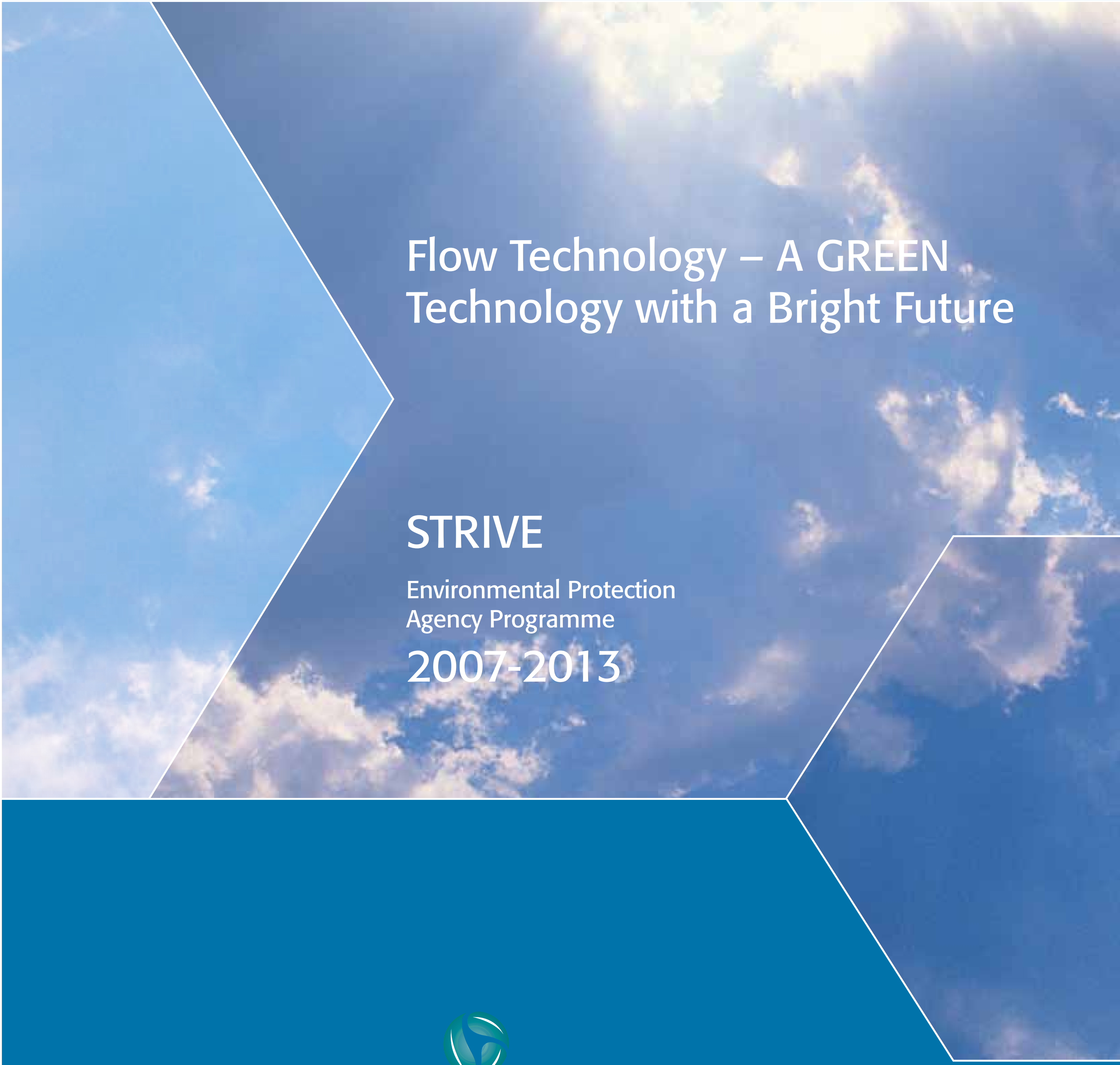

Flow Technology – A GREEN Technology with a Bright Future

STRIVE

Environmental Protection
Agency Programme

2007-2013

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

The EPA is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Community and Local Government.

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- Office of Communications and Corporate Services

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EPA STRIVE Programme 2007–2013

Flow Photochemistry – A GREEN Technology with a Bright Future

µ-Photochemistry – A New Resources-Efficient Synthesis Tool

(2008-ET-MS-2-S2)

STRIVE Report

Full Technical Report available for download on http://erc.epa.ie/safer/reports

Prepared for the Environmental Protection Agency

by

Department of Chemistry, Dublin City University

Authors:

Kieran Nolan, Alexander Yavorskyy, Michael Oelgemöller, Oksana Shvydkiv

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co.Wexford, Ireland

Telephone: +353 53 916 0600   Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

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The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Details of Project Partners and Project Team

Kieran Nolan
School of Chemical Sciences
Dublin City University
Dublin
Glasnevin D9
Ireland
Tel.: +353 01 700 5913
Email: Kieran.nolan@dcu.ie

Michael Oelgemöller
James Cook University
Molecular Sciences Building DB21,
Townsville Campus
Townsville
Australia
Tel.: +61 7 4781 4543
Email: michael.oelgemoeller@jcu.edu.au

Mirek Macka
University of Tasmania
Chemistry Building
Sandy Bay Campus
Hobard
Tasmania
Australia
Tel.: +61 3 6226 6670
Email: Mirek.Macka@utas.edu.au

Klaus Jaehnisch
Leibniz Institute for Catalysis at the
University of Rostock
A.-Einstein-Str. 29a
Rostock
Germany
Tel.: +49 381 1281 281
Email: Klaus.Jaehnisch@catalysis.de

Alexander Yavorskyy
School of Chemical Sciences
Dublin City University
Dublin
Glasnevin D9
Ireland
Email:alexander.yavorskyy@dcu.ie

Oksana Shvydkiv
School of Chemical Sciences
Dublin City University
Dublin
Glasnevin D9
Ireland

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Executive Summary[1]

The production of a chemical product, such as a typical pharmaceutical compound, relies to a large degree on chemical processes. All these individual processes produce significant amounts of waste and consume vast amounts of energy. As an example, it is estimated that between 25 and 100 kg of waste is generated for every 1 kg of active pharmaceutical product synthesised (Dunn et al 2004). In addition, the handling and storing of large quantities of hazardous materials require strict safety precautions to avoid contamination of soil, water or air. Besides the generation of waste, the high energy demand of most industrial processes contributes to climate change. The overall goal is to have a more efficient use of resources: water, energy and materials.

In Europe, the flagship Europe 2020 Policy supports the shift towards a resource-efficient, low-carbon economy to achieve sustainable growth (EU Commission, 2011). Furthermore, within its 2020 Vision document the Environmental Protection Agency has identified "Limiting and adapting to climate change" as its first priority (EPA, 2007). To achieve this challenging goal, the EPA has urged:

- "Energy efficiency must be integral to industrial and commercial activities, …" and
- "Ireland needs to be at the forefront of adopting new approaches and low-carbon technologies …".

Since the rapidly expanding chemical industry in Ireland will continue to contribute to carbon emissions, the development and implementation of novel energy-efficient processes is vital. On a national level, there is an increasing imbalance between the current needs of industry, society and the environment. Therefore, each contribution to minimising the waste and energy demands by chemical industries and research laboratories is highly beneficial and urgently needed.

The goal of this project, 'μ-Photochemistry a New Resources Synthesis Tool', was to address these issues – by both developing and applying the concept of energy-efficient flow microphotochemistry in both the research laboratory and the broader chemical industry.

Microphotochemistry is a novel research area of the twenty-first century that arises from significant progress in micro- and nanotechnologies. Microphotochemistry combines established techniques in organic photochemistry and continuous flow microsystem engineering with advances in light technology. Microphotochemistry can be considered to be an environmentally conscious methodology, contributing to the rapidly expanding field of 'green chemistry', by reducing the volume of waste, improving energy efficiency and product selectivity.

The first stage of this project was the establishment of a high-profile international photochemistry research cluster centred at Dublin City University (DCU) with partners at the Leibniz Institute for Catalysis, Rostock, Germany (Dr Klaus Jaehnisch) and James Cook University, Australia (Prof Michael Oelgemöller).

The present project has allowed for the creation of new technologies that not only address environmental needs, but also offer chemical manufacturers substantial process cost savings and improved product yield outputs.

This project investigated the microscaling of a series of photo-induced electron transfer and photodecarboxylative additions initially using commercially available microreactors. It was found that not only can typical photoaddition reactions be successfully scaled down to a microdwell reactor, but that in many cases yields of these reactions are greatly improved over the large-scale Rayonet reactors. However, the commercial availability of a large range of microreactors that can be used in photochemistry are somewhat limited. Furthermore, commercially available microreactors are based on a square chip design and are expensive. It was hypothesised that a coiled design, where a microcapillary can be wrapped around a commercial light source, would be advantageous since this would allow control of the path length of the reactor and also be far cheaper to build in comparison to commercial chip systems. A prototype dual-capillary reactor was constructed and then comparative synthetic studies between the new reactor and the commercially

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[1] Metadata and datasets associated with this report can be found on the EPA SAFER website at: http://erc.epa.ie/safer/iso19115/displayISO19115.jsp?isoID=3002

available systems were carried out. It was found that the new prototype reactor gave comparable performances to the commercial devices but with the advantages of low cost and the elimination of water as coolant.

With the success of the new prototype reactor a new multi-capillary tower reactor was constructed. This new reactor has the capacity to either run ten separate reactions simultaneously (as a parallel reactor) or can be used as a scale-up system where a single reaction mixture can be run through all ten capillaries simultaneously. It was possible to validate both applications with the new reactor, demonstrating its applicability in both parallel synthesis and scale-up chemistry.

Overall, the new multi-capillary tower reactor can be used not only as a small-scale R&D tool for laboratory-based production of chemicals, but has excellent potential as a multi-kilo chemical production tool for the chemical industry, offering reduced waste streams, a safer working environment, a reduced carbon footprint and a significant reduction in water usage.

The project also investigated photooxygenation reactions, a commercially important class of reaction, initially using commercially available microreactors. It was found that transferring bulk photooxygenations to a microflow platform offers the following advantages:

- Potential elimination of water as a coolant;
- Peroxides are an explosion hazard: using a microflow platform, only small quantities of peroxide is being produced at any one time;
- Low-energy light sources can be used in place of halogen lamps due to the shorter path length in a microchannel;
- Schlenck flasks in combination with halogen lamps have unfavourable light penetration properties;
- Halogen lamps can generate large amounts of heat that can facilitate thermal decomposition reactions.

The synthesis of the potentially explosive endoperoxide ascaridole was optimised and carried out in safer and controllable conditions in the commercial reactors with outstanding yields. Because the commercial devices are limited with respect to dimensions, the development of a new reactor – the 'bubble reactor' to be used in photooxygenation reactions – was initiated. The construction of this new reactor was quite inexpensive relative to the commercial devices and again it was possible to eliminate the usage of water as coolant. Furthermore, this reactor allows for larger-scale synthesis than the commercial devices. Comparison studies on the new reactor revealed a comparable performance with the commercial reactors and a far superior performance compared to the traditional batch reactors.

Overall, the advantages of the new bubble reactor are that it is:

- cost effective;
- easy to assemble;
- provides sufficient product quantities;
- suits a wide range of reactions;
- can be integrated into systems for greater accuracy and quality control; and, finally
- does not require water for cooling.

Overall, the project not only demonstrated that the ‘microphotochemistry approach’ is superior than the ‘traditional batch’ approach, but it also allowed the development of new energy-efficient/water-free reactors that are not only capable of small-scale synthesis but have the potential for application in industrial scale-up/process chemistry.

Given the significant results obtained with the new bubble reactor, design changes to the dual-capillary reactor are now being pursued – to apply the ‘bubble’ concept of the bubble reactor, by introducing a microcapillary air ‘bleed’ into the system. Initial results indicate that this system has a performance superior to the commercially available falling film reactor.

The next and final stage for this chemistry is industrial application. The new technology developed in this project makes photochemistry a far more attractive and ‘green’ tool since it removes the need for: (i) high energy lamps and (ii) water as a coolant, and (iii) it guarantees high-atom efficiency, thereby reducing waste by-products.

Presently there are companies in Ireland (Henkel Loctite) that are interested in peroxides (for polymerisation) that are prepared from renewable feed-stocks. The work reported here demonstrates that not only is it possible to achieve this goal, but that a ready-made green technology that can be adopted to industrial process needs is available. More funding is necessary to launch this technology into industry.

Ideally, a dedicated demonstration laboratory should be established to convince/convert industry to this new technology. If this is not undertaken within the next two years, the lead that has been created in green photochemistry in Ireland may be lost.

1 Introduction

Microphotochemistry is a novel twenty-first century research area that has arisen from significant progress in micro- and nanotechnologies. During the last few years, the interest in miniaturisation has increased significantly in all areas of science, technology and engineering due to a general tendency for greener industrial research processes. Microphotochemistry combines established techniques in organic photochemistry and continuous flow microsystem engineering with advances in light technology. It is also considered to be an environmentally conscious methodology, contributing to the rapidly expanding field of 'green chemistry', by reducing the volume of waste, improving energy efficiency and product selectivity (Coyle and Oelgemöller, 2008).

For photochemical processes usage of microstructured/continuous-flow devices have important benefits compared to the conventional/batch reactors:

- The thin liquid layers within a microchannel plate allow extensive penetration by light;
- The large irradiated surface-to-volume ratio provides efficient light-energy transfer and illumination homogeneity;
- The flow-through design avoids undesired side reactions and/or decompositions of product;
- The small irradiation aperture allows the usage of any light source, including miniaturised light sources such as light-emitting diodes (LEDs);
- The small experimental scales reduce the amounts of waste and materials;
- The combination of microreactors into serial or parallel clusters can allow for process scale-up to multigram–kilo scales;
- The flow-through design can reduce heat build-up during irradiation, potentially eliminating the need for water as a *coolant*.

The current project aimed to develop a novel resource- and energy-efficient approach to photosynthetic chemistry. It set out to explore how miniaturisation can revolutionise photochemical synthesis with the goal of improving product yields, product purity, reducing reaction times relative to batch reactors and reducing the quantity of coolant used.

To demonstrate the advantage of microphotochemistry as a new technique, a series of *homogeneous* and *heterogeneous* model transformations was selected for evaluation. Reactions of particular interest to the project team were:

- Photoelectron transfer reactions (PET) leading to new C-C bond formations with phthalimides (Gallagher et al., 2010; Griesbeck and Mattay, 2005; Griesbeck and Oelgemöller, 2000; Griesbeck and Oelgemöller, 1999);
- Stereoselective radical additions to alkenes leading to the formation of new C-C bonds (Hoffmann, 1994; Hoffmann et al., 1994); and
- Heterogeneous (gas-liquid) photooxygenations (Clennan and Pace, 2005; Suchard et al., 2006).

To initiate the research programme, a series of commercially available microreactors was selected – specifically the Mikroglas dwell device (manufactured by Mikroglass Chemtech, Fig. 1.1b), microchip (manufactured by Micronit Microfluidics BV, Fig 1.1c). We wished to evaluate the performance of these reactors with respect to batch systems (Rayonet reactor shown in Fig. 1.1a) with our selected reactions. Once this work was completed the development of new improved microflow reactors was envisaged, which would not only perform photochemical transformations on the microscale level, but have the potential to be used as a process chemistry tool for the industrial production of large quantities of product.

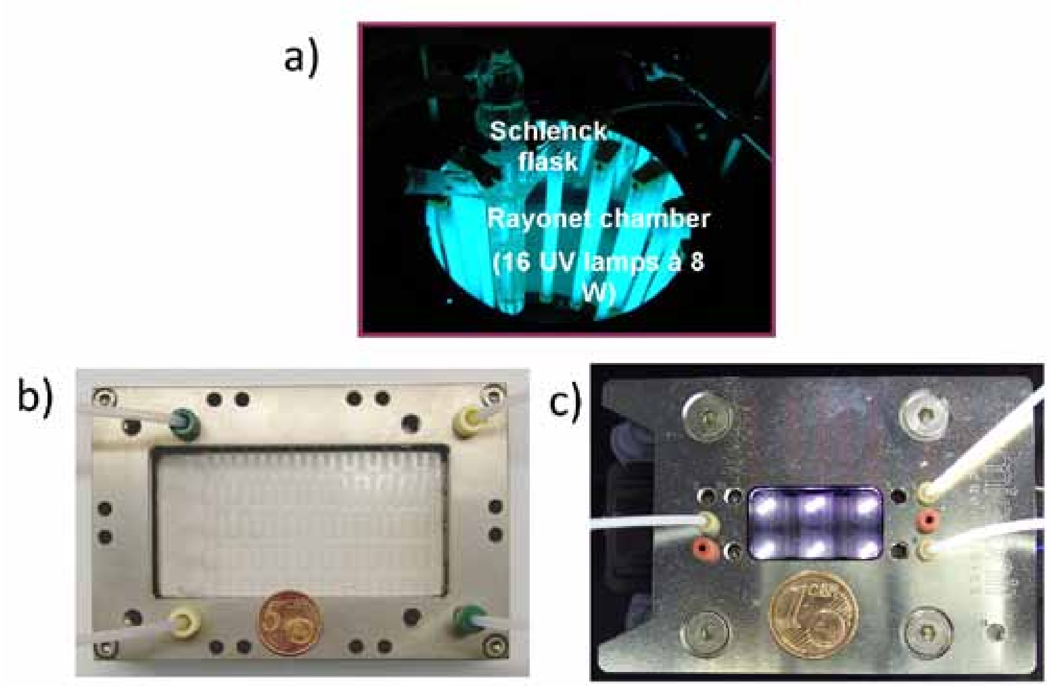


Figure 1.1. (a) Rayonet reactor which is a typical batch reactor system used in photochemistry (16 UVA lamps (16 × 8 W), 15mL volume; (b) The commercial Mikroglasdwell device (Mikroglas Chemtech) (5 UVA-lamps [5 × 8 W], internal volume 1.68mL); (c) Commercial Micronit Microfluidics reactor (6 × 75 mW LEDs, internal volume 13μL).

2 Stage 1

2.1 Comparison Study of the Mikroglas Dwell Device versus Rayonet Batch Reactor

The first noteworthy difference between the Rayonet and the mikroglas dwell device (manufactured by Mikroglas Chemtech*)* was the number of lamps used for irradiation. The Rayonet reactor functioned with 16 UVB fluorescent tube lamps, whereas the mikroglas dwell device used only 5. To investigate energy savings it was important to examine the reaction efficiency in the Rayonet when operated with the same number of lamps as the dwell device. One key advantage of the mikroglas dwell device in comparison to the Rayonet reactor is its perfect light penetration: the microstructured channel of the mikroglas dwell device has a large irradiation area (23 cm^2) over a small internal volume (1.68 ml). This parameter is very important for photochemical reactions as a larger irradiated surface provides more light to the reaction media. Moreover, the mikroglas dwell device channel is fabricated in the Foturan glass plate, which is UV transparent and additionally supplies light distribution that surrounds the channel. In contrast, the conventional Schlenck flask (100 ml and 50 ml volume), which is used as the reaction vessel in the Rayonet reactor, has an irradiation surface of only 274.31 cm^2 and 85.41 cm^2, respectively. This creates a 5 to 8 times smaller irradiated surface to volume ratio for the Schlenck flasks compared to the mikroglas dwell device channel. Furthermore, a significant influence on the photoreaction efficiency is the light source used per area unit. Thus, 5 fluorescent tube lamps of a mikroglas dwell device provide more light energy to the solution in a microchannel (1.74 W cm^{-2}) than 16 Rayonet lamps (0.47 or 1.50 W cm^{-2}) provide to a Schlenck flask. The irradiated area to volume ratio for the Schlenck flask compared to the mikroglas dwell device is 171 m^2 m^{-3} to 1369 m^2 m^{-3}. A comparison of the penetration profiles in acetone solution (Fig. 2.1a) for the microchannel (mikrolas dwell device) vs. the Schlenck flask (Rayonet reactor) reveals clearly that the narrow depth of the microchannel (0.5 mm) allows extensive penetration of light, despite the high

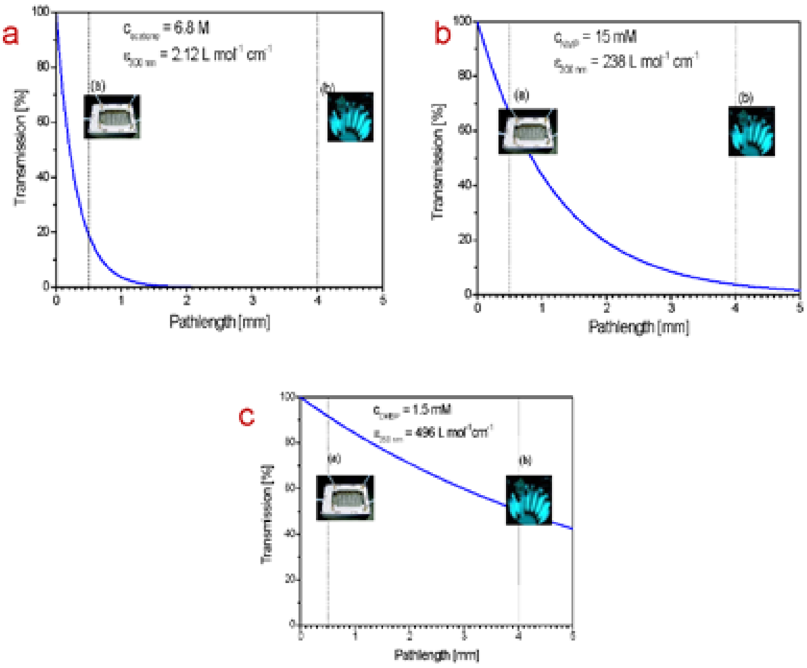


Figure 2.1. (a) Light-penetration profile for a 6.8 M acetone solution at 300 nm; (b) Light-penetration profile for a 15 mm nmP solution at 300 nm; (c) Light-penetration profile for a 1.5 mm - solution at 350 nm dimethoxybenzophenone (DMBP). The vertical broken line (a) represents the path length in the mikroglas dwell device and the dotted line (b) the effective path length in the Schlenck flask.

concentration of acetone (6.8 M). In contrast, complete absorption of light is achieved in the Schlenck flask with an average path length of about 4 mm (considering a circular arrangement of 16 lamps around the cylindrical vessel incorporated with a cold finger).

To compare the efficiency of the different photoreactors it is necessary to use the concept of Space-Time-Yields (STY). Space-Time-Yields are dependent on the reactor geometry and are determined by the following equation (Eq. 2.1):

$$STY = n_R / (V_R \times t) \qquad \text{(Eq. 2.1)}$$

where n_R is the amount of reactant that is converted to product within reactor volume (V_R) and (t) is irradiation time (Fig 2.1).

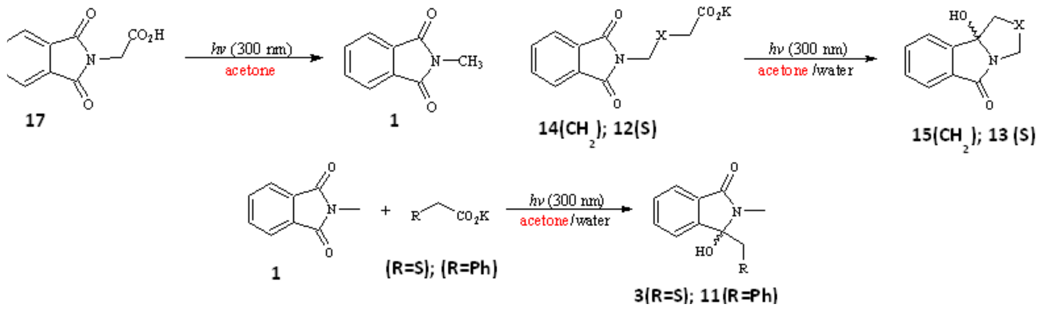
2.2 Results for the Reactions with Phthalimide in a Rayonet Reactor vs Mikroglas Dwell Device

Scheme 1 outlines the series of reactions (Hatoum et al., 2009a; Hatoum et al., 2009b; Griesbeck and Oelgemöller, 2000) that were screened in both the batch reactor and the mikroglas dwell device. Table 2.1 depicts the STY comparisons for all reactions conducted.

It is quite apparent from the tabulated results that the *mikroglas dwell device outperforms the batch reactor based on STYs*. Among all transformations that were studied the photobenzylation to **11** furnished the highest STY of *ca.* 0.69 after only 21 min.

On the back of this success with the mikroglas dwell device, it was decided to further ‘microscale’ the chemistry by employing a commercially available microchip (manufactured by Micronit Microfluidics BV). A microchip reactor was set-up at Dublin City University (DCU) and is shown in Fig. 2.2.

The chemistry used to evaluate the microchip reactor performance was the photoinduced addition of isopropanol to 2(5H)-furanones which is an attractive complement to the Michael addition reaction (Scheme 2) (Jansen and Ferringa, 1995; Hoffman, 1994). In contrast to the C-C bond formation via typical thermal Michael addition reactions, the arrangement of the same bond type via photoaddition of radicals to α,β-unsaturated carbonyl compounds represents a more environmentally friendly procedure with respect to high atom efficiency and the elimination of catalysts. The generation of the corresponding radicals is entirely



Scheme 1. Phthalimide reactions examined in the current project.

Table 2.1. Space-time yields (STY) for five acetone-sensitised photodecarboxylation reactions.

Reactor	Time [min.]	STY [mmol L^{-1} min^{-1}] Reaction				
		1 + 8a → 3	1 + 10 → 11	12 → 13	14 → 15	17 → 1
Rayonet	21	0.14	0.66	0.26	0.33	0.14
Dwell device	21 (175^{b})	0.24	0.69	0.28	0.24	0.31
Rayonet	40	0.17	0.38	0.22	0.20	0.15
Dwell device	40 (333^{b})	0.25	0.38	0.26	0.26	0.28
Rayonet	60	0.22 (0.04^{a})	0.25 (0.07^{a})	0.18 (0.05^{a})	0.17 (0.05^{a})	0.15 (0.06^{a})
Dwell device	60 (500^{b})	0.25	0.25	0.20	0.19	0.23

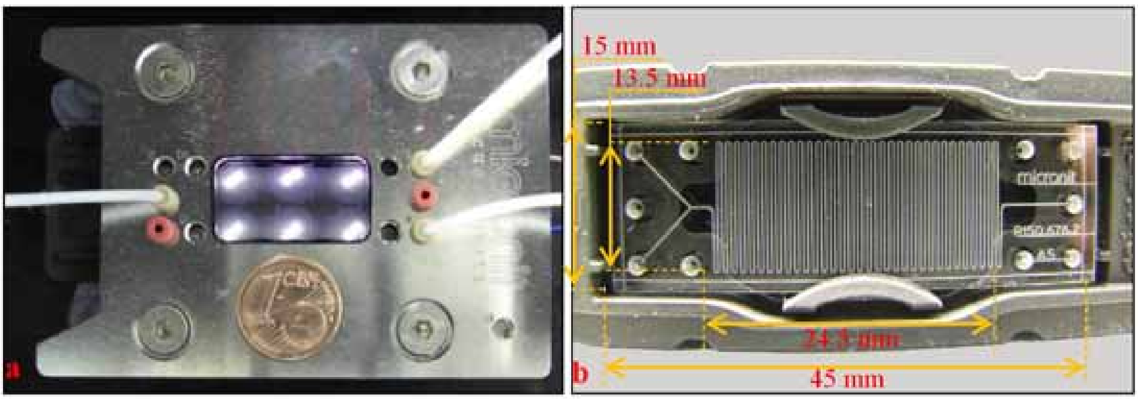
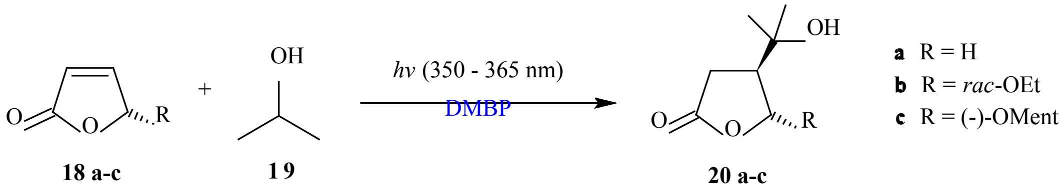


Figure 2.2. Microchip by Micronit Microfluidics: (a) compared to 1 cent coin; (b) glass plate with embedded reaction channel.



Scheme 2. Photo-induced addition of isopropanol to 2(5H)-furanones.

controlled by the 'flick of a light switch'. Radicals that are required for this phototransformation could be generated directly from an alcohol solvent, and acetone could be used as the photosensitiser (Scheme 2)

The volume of the microchip reaction vessel was just 13 µl. Another key difference between the microchip set-up and the previously used Rayonet and mikroglas dwell was the type of light source employed for irradiation. In the microchip system an array of 6 × 365 nm low-energy high-power LEDs were used, while in all previous set-ups fluorescent tube lamps were utilised.

The results for the photoinduced addition of isopropanol to 2(5H)-furanones in the microchip reactor are outlined in Table 2.2; for comparison, the same reaction was carried out in the mikrolas dwell device and these results are listed in Table 2.3.

Table 2.2. Results obtained in the LED-driven microchip.

Entry	Flow rate, [µl/min]	Residence time [min]	Conversion [%][a]		
			R = H (20a)	R = OEt (20b)	R = OMent (20c)
1	13	1	58	60	59
2	5.2	2.5	89	100	100
3	2.6	5	100 (90[b])	100 (90[b])	100 (87[b])
4	0.65	20	100	–[c]	–[c]

[a] Determined by ^{1}H-NMR spectroscopy; [b] conversions under batch conditions in the Rayonet reactor; [c] not determined.

Table 2.3. Results obtained for the microdwell reactor.

Entry	Flow rate, [ml/min]	Residence time [min]	Conversion [%][a]		
			R = H (20a)	R = OEt (20b)	R = OMent (20c)
1	0.336	5	81 (90[b])	99 (90[b])	98 (87[b])
2	0.168	10	100	100	100

[a] Determined by ^{1}H-NMR spectroscopy; [b] conversions under batch conditions in the Rayonet reactor; [c] not determined.

Complete conversions were obtained at 2.5 min for 5-alkoxy-2(5*H*)-furanones **18b** and **18c** (Table 2.2, entry 2) and at 5 min for unsubstituted 2(5*H*)-furanone **18a** (Table 2.2, entry 3). In contrast, the equivalent experiments performed in the Rayonet reactor and under continuous-flow conditions in the mikroglas dwell device gave incomplete conversion rates for the same residence time of 5 min.

The microchip is indeed superior to both the Rayonet and mikroglas dwell with respect to shorter reaction times and higher yields.

2.3 Critical Evaluations of the Commercially Available Microflow Reactors

One essential drawback of the microreactor setup(s) is the long experimental time required to pump the entire reaction mixture and additional solvent for ‘wash-out’ through the microchannel. Thus, over 2 hours (175 min) are needed to transfer 14 ml (reaction mixture 10 ml and solvent 4 ml) of liquid through the mikroglas dwell device microchannel at a flow rate of 0.08 ml/min, which corresponds to a residence time of 21 min. For a prolonged irradiation time of 1 hour the experimental time is significantly extended to 8.5 hours.

The significant impact of continuous flow reactors on improved reaction efficiency was demonstrated clearly in nearly all experiments, with cleaner products (no or few impurities) and higher yields. The reason for cleaner product production in comparison to the Rayonet reactor is that exhaustive irradiation in the Rayonet reactor (transmission more than 50%) results in the photoreduction and photopinacolisation of some of the sensitisers used (for example, dimethoxybenzophenone [DMBP]). Whereas in the microreactor, the surplus amount of sensitiser was continuously removed from the irradiated area. Consequently, the side reactions of the sensitiser – photoreduction and photopinacolisation – are reduced significantly in the microreactor experiments.

However, the above-described experimental platforms of the mikroglas dwell device and the LED-microchip are commercially available systems and thus the design and parameters of their reaction channels or vessels were fixed and pre-set by the manufacturer. Frequently, such parameters do not match the requirements for planned experiments and the project team found itself limited by the available commercial platforms. For example, the path length of the reaction channel was confined strictly by the size of the irradiation plate where the channel was embedded. Moreover, parallel experiments or experimental scale-up could not be achieved with these microreactors without purchasing more pumps and costly chips (price of a mikroglas dwell device is €4,000 and price of a single microchip is about €1,000).

At this point in the project the design of a new *dual-capillary reactor* was initiated.

2.4 The Creation of the Dual-capillary Photoreactor

This new design for the dual-capillary reactor is based on a three-dimmensional coil platform, which is a departure from the traditional two-dimmensional square chip. In the case of the coil platform the dimensions of the reactor are limited by the length of the lamp used and not by the size of a window plate, as is the case with the dwell and microchip reactors. Furthermore, it is also possible to introduce more than a single reactor channel – for example, two individual channels can be used. For this new platform to be successful the reactor channel must be composed of a transparent, flexible and chemically stable material. It was found that polytetrafluoroethylene (PTFE) capillaries meet all of these needs. Tetrafluoroethylene capillaries are UV transparent, chemically resistant flexible and *cheap*, offering a suitable alternative to common silicate reactor channels. The price for PTFE capillaries is just €80 for 100 metres; furthermore, PTFE capillaries are available in various diameters and wall thicknesses. One key design difference between the new prototype reactor and the commercial reactors is that water will be replaced as a coolant by simply employing a low-energy fan.

A dual microcapillary reactor (Fig. 2.3) was designed in-house by Dr Alexander Yavorskyy. This photoreactor was constructed to demonstrate the potential of microstructured devices for product-scale and parallel synthesis.

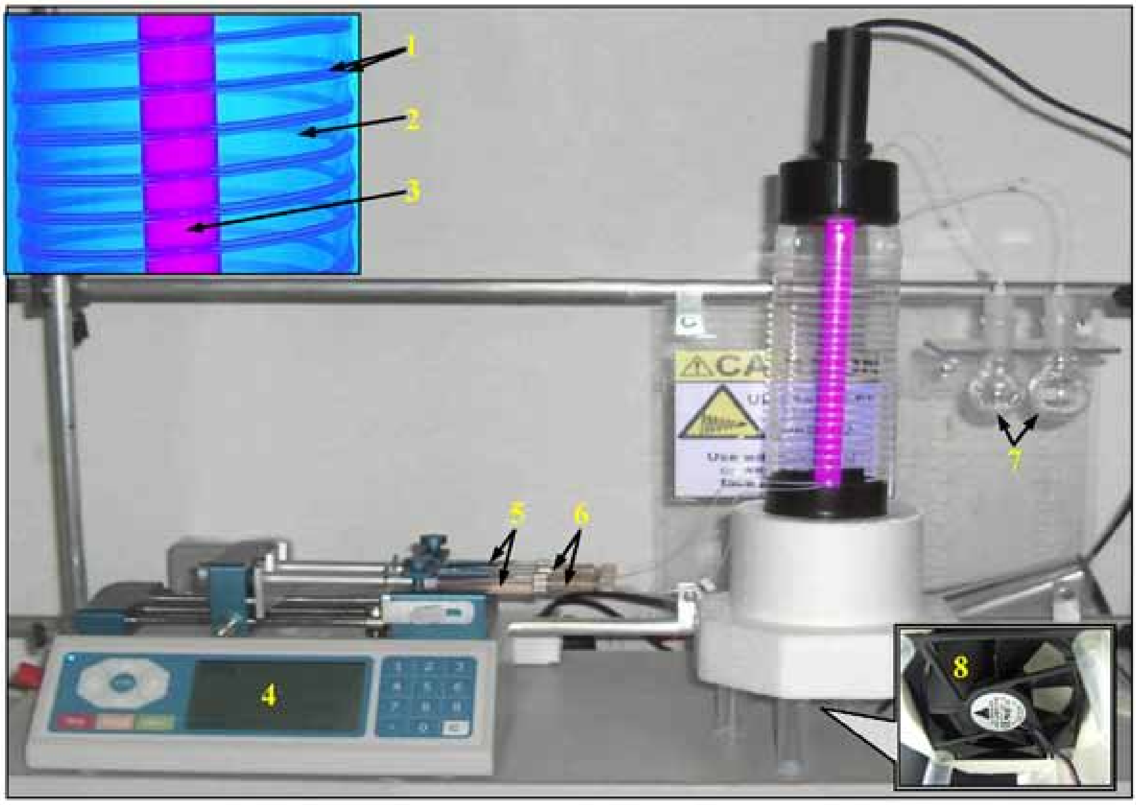


Figure 2.3. Dual-capillary microreactor setup: (1) two parallel polytetrafluoroethylene (PTFE) capillaries; (2) Pyrex glass cylinder; (3) UVA lamp; (4) programmable dual-syringe pump; (5) two syringes for 5 ml; (6) two PTFE adaptors; (7) collection flasks; (8) cooling fan.

The new reactor design was screened using the photoinduced addition of isopropanol to 2(5H)-furanones. A comparison of the performance of the reactors (commercial and dual-capillary) used in the photoaddition of isopropanol to 2(5H)-furaones is shown in Fig. 2.4. The LED-microchip yielded the highest conversions in the shortest residence times. Both the commercially available mikroglas dwell device and the new dual-capillary flow reactor showed similar efficiency and almost complete conversions for a residence time of only 5 min, which is outstanding.

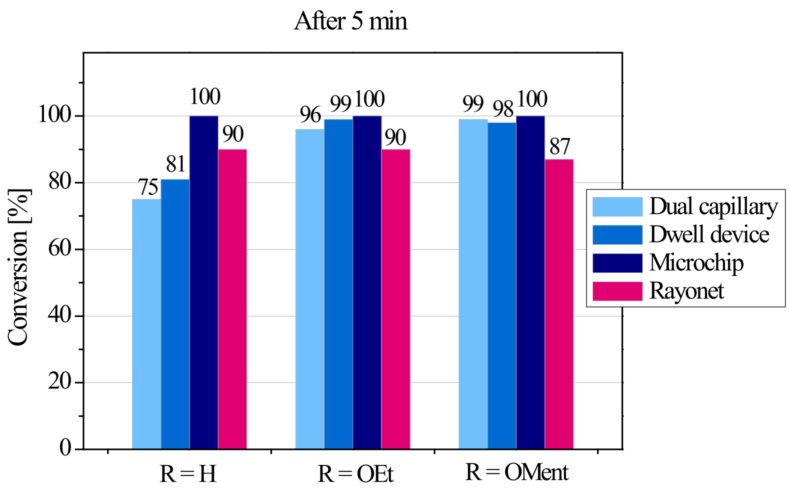


Figure 2.4. Comparison of 2(5H)-furanones 18a–c conversion rates in different experimental set-ups at fixed residence time of 5 min.

Figure 2.5. (a) Multi-microcapillary tower set-up: (1) ten parallel fluorinated ethylene propylene (FEP) copolymer capillaries; (2) two Pyrex glass cylinders wrapped with five FEP capillaries each (towers); (3) two UVA fluorescent lamps; (4) black paper membrane; (5) programmable syringe pump; (6) ten syringes for 10 ml each; (7) ten polytetrafluoroethylene (PTFE) shut-valves; (8) ten collection flasks; (9) two cooling fans; (10) styrofoam base; (b) multi-microcapillary reactor protected from ambient light during the experiment: (11) black fabric shutter; (12) black paper shields; (13) five PTFE adaptors.

The highest efficiency of the studied photochemical reactions was again with the LED-microchip: its small size and reaction volume of just 13 µl makes the LED-microchip an advantageous system for pharmaceutical research and development, where only small amounts of materials are required for biological screening.

However, if the desired product needs to be produced in gram-scale quantities we believe that the dual-capillary flow reactor has potential based on these results. The dual-capillary flow reactor, as a prototype, has shown excellent potential for production scale-up.

2.5 The Design and Evaluation of a New Multi-capillary Flow Reactor

Encouraged by the simplicity of the dual-capillary flow reactor design and its high efficiency, it was decided to build on this work further. As Fig. 2.3 shows, the original design of the dual-capillary flow reactor, although outstanding in performance, allows room for improvement. Firstly, the irradiated area of the glass cylinder was not optimally used. More than 5 mm of vacant space was left between each of the windings of the PTFE capillaries. Secondly, the length of the utilised lamp for irradiation was just 26.5 cm: there are equivalent lamps available on the market that are longer (60 cm) and therefore offer a longer capillary length.

Considering the above-mentioned two points it was possible to construct a new *multi-microcapillary flow reactor tower* (Fig. 2.5) which was also designed by Dr Alexander Yavorskyy. Again, *water is eliminated as a coolant*.

As can be seen in Fig. 2.5 and from the description of the experimental set-up, the new multi-microcapillary flow reactor tower has excellent potential for:

- Performing ten parallel photochemical syntheses simultaneously;
- Fast optimisation for any single experimental procedure;
- Synthesis of small compound libraries (for use in drug development);
- Gram-scale production and validation/standardisation of photochemical processes (manufacturing and process optimisation).

One of the main purposes of the tower reactor was its application for parallel experiments. Therefore, it was important to show that both towers and all ten capillaries were working with the same efficiency. To realise this task, the 4,4’ DMBP sensitised photoaddition of isopropanol to unsubstituted 2(5*H*)-furanone **18a** was tested simultaneously in all capillaries at a fluid flow rate of 1 ml/min, which corresponded to a residence time of 5 min. The conversion rates of **18a** were similar for all capillaries when the reactions were run simultaneously and were generally in the range of 67–73%. The standard deviation of conversion was just 3.2% between the different capillaries. This achievement demonstrates that the results obtained in the tower reactor are highly reproducible between the ten capillaries with a 4.5% relative standard deviation (RSD). Moreover, excellent reproducibility was observed, not only between the individual capillaries but also between the independent experiments.

2.6 Reaction Scale-up with the New Multi-capillary Reactor – Toward Process Chemistry

The single experimental capacity of the tower reactor was 100 ml of test solution, which is equivalent to the typical capacity of a Schlenck flask.

In order to evaluate the energy efficiency of the multi-capillary reactor and compare it to that of the conventional Rayonet reactor, the energy consumption per hour of operation was measured using a commercially available domestic electricity meter. The Rayonet reactor (with 16 lamps) consumed 0.179 kW/h (Table 2.4, entry 1) which is almost three times larger than the sum of the energy consumption (0.063 kW/h) for all of the devices involved in the multi-microcapillary tower reactor set-up (Table 2.4, entry 2). However, it is important to note that the total operation time of both systems for the production of the same amount of product was not equivalent. For example, in the multi-capillary reactor, the production of 451.7 mg of product **20a** the operation time was 40 min (residence time just 10 min). In the Rayonet reactor the residence time was always equivalent with the operation time and the same amount of product could be produced after 20 min. Therefore, to determine if there is real difference in energy consumption between the multi-capillary reactor and the batch reactor, the quantity of energy used by each system to produce 1 kg of product was calculated. The numbers obtained show that in the multi-capillary tower reactor, despite its longer operation time, 1 kg of product could be produced with 30% of the electrical energy compared to the batch reactor (Table 2.4). Moreover, due to the significant generation of heat by the 16 lamps in the Rayonet reactor, cooling water is required. The water consumption was subsequently determined for the Rayonet reactor to be to be 1–4 L/min. In the case of the tower reactor, the fluorescent lamp generated far less heat and it was possible to cool the tower reactor by using simple cooling fans – again, *no water is required.*

Table 2.4. Comparison of energy consumption by the batch Rayonet reactor and continuous flow multi-capillary system.

Entry	Appliance	Energy consumption, [kW/h]	Operation time, [h][a]	Total energy consumption, [kW][b]	
1	Rayonet reactor	0.179	737.9	132	
2	2 fluor. lamps	0.046	1475.9	67.9	93
	2 cooling fans	0.009		13.3	
	Syringe pump	0.008		11.8	

[a] Operation time to produce 1 kg of product; [b] total energy consumption to produce 1 kg of product.

3 Stage 2

3.1 Introduction

Dye-sensitised photooxygenations involve the reaction of photochemically produced singlet molecular oxygen with unsaturated compounds to give rise to oxygen-peroxide containing molecular entities. The three main classes of photooxygenations involving singlet oxygen are: (i) ene-reactions (Schenck-ene reaction), (ii) [2+2]-cycloadditions and (iii) [4+2]-cycloadditions. *Photooxygenations* are a versatile, clean alternative to oxidations with metal oxides since only catalytic amounts of an organic dye and air are required (Clennan and Pace, 2005). Furthermore, due to the absorption of the dyes in the visible region of the solar spectrum these reactions can potentially be performed solarchemically with sunlight: however, most photooxygenations are carried out 'indoors'. A typical indoor photooxygenation set-up is shown in Fig. 3.1.

Transferring bulk photooxygenations, as shown in Fig. 3.1, to a microflow platform offers the following advantages:

- Potential elimination of water as a coolant;
- Peroxides are an explosion hazard by using a microflow platform only small quantities of peroxide is being produced at any one time which is in contrast to the batch system;
- Low-energy light sources can be used in place of halogen lamps due to the shorter path length in a microchannel;
- Schlenck flasks in combination with halogen lamps have unfavourable light penetration properties;
- Halogen lamps can generate large amounts of heat that can facilitate thermal decomposition reactions.

At the outset of this project, two microflow devices were commercially available; the mikroglas dwell device (as described above) and the falling film reactor (FFMR-standard by IMM, Mainz). Both systems were initially examined using the [4+2] photooxygenation of alpha-terpinene to ascaridiole as the model reaction (Scheme 3).

3.2 Evaluation of the Commercially Available Falling Film Reactor and Mikroglas Dwell Device

The initial stage was the construction of the falling film reactor system, which is shown in Fig. 3.2.

The results obtained showed that the investigated photochemical reaction is very fast, and complete conversion could be achieved in the falling film microreactor after a residence time of only 32 seconds. The highest selectivity to ascaridole of 80% to 90% was reached at an α-terpinene concentration of 5 mmol at room temperature (20°C).

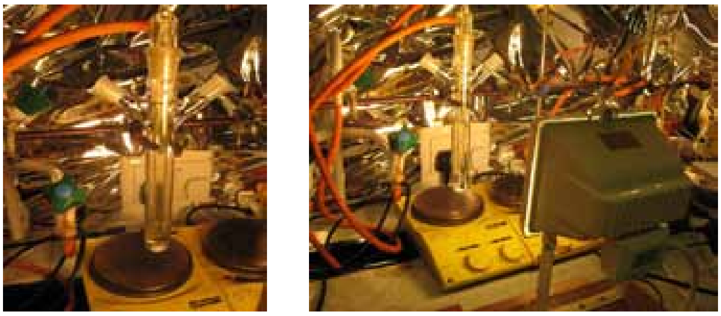


Figure 3.1. Indoor photocatalytic reaction set-up with Schlenck flask, and inserted cooling finger (water is used as coolant) situated over a stirring plate with irradiation by a Halogen lamp.

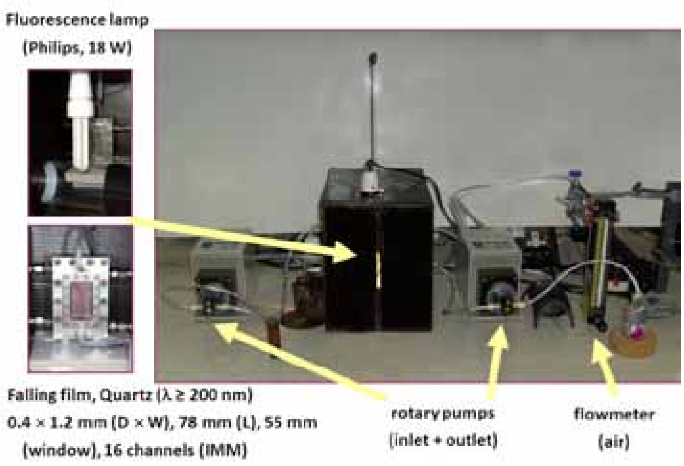
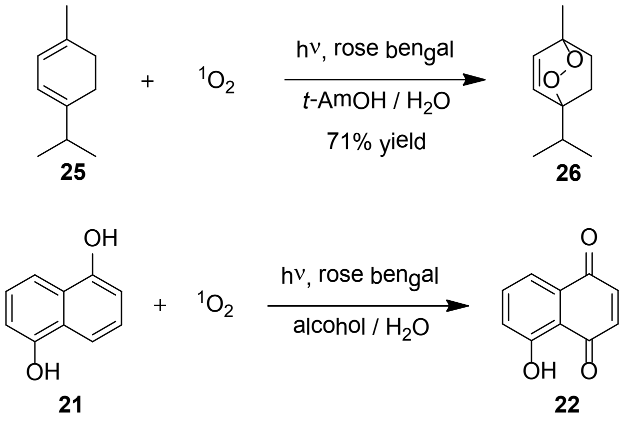


Figure 3.2. Falling film reactor set-up at Dublin City University.

Photooxygenations were then attempted in the mikrodlas dwell device using the Luzchem panel with fluorescent lamps. The reaction that was studied was the photooxygenation of 1,5-dihydroxynaphthalene (**21**) to give juglone (**22**) (Scheme 3).



Scheme 3. Photooxygenation of α-terpinene (25) to ascaridole (26) carried out in the falling film reactor and the photooxidation of 1,5-dihydroxynaphthalene (21) to give juglone (22).

The experimental procedure required the reaction solution to be air saturated before being pumped through the reactor. Unlike the falling film reactor there is no gas-film/liquid interface in the mikroglas dwell device: therefore, the only source of oxygen is from dissolved air. Rose bengal was used as the sensitiser. Conversions of only 10% were achieved with a residence time of 42 min. It is evident that dissolved air may not be enough for efficient conversion in the mikroglas dwell device, and consequently further studies using this reactor were discontinued.

3.3 New Reactor Designs for Photooxygenations – The Bubble Reactor

Given the discovery that dissolved air in the reaction medium is insufficient for complete conversion in the mikroglas dwell device, it was envisaged that the design and construction of a new prototype reactor would afford:

- Continuous air supply;
- Optimum gas liquid interface (similar to falling film reactors);
- Optimum light penetration.

The design of the new photo reactor (Fig. 3.3) comprises a radiation-permeable (in this case 1.5 m long and 5–7 mm outside diameter providing up to 25 ml of reaction volume) glass tube that contains a reaction medium which is irradiated by two 60 W white fluorescent lights from both sides of the tubing. Photochemical reactions are carried out by pre-filling the reaction mixture to be irradiated into the glass tube using a specially adapted vacuum pump. For oxygenation reactions, an extra adjustment has been made to provide a continuous flow of air into the reaction medium through a specially designed capillary nozzle.

Advantages of the new white fluorescent lamp photoreactor are:

- Very cheap and easy to assemble design. Uses energy efficient and cost-effective 60 W domestic type fluorescent lamps. The unit could be easily disassembled for light-source replacement/change according to particular needs;

- The reaction volume of up to 25 ml provides sufficient quantities of product (for research and semi-production purposes);
- Suitable for a wide range of reactions, including reactions that require (aeration) oxygenation;
- The inline detection cell (colorimeter) can be integrated into the system for accurate metering, conversion quantification and product-quality control;
- *No water is required for cooling.*

The air flow pattern had a significant influence on the photooxygenation reaction. Bubble flow (small bubbles) conditions required prolonged irradiation times – many hours – in order to reach high conversions of **21**. In contrast, high to complete conversion values were achieved after just 1 hour under slug flow conditions (Fig. 3.4). The different performances between reactions conducted in slug flow and bubble flow was striking. The slug flow pattern results in the formation of a thin liquid film (<0.5 mm) along the side of the air bubbles (Fig. 3.4). Consequently, the specific surface area of the liquid phase is increased significantly which subsequently results in an improved mass transfer.

To evaluate this new reactor system, the photooxygenation of **21** using rose bengal as a sensitiser was selected as a model transformation. Using an irradiation time of 1 hour and an air flow rate of 20 cm^3/min, the reaction performed in the column reactor in aqueous isopropanol showed a conversion of 91% and gave an isolated yield of **22** of 54%. In contrast, the reaction in the conventional batch reactor (Schlenk flask and

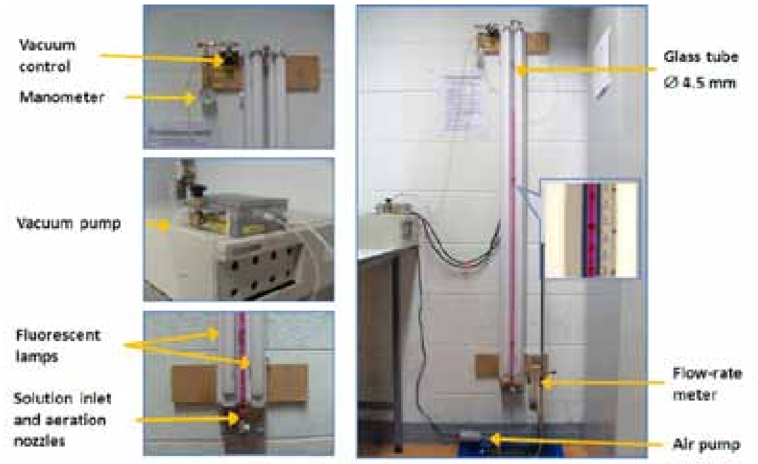


Figure 3.3. New glass column reactor.

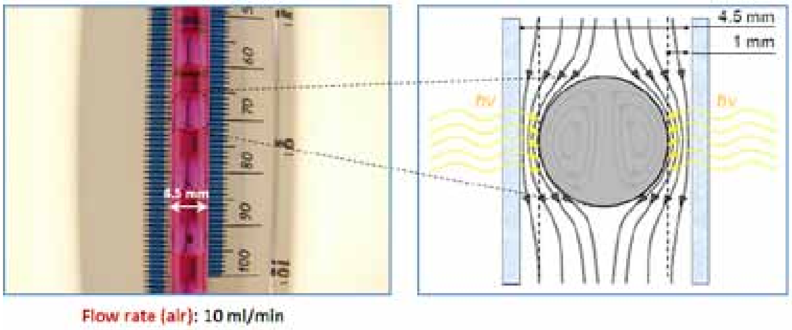


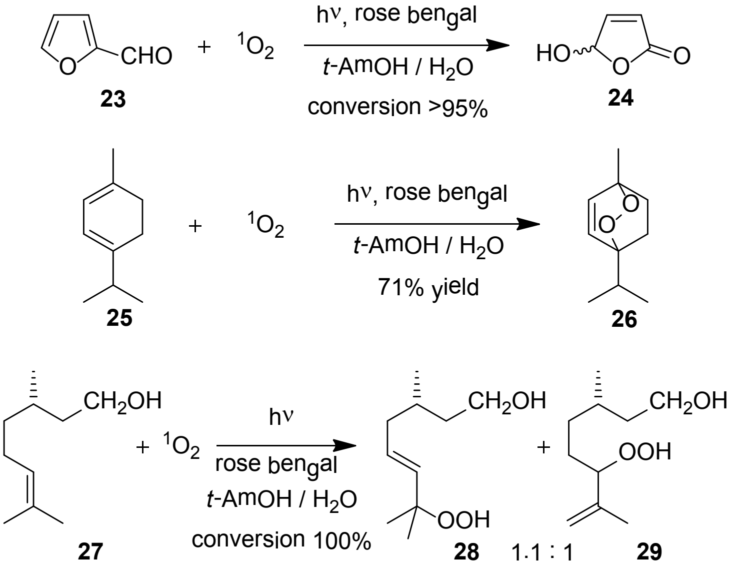
Figure 3.4. Images of the flow pattern formed inside the glass tube in different solvents (air flow rate: 10 cm^3/min; taken at a height of approximately 30 cm): (a) bubble flow in isopropanol/water (100 µm capillary); (b) slug flow in methanol/water (500 µm capillary); (c) slug flow in isopropanol/water (500 µm capillary); (d) slug flow in tert-amyl alcohol/water (500 µm capillary). (e) Representation of vertical slug flow pattern; (b) important dimensions.

halogen lamp, see Fig. 3.1) gave a conversion of 56% with an isolated yield for **22** of 39%.

The optimised irradiation conditions were subsequently transferred to other photooxygenation reactions (Scheme 4). The transformation of furfural **23** gave 5-hydroxyfuranone **24** in a conversion of >95%. Likewise, the [4+2]-cycloaddition of α-terpinene **25** gave ascaridole **26** in a yield of 71%. No trace of the commonly observed by-product *p*-cymene was detected in the crude product. The Schenck-*ene*-reaction of citronellol **27** is an important key-step in the industrial synthesis of the fragrance rose oxide. In the slug flow column reactor, complete conversion of **27** to a 1.1:1 mixture of the regioisomeric hydroperoxides **28** and **29** (the latter in a 1:1 mixture of diastereoisomers) was achieved within 1 hour. These examples clearly show the general suitability of the column reactor for preparative photooxygenations.

The efficiency of the reactor was furthermore evaluated using STY calculations. For the preparative irradiation performed in aqueous *tert*-amyl alcohol, a STY of 0.12 mmol/(L·min) was achieved.

In conclusion, the project team has developed an efficient and reliable column reactor for photooxygenation reactions. A slug flow pattern was easily achieved using an appropriate capillary for aeration of the reaction mixture. Superior conversions and yields were achieved because of the formation of a thin liquid film which allowed for an enlarged surface area, improved mass transfer and superior light penetration. Not only can this reactor now be used as a process system in the flow mode, but the team envisages that the 'bubble' concept will be applied in the future to the multi-capillary tower reactor which will aid in boosting the scale of the chemistry to that of a process reactor.



Scheme 4. Additional photooxygenations studied.

4 Concluding Remarks and Future Work

This project studied a series of homogeneous and heterogeneous photoreactions in a commercially available mikroglas dwell device, and a falling-film microreactor in order to evaluate the potential of micro-photochemistry. The project team also designed a new LED-driven microchip and applied it successfully to isopropanol additions to furanones. All results were compared to analogous experiments in conventional batch reactors. In all cases examined, the reactions performed in the chosen microreactors gave higher conversions or yields, thus proving the superiority of the microphotochemistry concept.

However, a major drawback to the commercially available microreactors was found – they have fixed-length reaction channels and are of a single-channel design. For this technology to be applied in process/ large-scale synthesis, 'numbering-up' – using an array of microreactors – is necessary. However, this strategy entails significant investment costs. To address the problem, the project team designed and tested a simple cost-efficient *continuous-flow dual microcapillary tower* that uses flexible FEP capillaries. The tower design also enables reactions to be carried out in parallel: this was demonstrated with the successful construction of a 10-capillary twin-tower which was tested for process optimisation, validation and library synthesis. In addition, a gram-scale product synthesis was performed in the multi-capillary tower reactor with a 30% energy saving compared to the batch reactor, and water was completely eliminated as a coolant, thus contributing to a greener chemical process.

The project team also demonstrated the value of the falling-film reactor in photooxygenation reactions. It found the falling film reactor not only to be far more efficient than the traditional batch reactor approach with respect to STY but that it also eliminates the danger involved in preparing large-scale quantities of peroxides, which is presently done in industry. With the success of the falling-film reactor the possibility of creating a new bubble reactor which can offer the benefit of microscale on a macroscale level was recognised. This newly designed reactor gave outstanding results with a broad cross-section of photooxygentation reactions. Furthermore, the team's newly designed reactor does not require a coolant, unlike the commercially available falling reactor, thereby reducing the environmental impact that is common with photooxygenation reactions.

The discoveries made in this project are now being applied to both the preparation of new materials (new arylated-fluoro phthalocyanines, application of silica and magnetic nanoparticles in photooxygenations) and further reactor development. Of particular note is the team's recent design change to the dual-capillary reactor, the 'bubble' concept of the bubble reactor has now been applied – by introducing a microcapillary air 'bleed' into the system allowing for efficient photooxygentation to be carried out under microflow conditions. Initial results indicate that this system has a performance equivalent to the falling-film reactor. This offers a cheaper, greener (no coolant) alternative.

This new breakthrough with photooxygenations will be transferred over to the new multi-capillary reactor, and an attempt to develop a photooxygenation process specific for industrial needs will be developed. The nanotechnology that the team will apply in its flow reactors involves the covalent immobilisation of sensitisers onto magnetic nanoparticles. It is believed that this approach will greatly improve existing technology since purification is still required to remove the photosensitisers from the photooxygentation reaction mixtures. By using sensitisers covalently bound to magnetic nanoparticles it will be possible to remove the sensitiser by simply applying a magnetic field. By eliminating purification, which can typically be a high-waste procedure with respect to materials and energy, the project team is reducing both the usage of valuable resources and the carbon footprint for the overall process. If successful, this will perfect new reactors and make them a highly attractive process tool for industry.

The next and final stage for this chemistry is industrial application. The new technology developed in this project makes photochemistry a far more attractive and *green* tool since there is no longer a need for: (i) high energy lamps or (ii) water as a coolant. In addition, high atom efficiency is guaranteed, thereby reducing waste by-products. All three achievements are in line with the policy outlined in flagship Europe 2020 and the EPA *2020 Vision* document.

Currently, there are companies in Ireland that are interested in peroxides (for polymerisation) that are prepared from renewable feed-stocks. The work reported here demonstrates that not only is it possible to achieve this goal, but that there is a ready-made green technology that can be adopted to industrial process needs. More funding would is required to launch this technology into industry, with the ideal situation being the setting up of a dedicated demonstration laboratory for industry to convince/convert them to this new technology. If this is not undertaken within the next two years the lead that we have created in green photochemistry in Ireland may be lost.

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Acronyms and Annotations

DMBP	4,4’-dimethoxybenzophenone
DCU	Dublin City University
FEP	Fluorinated ethylene propylene
LEDs	Light-emitting diodes
PET	Photoelectron transfer reactions
PTFE	Polytetrafluoroethylene
RSD	Relative standard deviation
STY	Space-Time-Yields

Appendix

Peer-reviewed Publications for Project Work

Parallel microflow photochemistry: process optimization, scale-up, and library synthesis, Alexander Yavorskyy, Oksana Shvydkiv, Norbert Hoffmann, Kieran Nolan, Michael Oelgemöller, *Organic Letters*, **2012, 14,** 4342–5.

Synthesis of Juglone (5-hydroxy-1,4-naphthoquinone) in a falling film microreactor, Oksana Shvydkiv, Michael Oelgemöller, Kieran Nolan, *Journal of Flow Chemistry*, **2012,** 2, 52–5.

Green photooxygenations in a bubble column reactor, Alexander Yavorskyy, Oksana Shvydkiv, Carolin Limburg, Kieran Nolan, Yan M. C. Delauré, Michael Oelgemöller, *Green Chemistry*, **2012**, 14, 888–92.

Microphotochemistry – a reactor comparison study using the photosensitized addition of isopropanol to furanones as a model reaction, Oksana Shvydkiv, Alexander Yavorskyy, Su Bee Tan, Kieran Nolan, Norbert Hoffmann, Ali Youssef and Michael Oelgemöller, *Photochem. Photobiol. Sci.*, **2011**, 10, 1399–404.

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Photosensitized addition of isopropanol to furanones in a 365 nm UV-LED microchip, Oksana Shvydkiv, Alexander Yavorskyy, Kieran Nolan, Ali Youssef, Emmanuel Riguet, Norbert Hoffmann, Michael Oelgemöller, *Photochem. Photobiol. Sci*. **2010,** 9 (12), 1601–3.

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Conference Presentations

‘Microphotochemistry-photochemistry in Microstructured and Continuous Flow Devices’, O. Shvydkiv, A. Yavorskyy, K. Nolan, M. Oelgemöller, 63rd Irish Universities Chemistry Research Colloquium 2011, University College Dublin, Dublin (Ireland), 23–24 June 2011.

‘Microphotochemistry-photochemistry in microstructured and continuous flow devices’, O. Shvydkiv, A. Yavorskyy, K. Nolan, M. Oelgemöller, , RSC Photochemistry and Photochemical Techniques meeting, University College Dublin, Trinity College Dublin, Dublin (Ireland), 16–18 May 2011 (Winner of Best Presentation Award for Postgraduate Students: Oksana Shvydkiv).

‘Micro-photochemistry – a New Resources-Efficient Synthesis Tool Approach’ O. Shvydkiv, A. Yavorskyy, K. Nolan, M. Oelgemöller, Green Chemistry in Ireland: including highlights of Environmental Technology projects funded by the EPA, Dublin City University, Dublin, Ireland, 15 April 2010.

‘Micro-flow photochemistry – new reactor design’, A. Yavorskyy, O. Shvydkiv, M. Macka, M. Oelgemöller, K. Nolan, EPA National Research Conference, Croke Park Conference Center, Dublin, Ireland, 23 June 2010, poster presentation

‘Microphotochemistry: Photodecarboxylations of Phthalimides and Photooxygenations of alpha-Terpinene as Model Reactions in Microstructured Reactors’, O. Shvydkiv, A. Yavorskyy, K. Nolan, M. Oelgemöller, Central European Conference on Photochemistry – CECP 2010, Bad Hofgastein (Austria), 8 February 2010.

‘Microphotochemistry – The Photochemistry of the Future?’, M. Oelgemöller, O. Shvydkiv, A. Yavorskyy, S. Gallagher, K. Nolan, 6th Asian Photochemistry Conference, Wellington (New Zealand), 14–18 November 2010.

Website

Micro-photochemistry – a New Resources-Efficient R&D Approach, Available at: http://www.dcu.ie/chemistry/m-PCC/

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomhnithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil, Pobal agus Rialtais Áitiúil.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail;
- scardadh dramhuisce.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

ENVIRONMENTAL PROTECTION AGENCY
PO Box 3000, Johnstown Castle Estate, Co. Wexford, Ireland
t 053 916 0600 f 053 916 0699
LoCall 1890 33 55 99
e info@epa.ie w http://www.epa.ie

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government