KATHOLIEKE UNIVERSITEIT LEUVEN

Process Intensification using light energy

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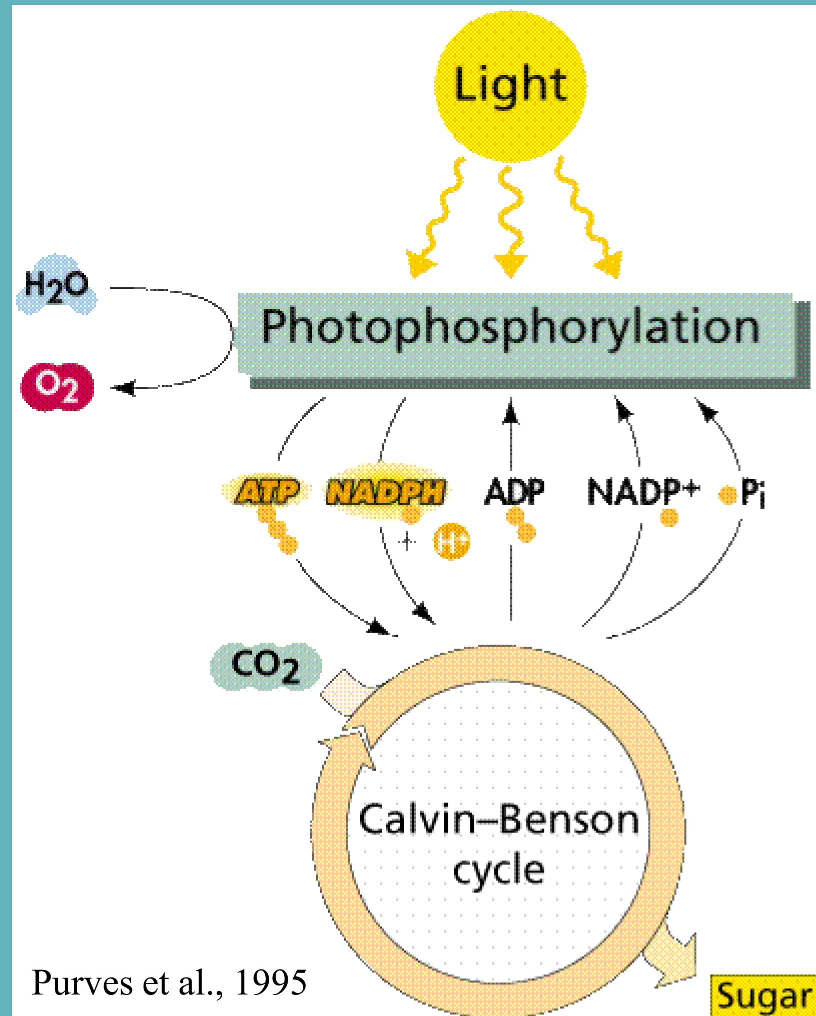
Content

- Photochemistry, photocatalysis, photosynthesis
- 3 case studies
  - Optical Fiber (Monolith) Reactor (OFMR)
  - Internally Illuminated Microreactor (IIMR)
  - Light Efficient Foils for open algae ponds (LEF)

Light

- Light = the main form of energy for plants



Purves et al., 1995

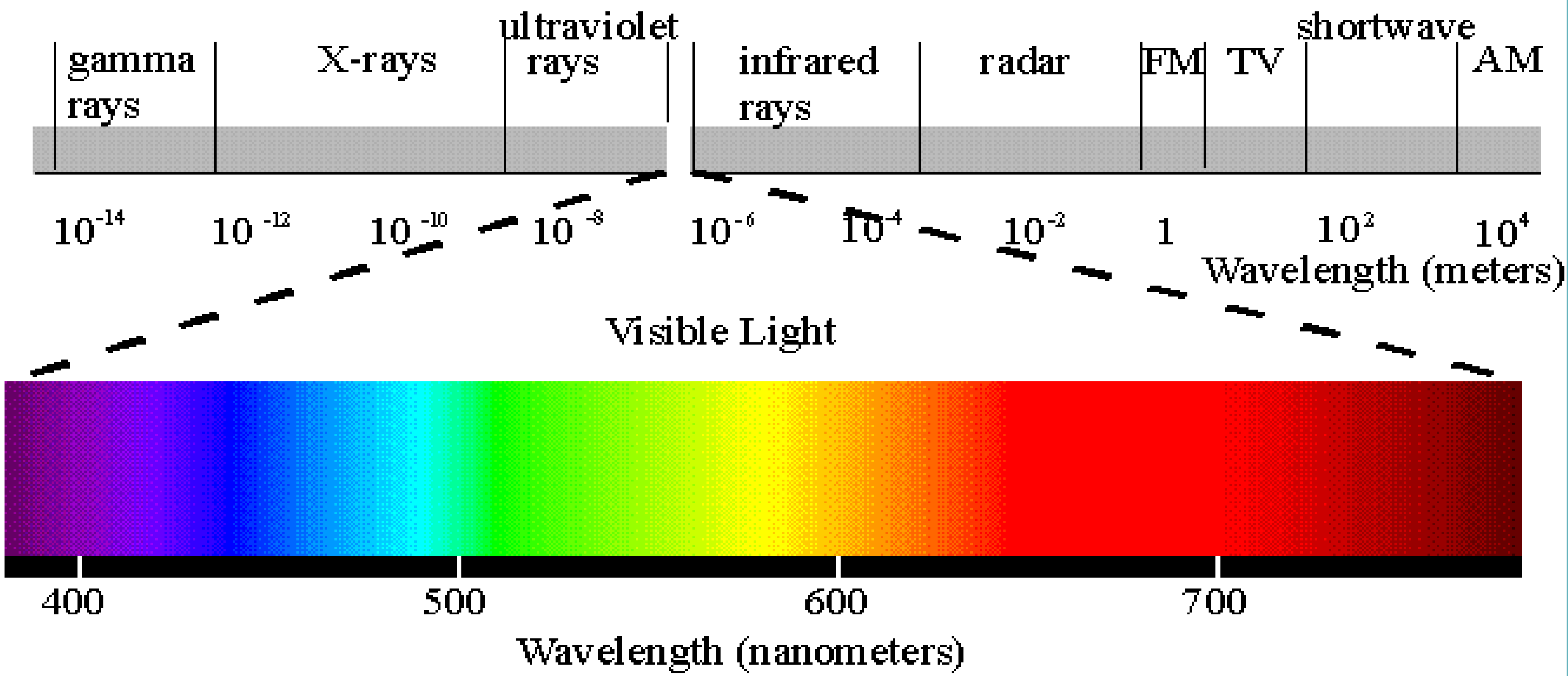
Light

- Light = an alternative form of energy for industry

Use of sunlight in photocatalytic pilot installation in Almeria, Spain (PSA, 2004)

Use of stripped optical fibers (TUD, 2006)

The Electromagnetic Spectrum



= Solar Energy

Photochemistry

Photochemistry can lead to more **sustainable** processes by:

- increased process selectivity to the required products
  - different chemistry
  - low/ambient process temperature

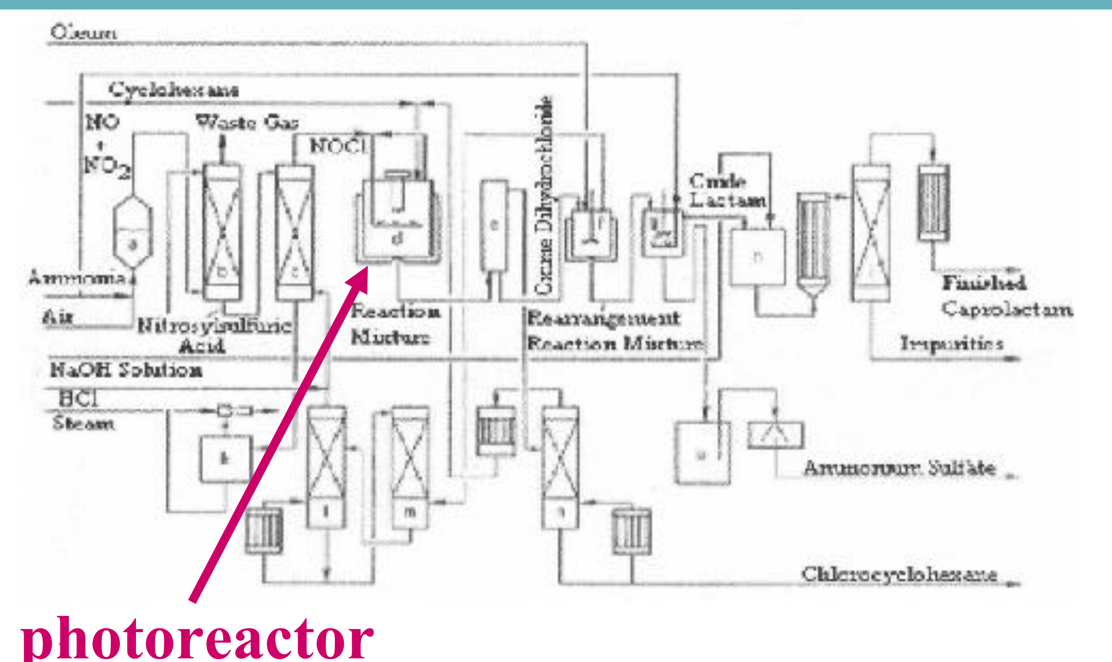
- decreased energy consumption in the process
  - low/ambient process temperature
  - use of solar light

Photochemistry in industry

Photochemistry is already implemented in industry, although limited

Some examples:

• photo-oximation of cyclohexane to cyclohexanone oxime (Toray, Japan)



• 170,000 ton/y (2003)

• conversion increases from 9-11% (others) to 80% (Toray)

• selectivity increases from 76-81% (others) to 86% (Toray)

• elimination of intermediate process steps

• from 1963 on

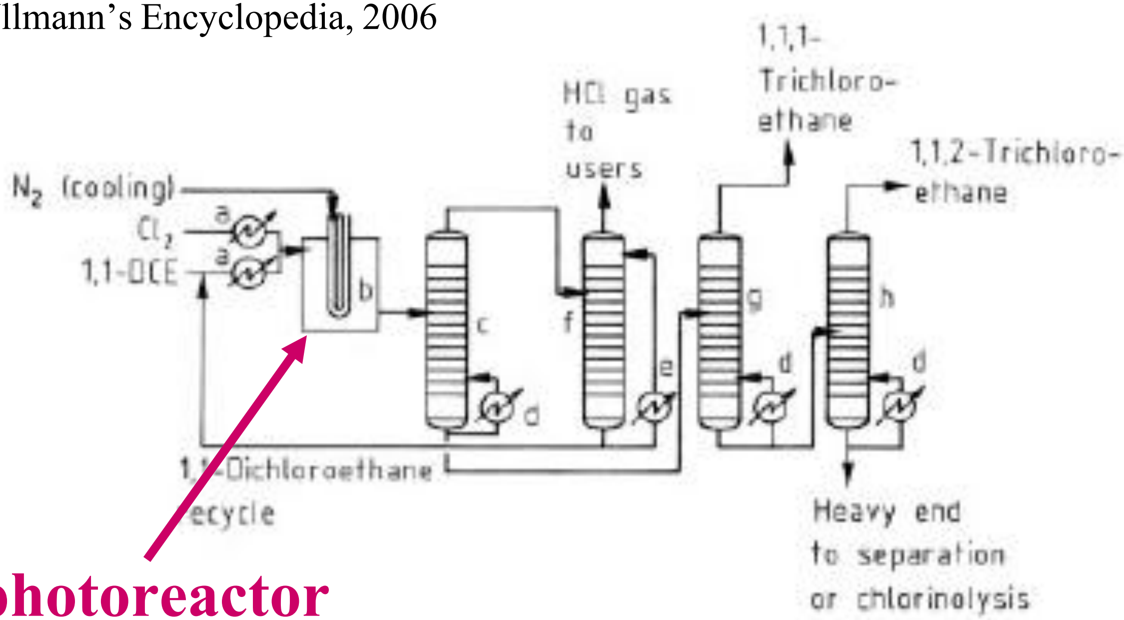
Photochemistry in industry

Photochemistry is already implemented in industry, although limited

Some examples:

• 1,1,1 trichloro-ethane from 1,1 dichloro-ethane

Ullmann's Encyclopedia, 2006



photoreactor

• 300,000 ton/y (1986)

• higher product yield, better selectivity than other processes

• lower process temperature than other processes (80-100°C vs. 350-450°C)

• main process route

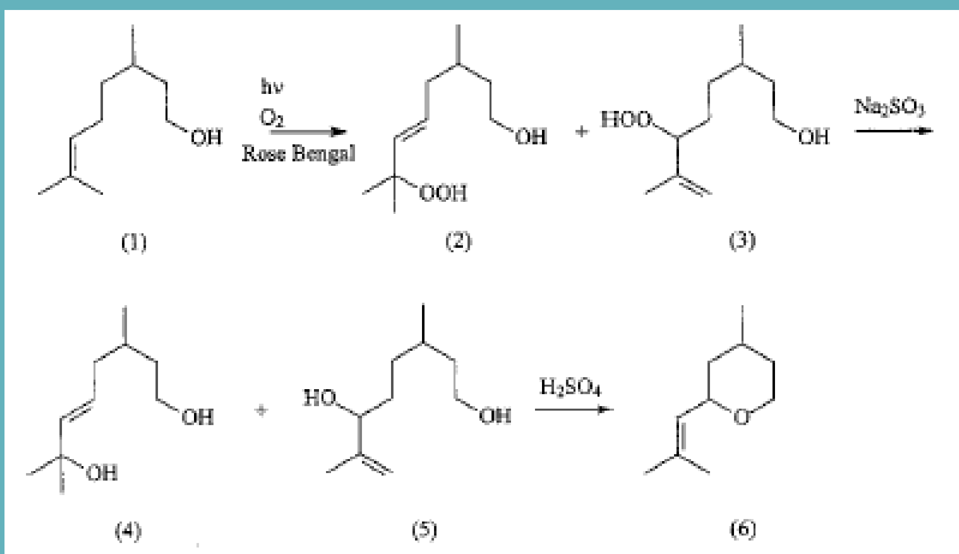
• 1950's to 1990's (production banned)

Photochemistry in industry

Photochemistry is already implemented in industry, although limited

Some examples:

• photo-oxidation of citronellol to rose oxide (Dragoco, Germany)



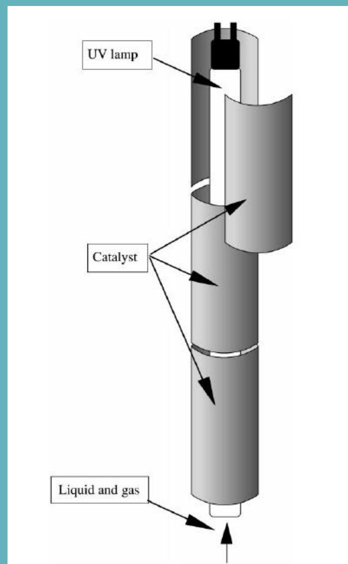
Monnerie & Ortner, 2001

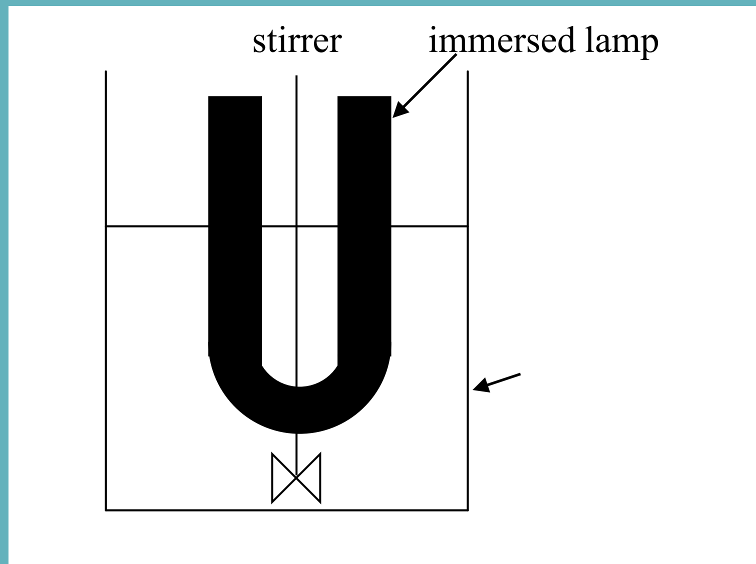
60-100 ton/y, main process route

Photochemistry in industry

Current design in industry:

slurry reactor / immersion reactor with pressure or excimer lamps



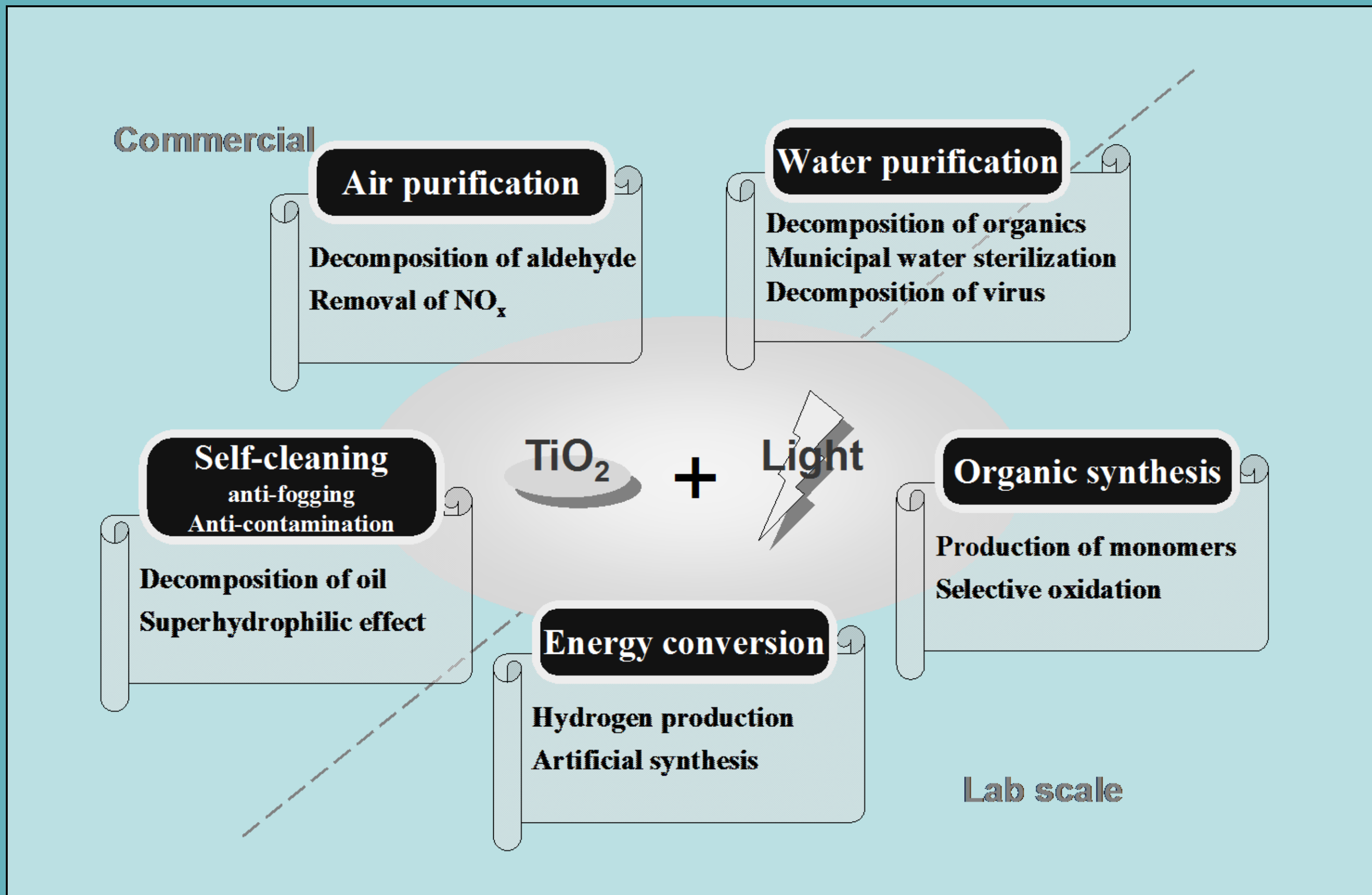


Photo(cata)lysis

- Photolysis
  - – No catalyst
  - – Deep UV (e.g. 250 nm) required – high energy

- Photocatalysis
  - – TiO2, ZnO, ... (doping)
  - – visible light + UV (e.g. 384 nm) – less demanding

Photocatalysis



Source: Guido Mul

Air Purification

$NO + O_2 \rightarrow NO_2 \rightarrow NO_3^-$

Source: Guido Mul

Water Purification

H_2O_2 + 'CH' → CO_2 + H_2O

No catalyst

Andijk

O_2 + 'CH' → CO_2 + H_2O

TiO_2

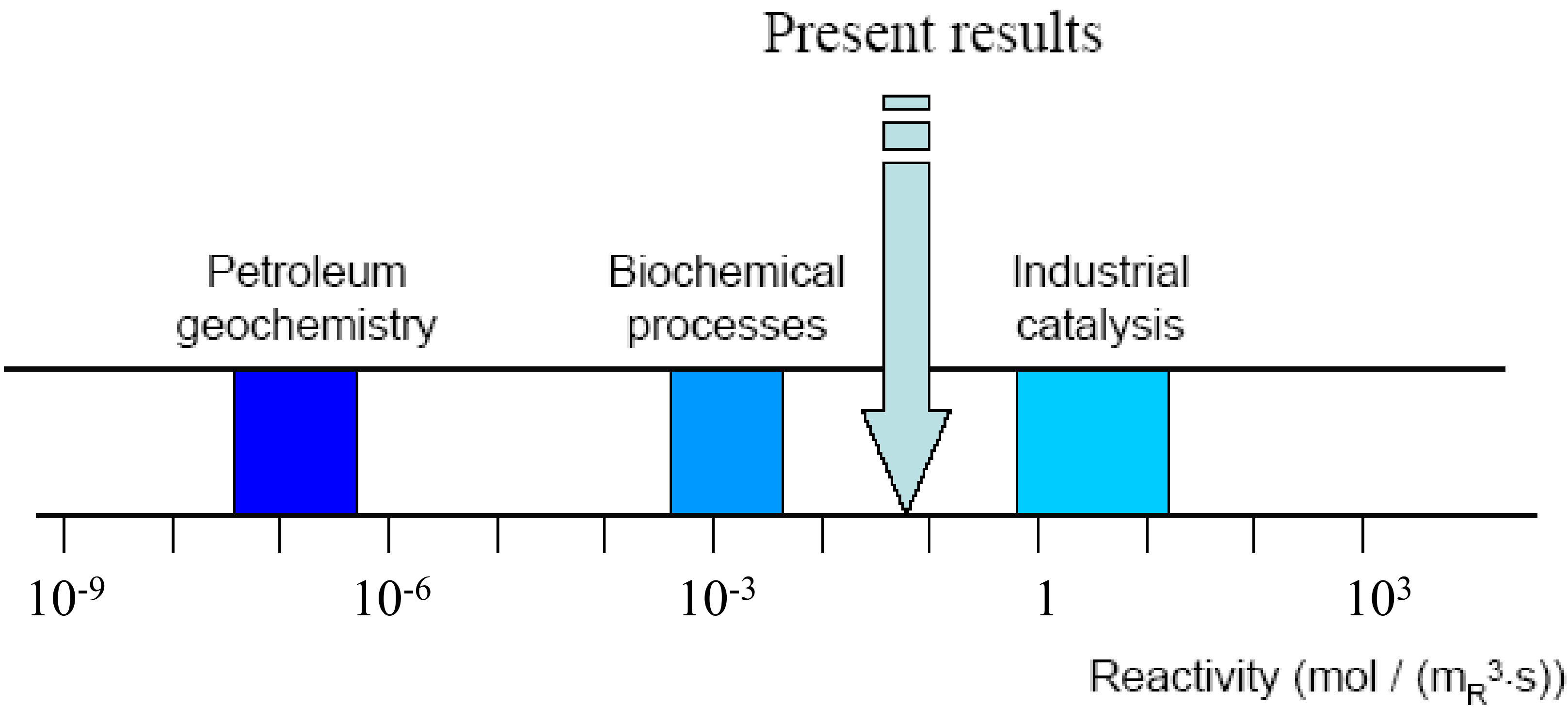
Spain

Source: Guido Mul

Photocatalysis in industry

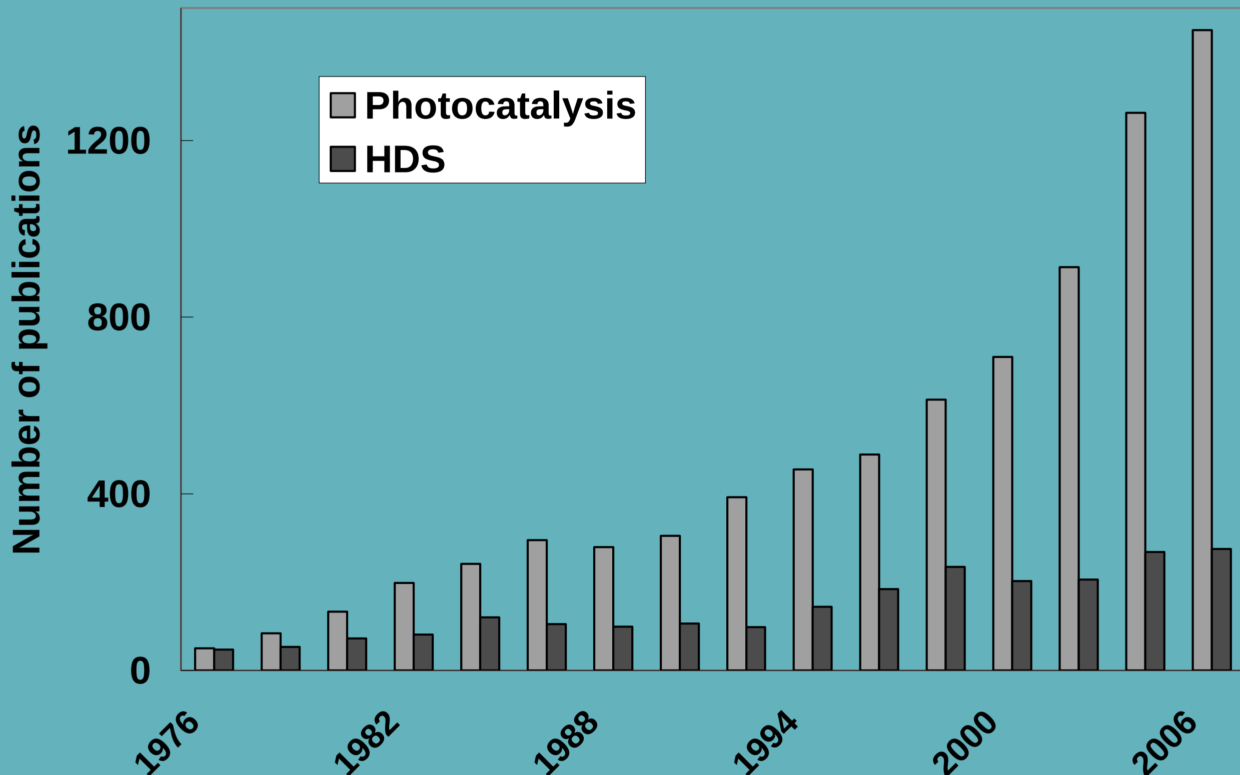
However, window of reality

Mul & Moulijn, 2006



Aim = 100 to 1000 times better → ***Intensification needed!***

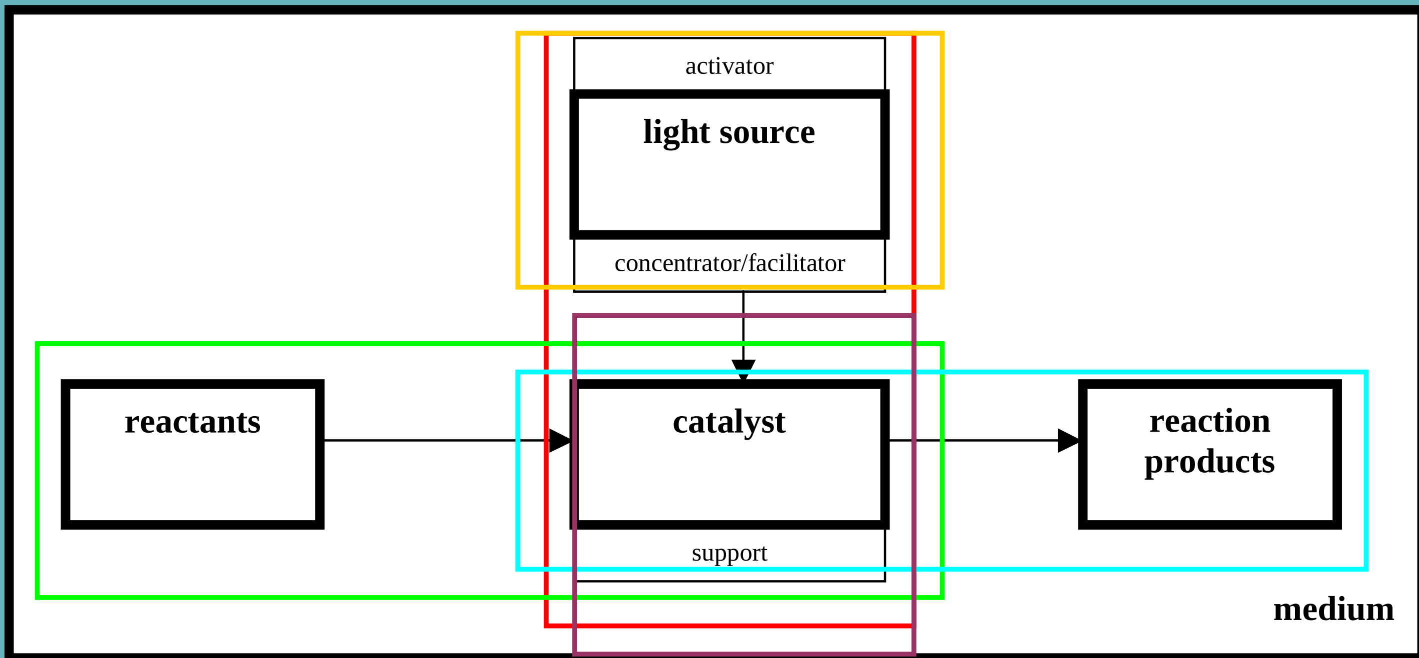
Increased interest



Source: Guido Mul

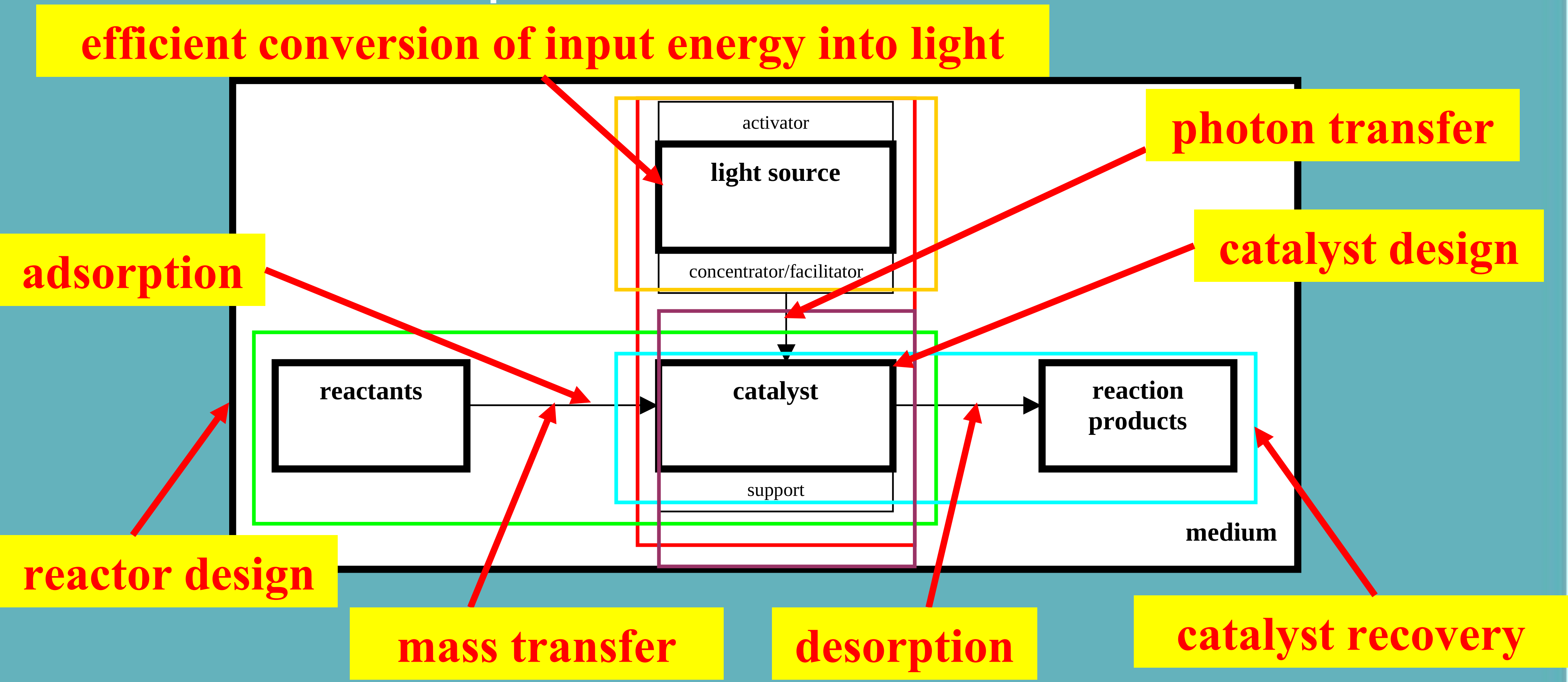
Photocatalytic reactors

- Basic components



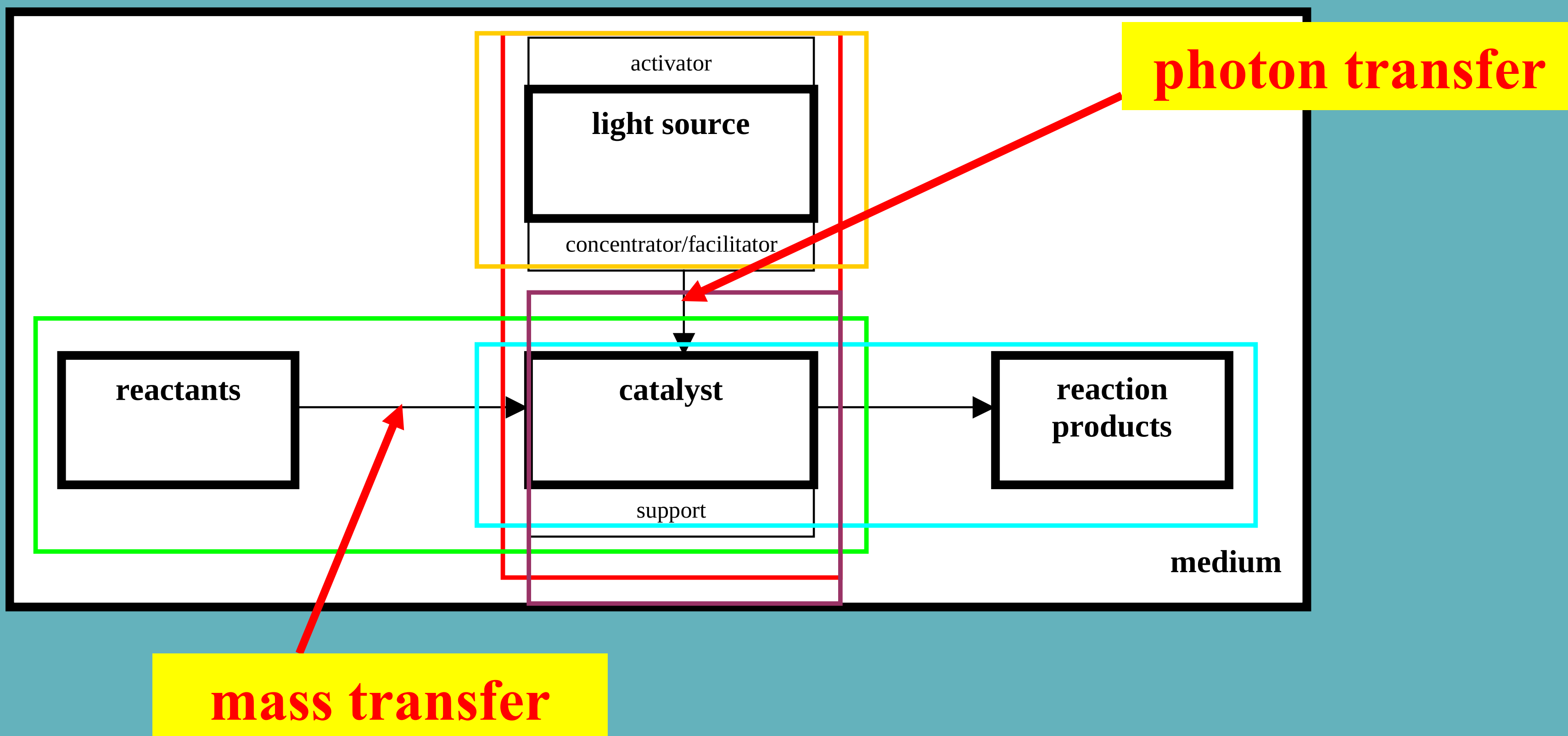
Photocatalytic reactors

- Basic components



Photocatalytic reactors

- Basic components



Photocatalytic reactors

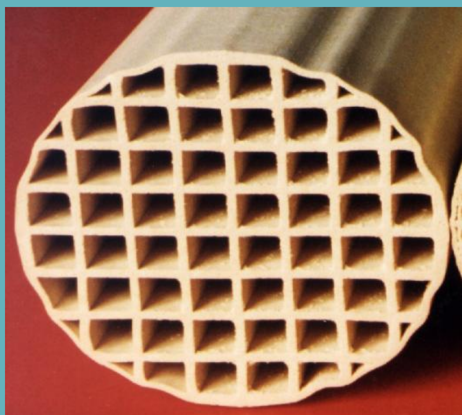
- Photon transfer
  - light intensity decays with distance
  - absorption on the way

solution is light source close to catalyst

- Mass transfer = OK in slurry reactors, but
  - expensive separation step
  - incomplete illumination

solution is immobilized catalyst
with excellent mass and photon transfer

Photocatalytic reactors



monolithic reactors

Improvement of mass transfer

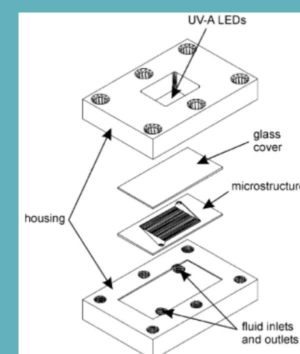
optical fibers

spinning disc reactors

microreactors

Improvement of light transfer

LED



Comparison of reactor configurations

Photocatalytic reactor	catalyst coated surface per reaction liquid volume (m^2/m^3)
slurry reactor	2631 8500-170000
(multi)annular/immersion reactor	27 69 133 170 340 2667
optical fiber/hollow tube reactor	46 53 112 210 1087 1920 2000
monolith reactor	943 1333
spinning disc reactor	50-130 20000-66000
microreactor	7300 12000 14000 250000

- Comparison based on catalyst coated surface per reaction liquid volume (m^2/m^3)
- The catalyst specific surface is not included in the comparison
- No evaluation of illuminated surface, illumination uniformity, minimization of energy loss on the way

- Microreactor and spinning disc reactor reach the values of slurry reactor
- Monolith reactor particularly suited for gas-liquid systems

Case 1: OFR

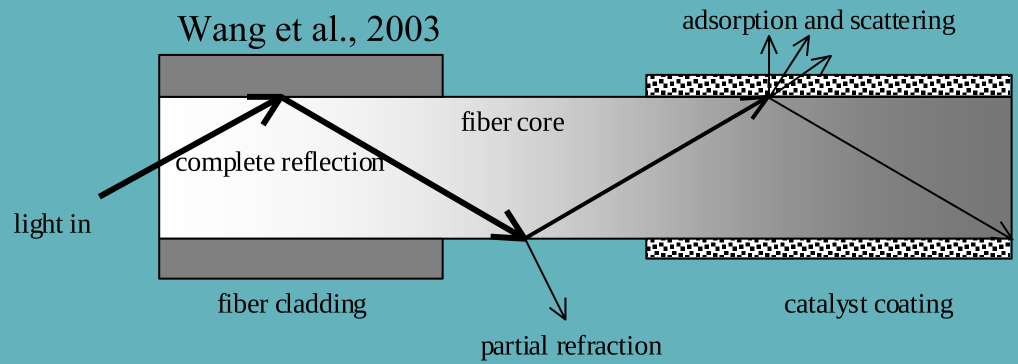
Optical fibers

Case 1: OFR

Optical fibers

10-fold increase of the illuminated catalyst surface per unit of reactor volume compared to an annular reactor (Lin et al., 2006)

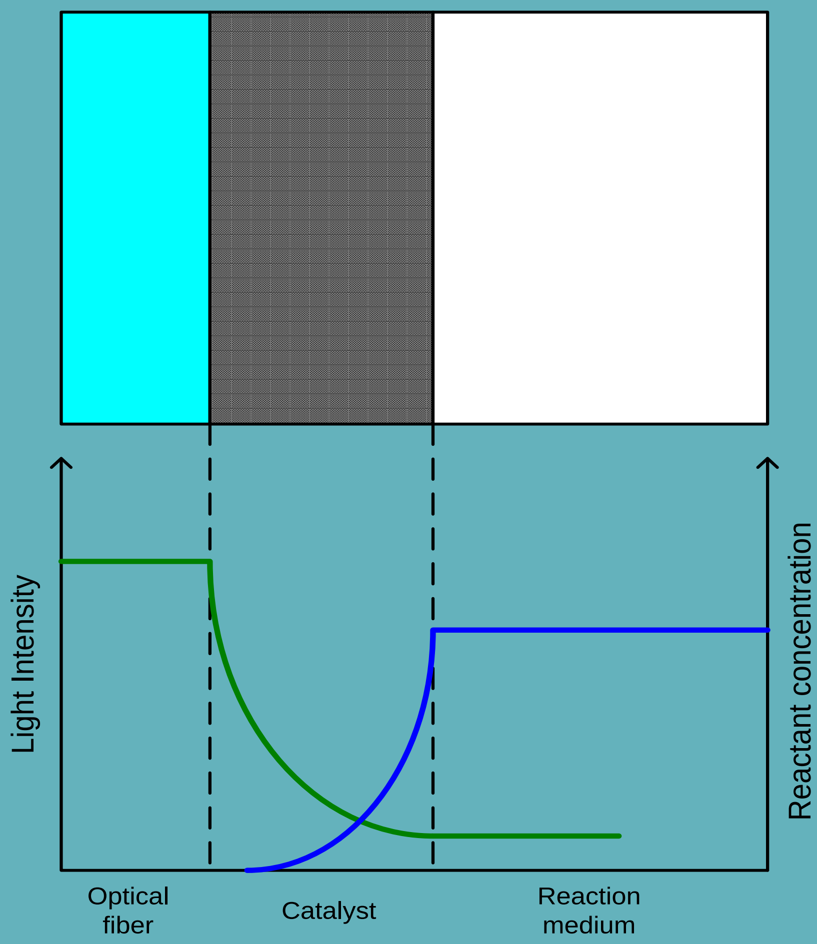
Wang et al., 2003



Drawbacks:

- Decay of light: maximum length is 10cm
- Back-irradiation
- Fiber volume

Optical Fiber Reactor



Problem:

Light absorption & rapid diffusion

- Layer thickness

Coating has 2 functions:

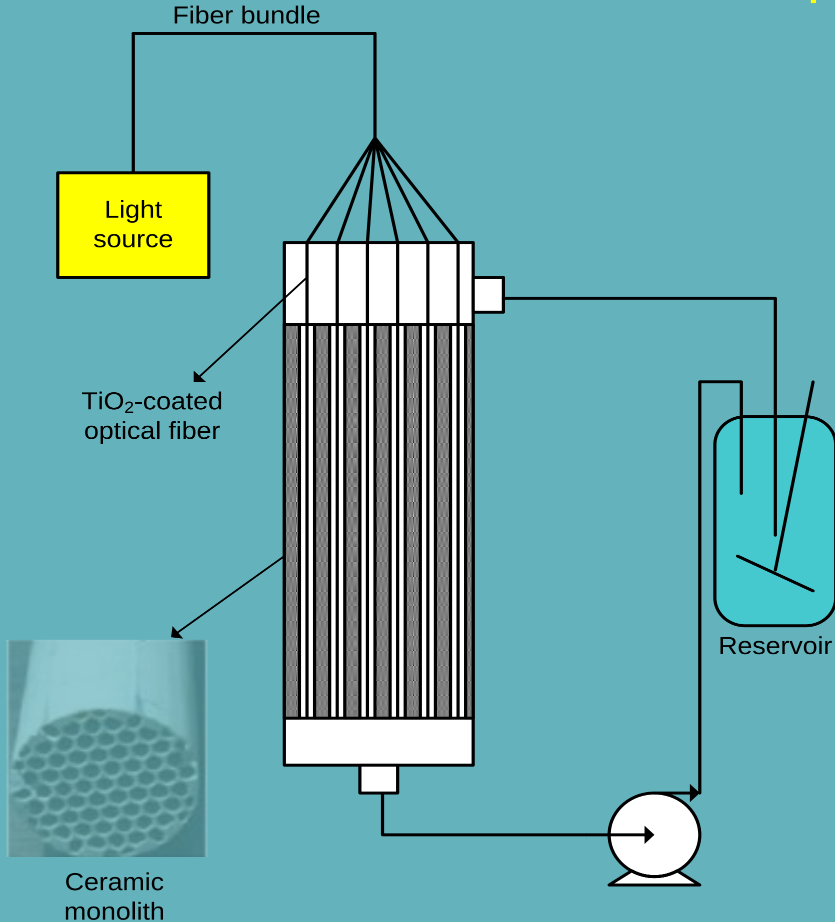
- catalyze surface reaction

- reflect light into the fiber

Fiber length limited to < 10 cm

(Carneiro, Mul, Moulijn)

Optical fiber monolith reactor 1.0



1. H. F. Lin, K. T. Valsaraj, J. Appl. Electrochem. 35 (2005) 699-708

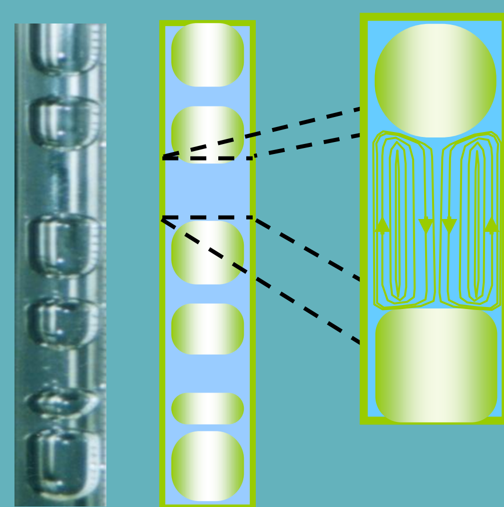
Optical Fiber Monolith Reactor[1]

wastewater treatment

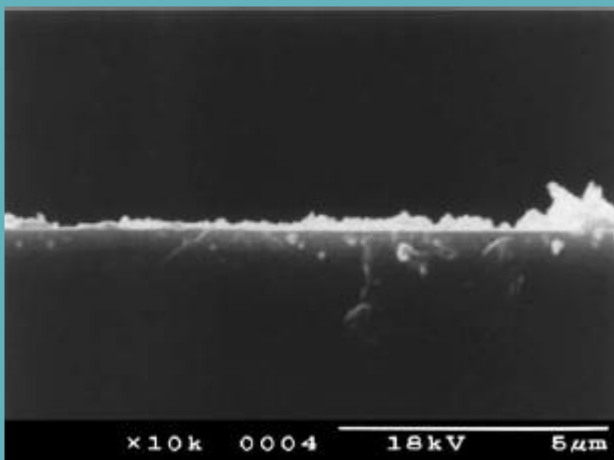
monolith merely distributor of optical fibers

Not exploited:

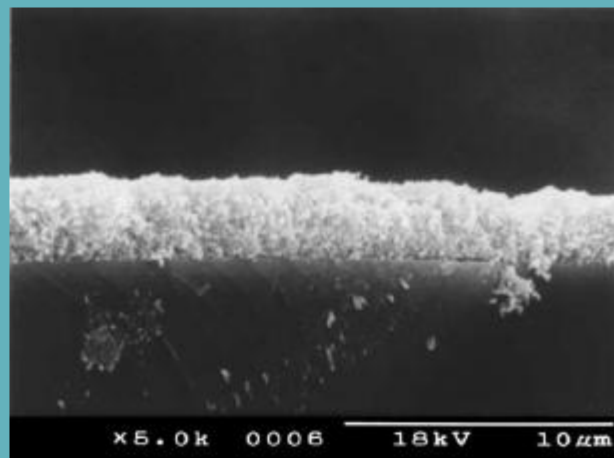
excellent mass transfer characteristics for gas/liquid systems



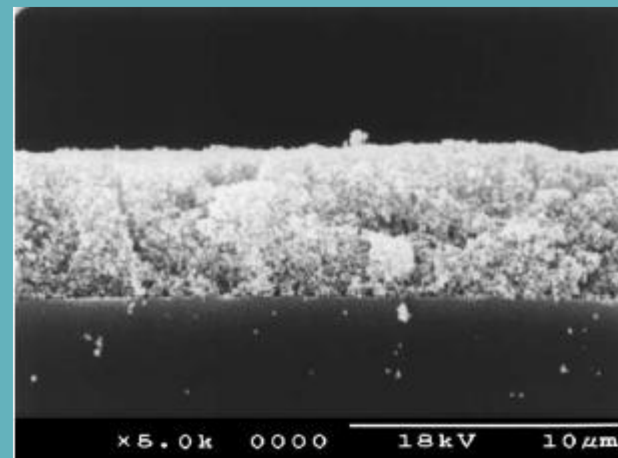
Optical fiber monolith reactor 1.0



1 coating



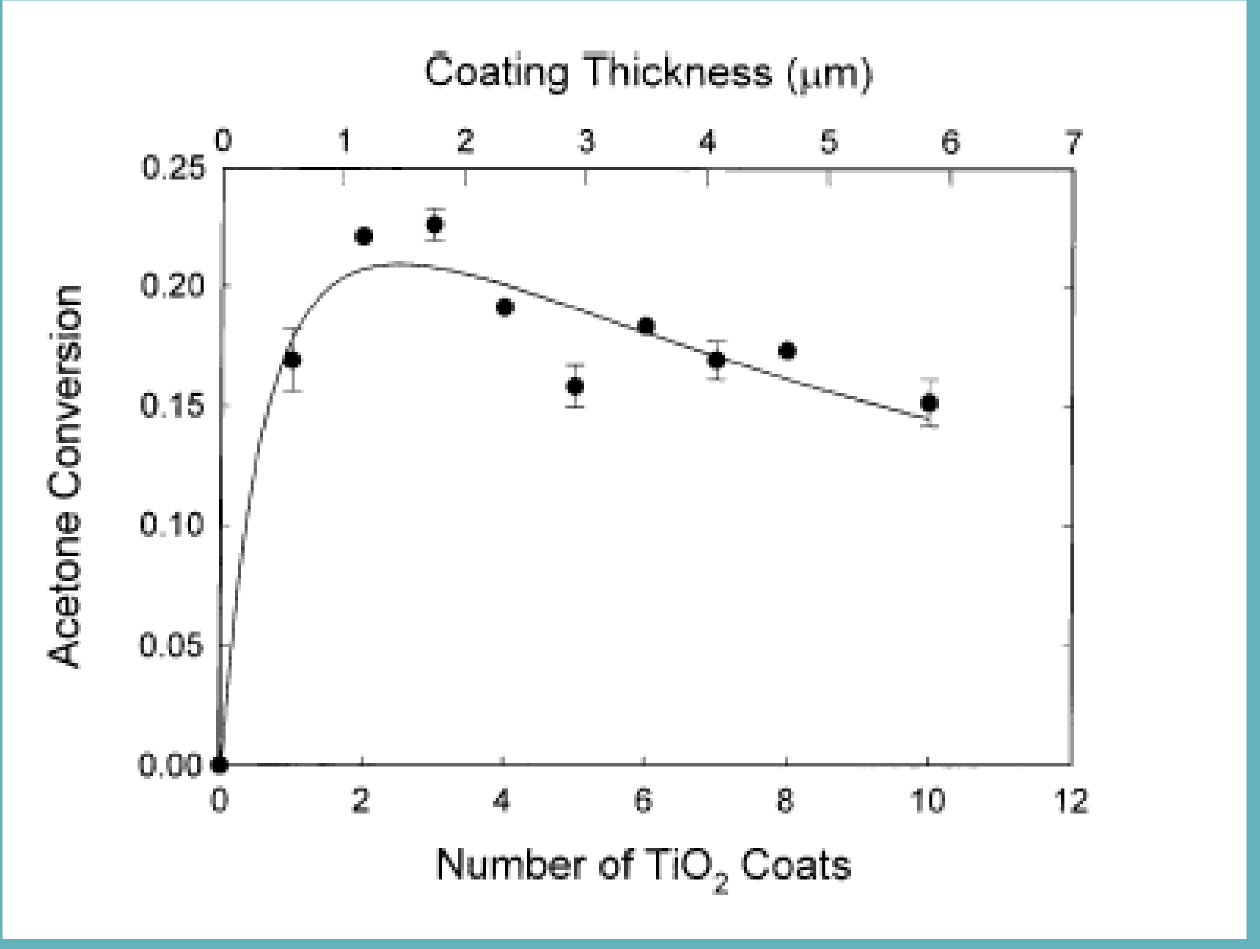
3 coatings



9 coatings

Choi et al. 2001

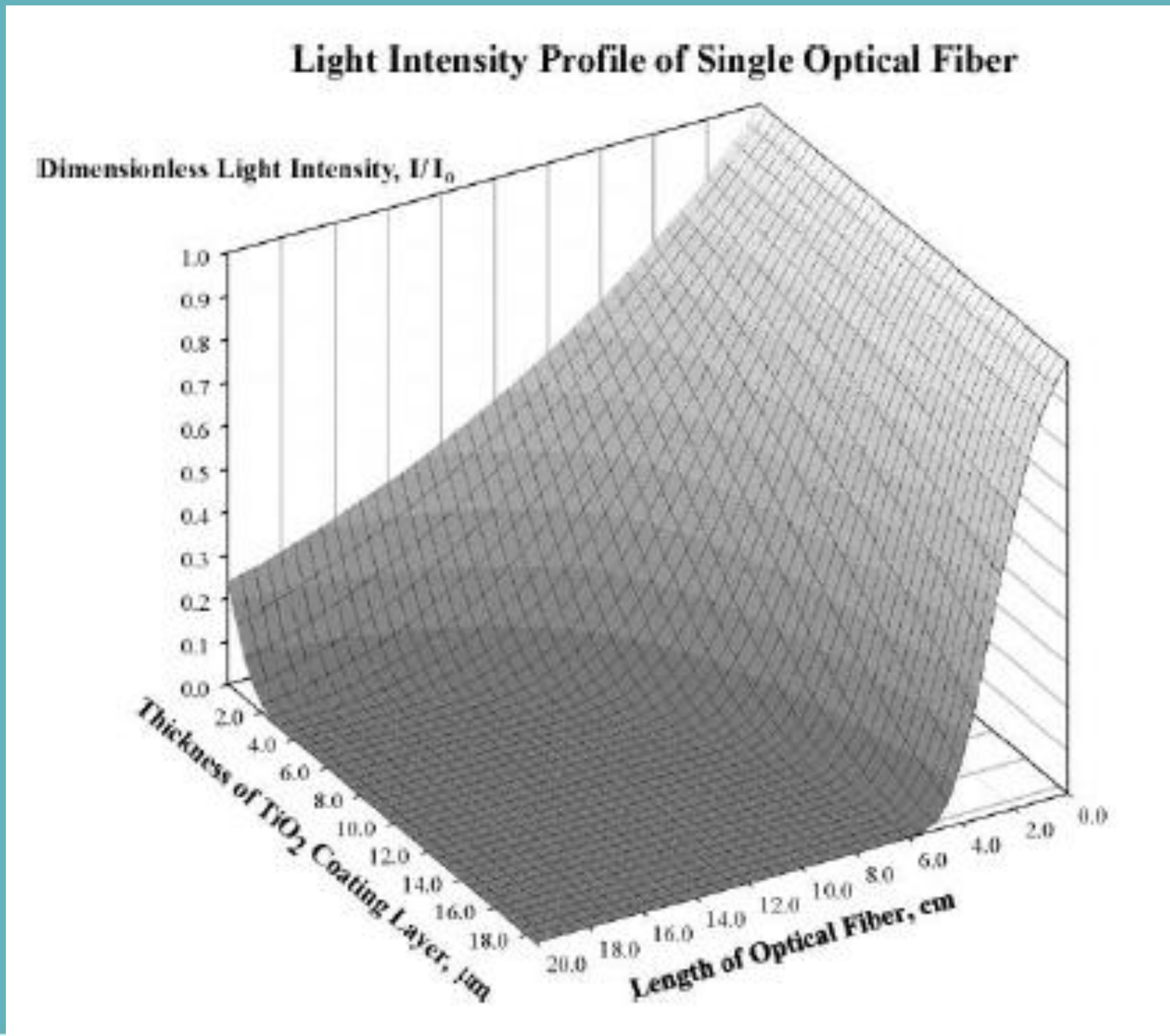
Optical fiber monolith reactor 1.0



An optimal catalyst coating satisfies sufficient light absorption with rapid reactant diffusion into the illuminated layer.

Choi et al. 2001

Optical fiber monolith reactor 1.0

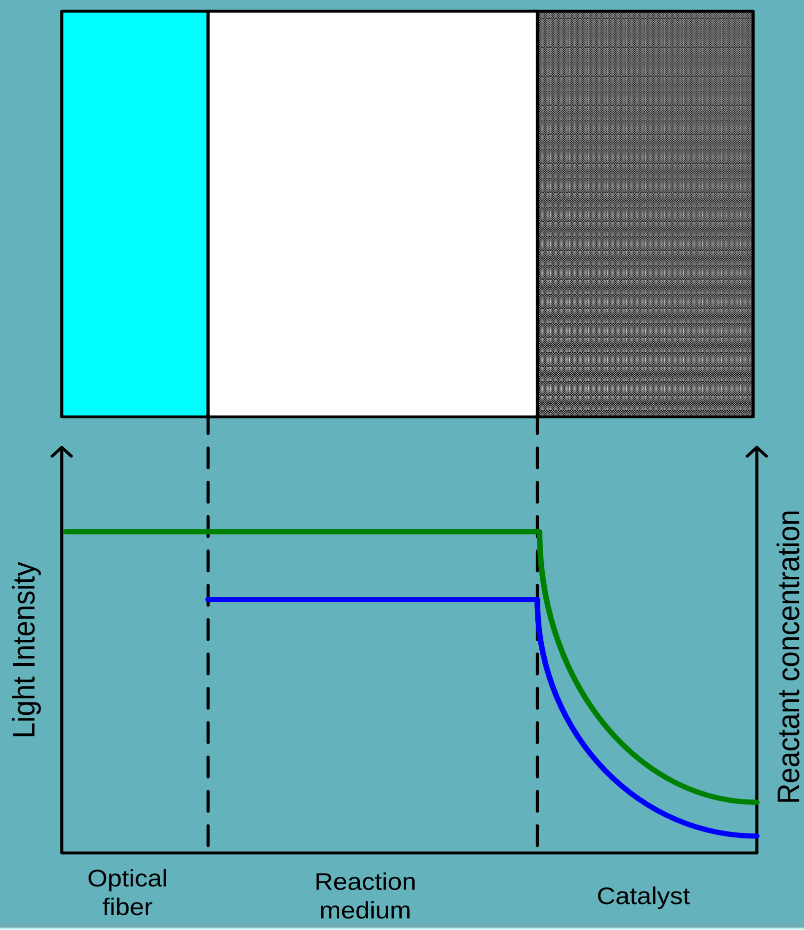


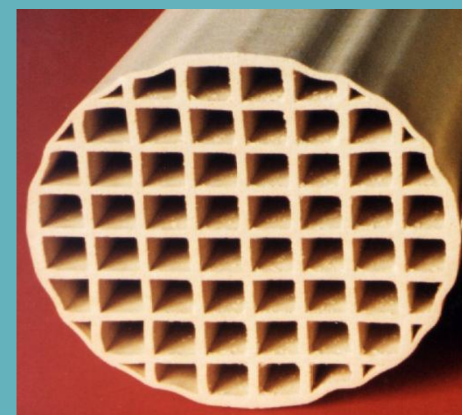
Wang and Ku, 2003

(Carneiro, Mul, Moulijn)

Optical fiber monolith reactor 2.0

Monolith: catalyst support





Advantages:

light propagation process in the fiber

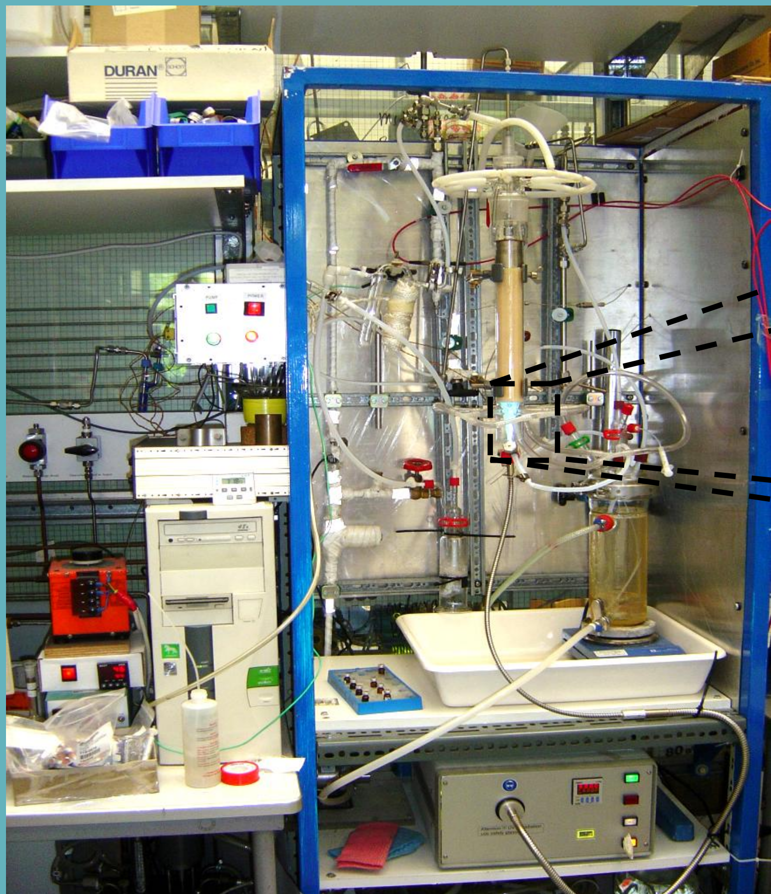
Is NOT DEPENDENT on

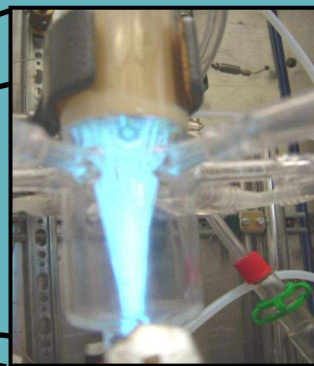
physical properties of the catalytic layer

Monolith multiphase advantages considered

(Carneiro, Mul, Moulijn)

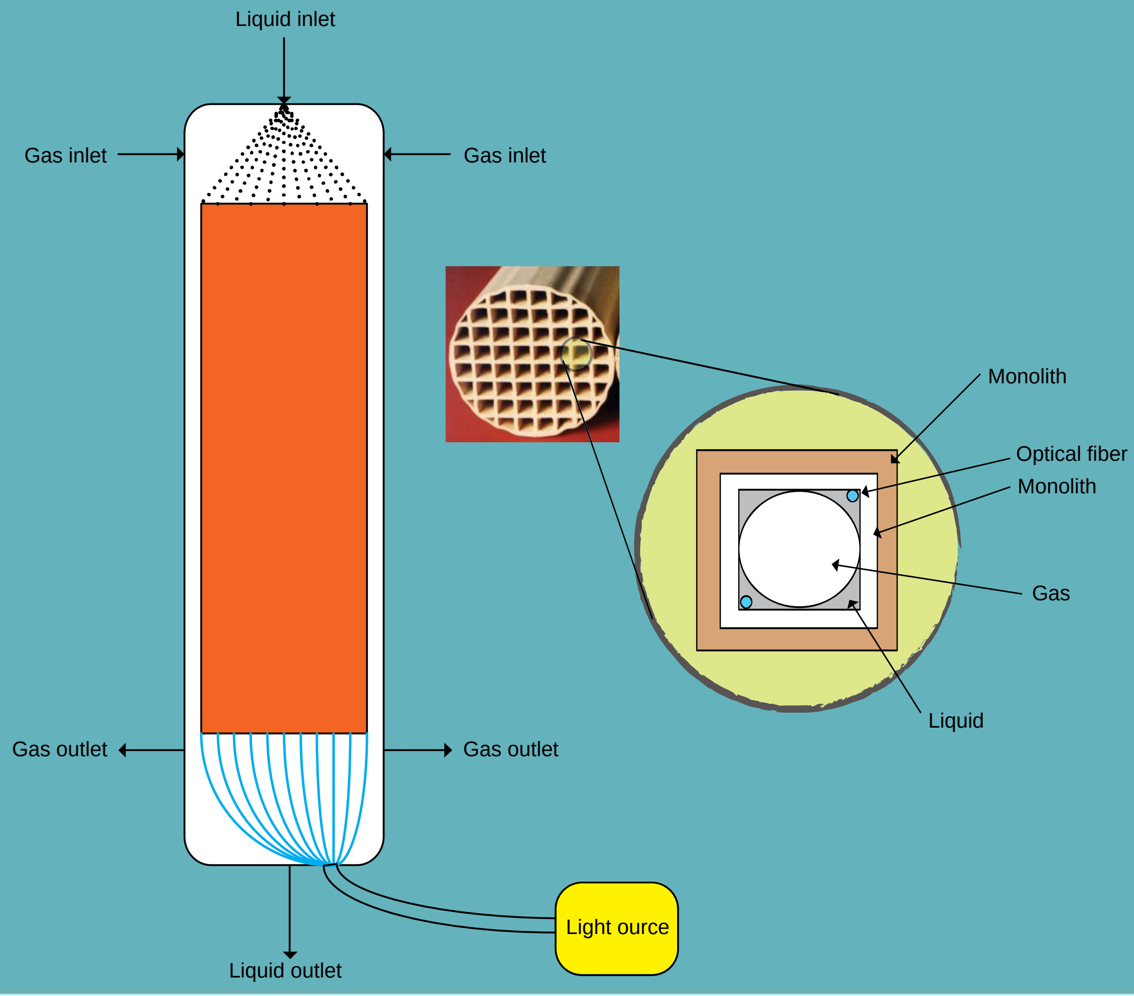
OFMR 2.0





(Carneiro, Mul, Moulijn)

OFMR 2.0



Operating conditions:

V = 800 mL

Film flow regime

Φ_{air} = 15 dm^3/min

Φ_{Liq} = 0.5 dm^3/min

16.7g TiO_2

Air presaturated with Chexane

Monolith:

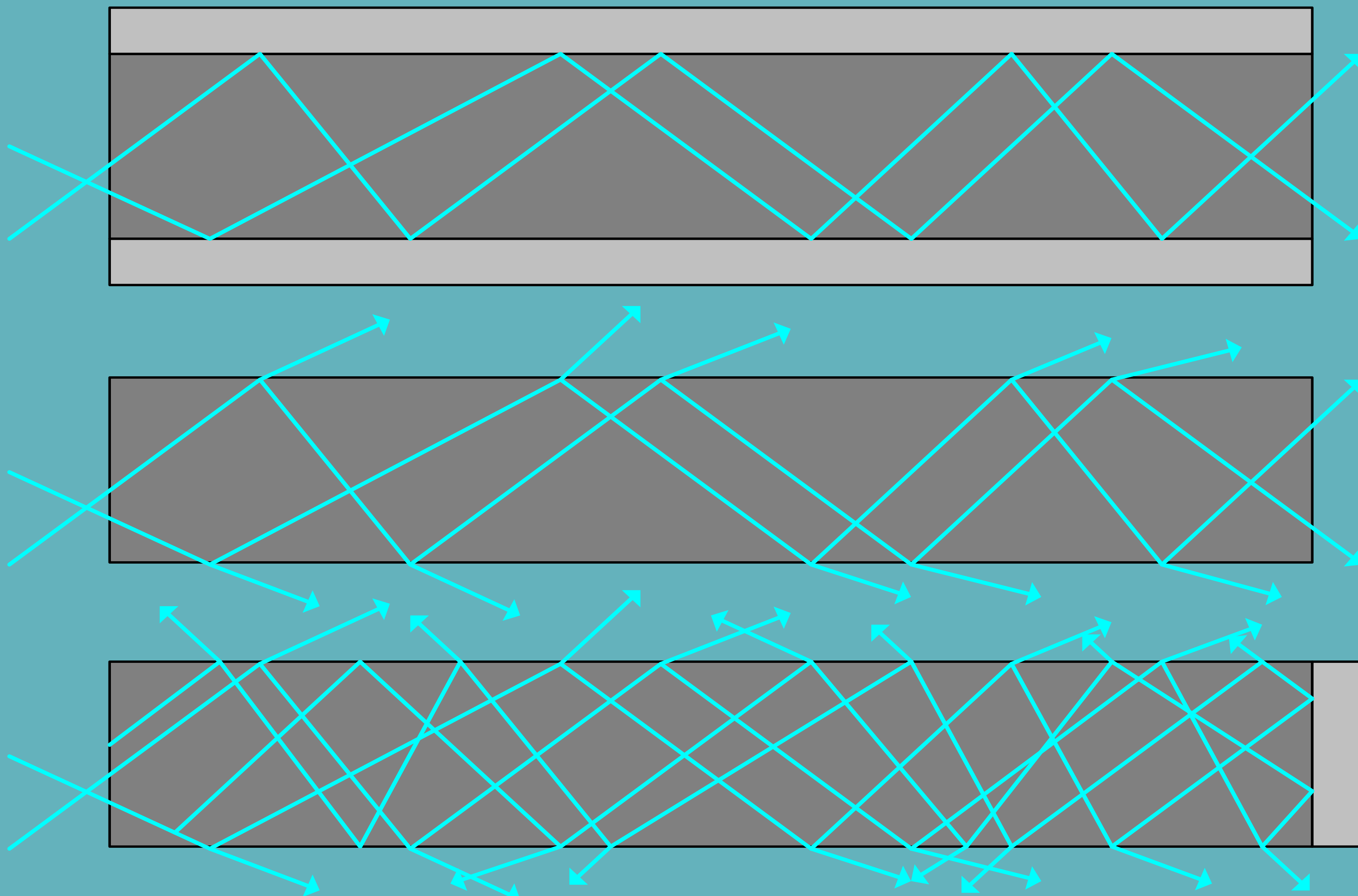
Cordierite

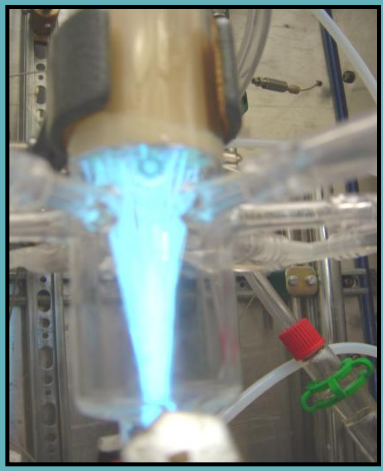
25 cpsi

L = 25 cm

(Carneiro, Mul, Moulijn)

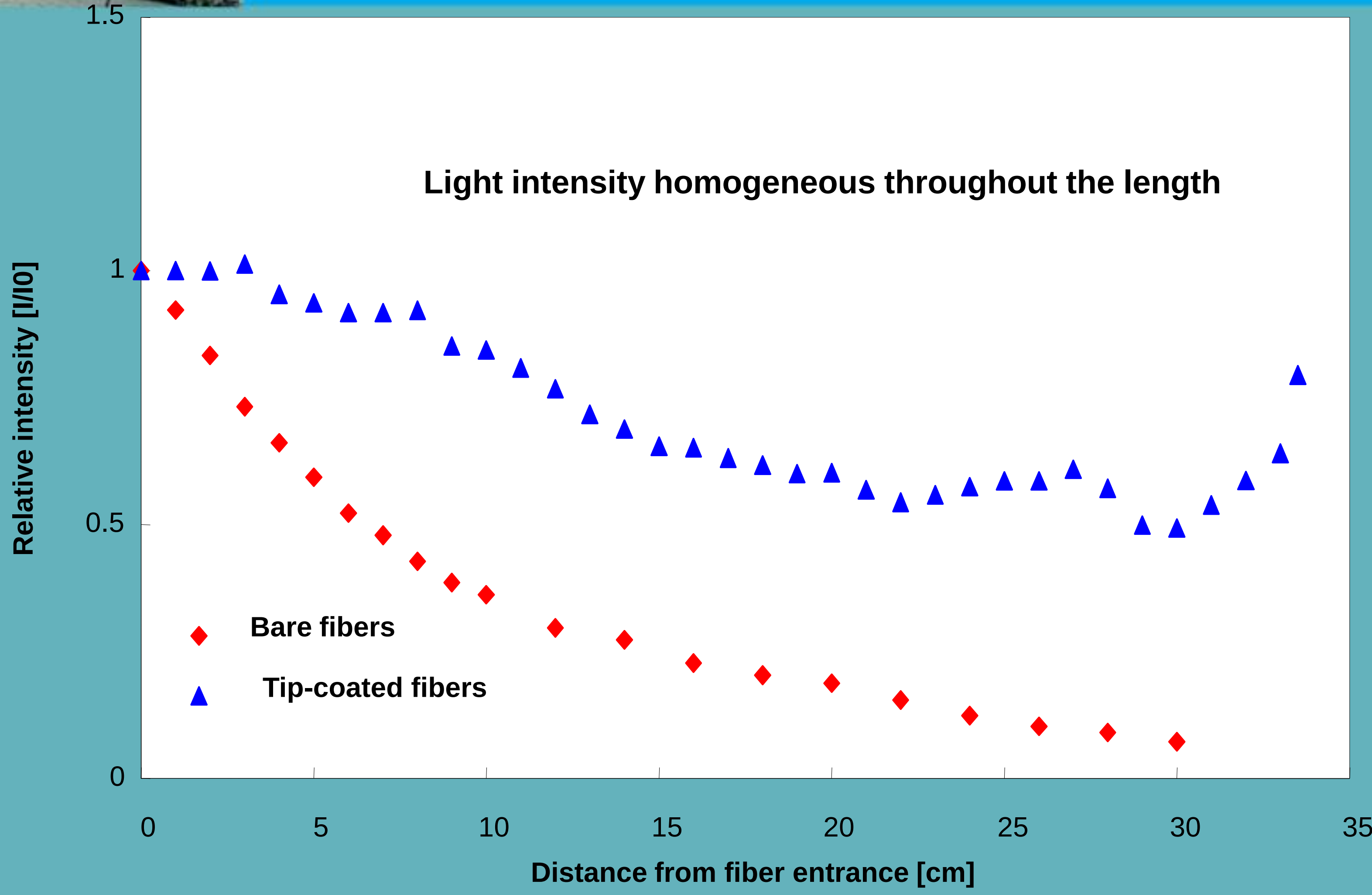
Side Light Fibers (OFMR 2.1)





(Carneiro, Mul, Moulijn)

Side Light Fibers



(Carneiro, Mul, Moulijn)

Reactor comparison

Top Illumination Reactor (slurry)

Side Light Fiber Reactor (slurry)

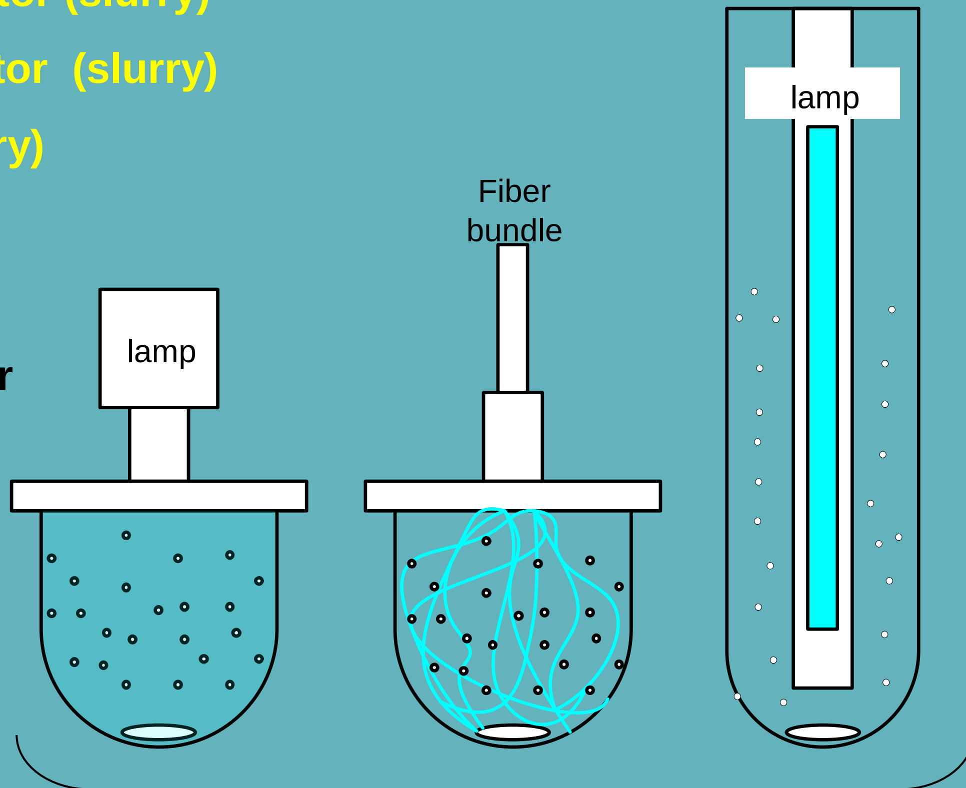
Annular Reactor (slurry)

OFMR a) Fiber Optic

b) Liquid

c) Catalyst layer

d) Monolith



1g/L catalyst

(Carneiro, Mul, Moulijn)

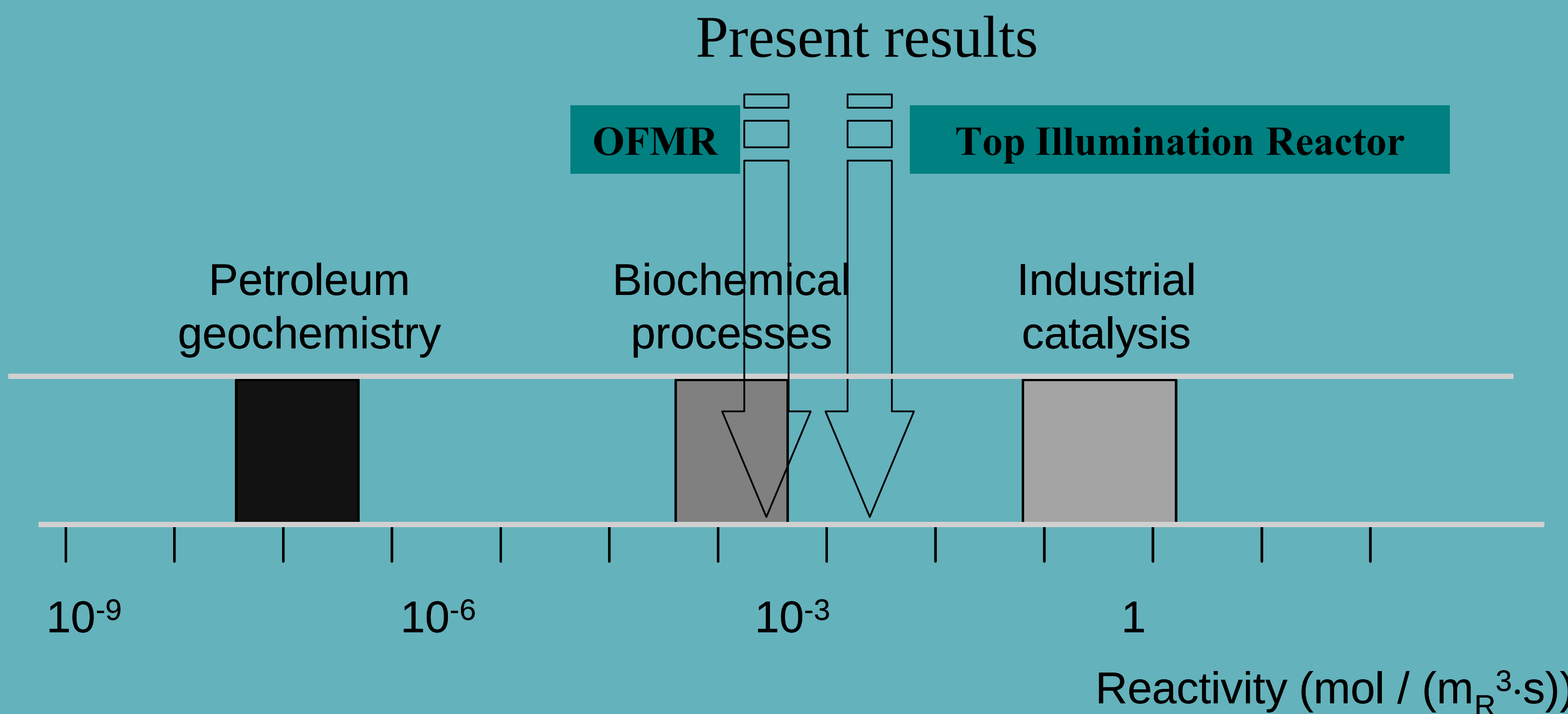
Results

Reactor	R^{in} [mol.s^{-1}]	ρ_p [Einst.s^{-1}]	ξ [mol.Einst^{-1}]	
Annular reactor	1.59×10^{-6}	1.96×10^{-4}	0.008	Low efficiency of light utilization
Side light fiber reactor	7.68×10^{-10}	3.69×10^{-7}	0.002	Low exposure of catalyst to light
OFMR	2.28×10^{-8}	3.69×10^{-7}	0.062	Bad desorption from catalyst
Top illumination reactor	1.20×10^{-7}	7.95×10^{-7}	0.151	… but slurry reactor, requiring post-separation of catalyst

$$\xi = \frac{\text{reaction rate (mol/s)}}{\text{photon flow (Einstein/s)}} = \text{photonic efficiency}$$

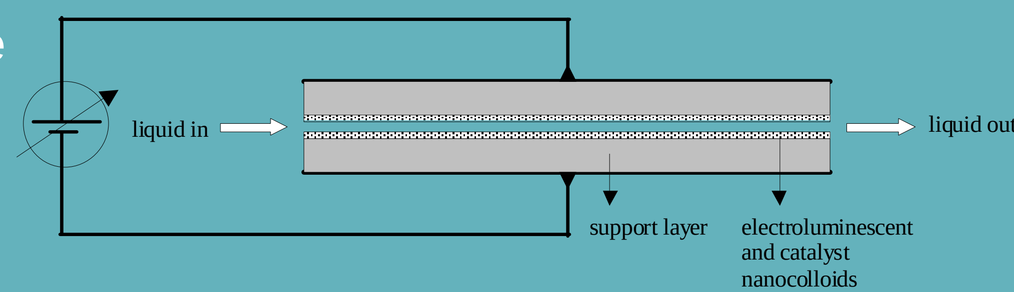
(Carneiro, Mul, Moulijn)

Further work needs to be done



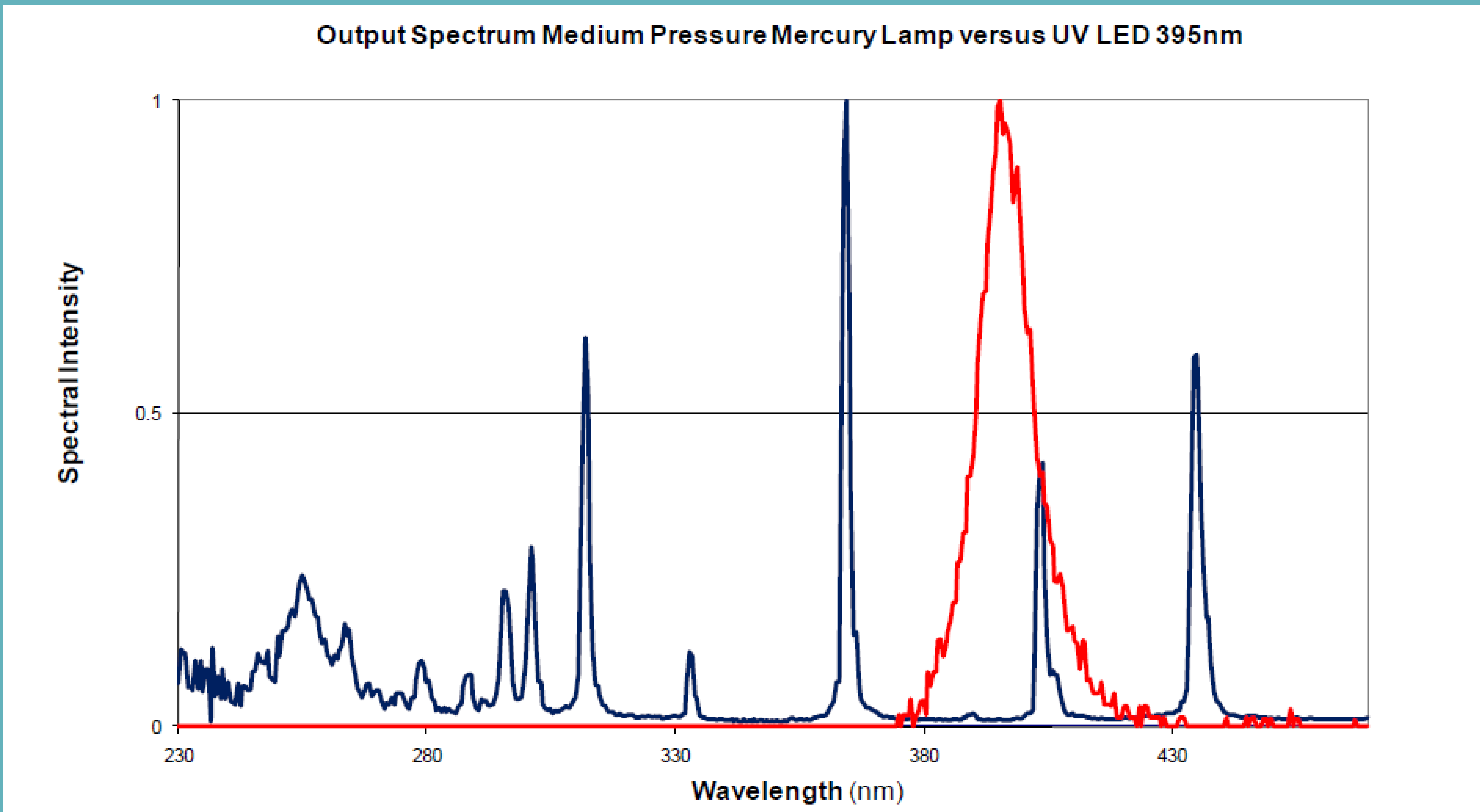
Case 2: IIMR

- Micro- and nanoscale illumination
  - LED devices
    - robust, long-lasting (up to 100000 hrs vs. 1000 hrs for conventional lamps)
    - low-energy consuming (100mW vs. 100-1000W for conventional lamps)
    - miniaturisation
  - Luminescent molecules interspersed with catalyst
    - physical integration on the nanoscale
    - very early research phase



Fedorov et al., 2002

LED emission



LED emission

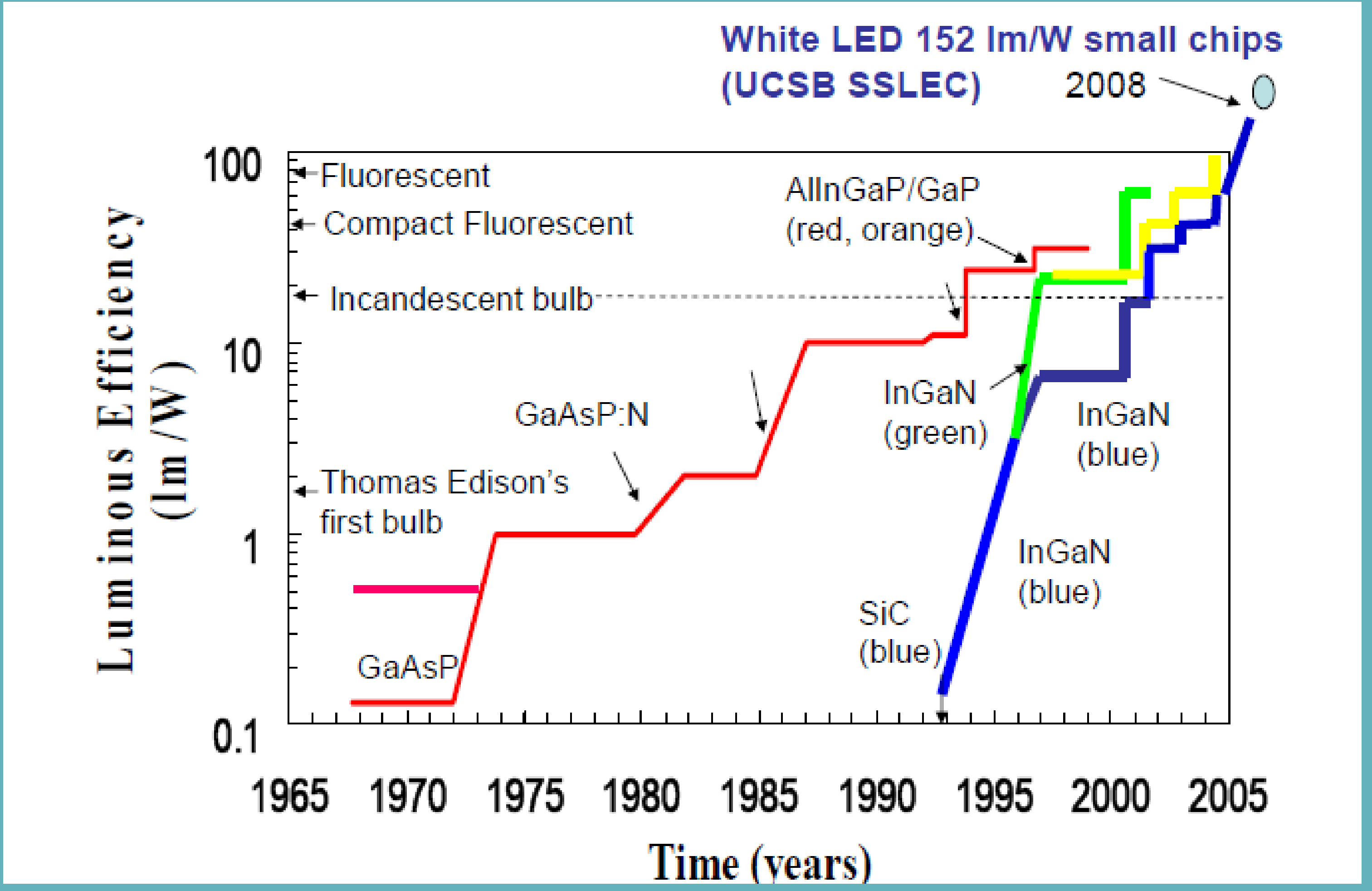
<u>Advantages of LED</u> compared to conventional (Hg) lamps:

- Higher spectral purity
- Less heat: UV LEDs operate at less than 60°C, Hg bulbs at a factor 10 higher
- Instant on/off: stable, full output within milliseconds
- Compact size: also more robust, long lifetime, less sensitive to break
- Safety and Environment: VOC free radiation (no Hg); no production of O3 (ozone) because no deep UV radiation

LED efficiency

Lamp Type	Overall Luminous Efficiency (LM/W)	Overall Luminous Efficiency (Percentage)
Incandescent		
5 W tungsten	5	0.7
40 W tungsten	12.6	1.9
100 W tungsten	17.5	2.6
Fluorescent		
5-24 W compact fluorescent	45-60	6.6-8.8
34 W tube	50	7
Halogen		
Glass	16	2.3
Quartz	24	3.5
LED		
White	20-70	3.8-10.2

LED efficiency



Optimal wavelength?

Alachlor degradation by UV with/without TiO_2

Wavelength (nm)	Total power consumption (W)	Photointensity (Einstein l^{-1} min^{-1})	Direct photolysis quantum yield	Photocatalysis quantum yield	Photolysis rate constant (min^{-1})	Photocatalysis rate constant (min^{-1})
254	70	1.80×10^{-4}	0.095	0.12	0.088	0.112
300	210	6.64×10^{-3}	0.051	0.54	0.012	0.128
350	240	3.24×10^{-2}	0.008	0.21	0.005	0.129

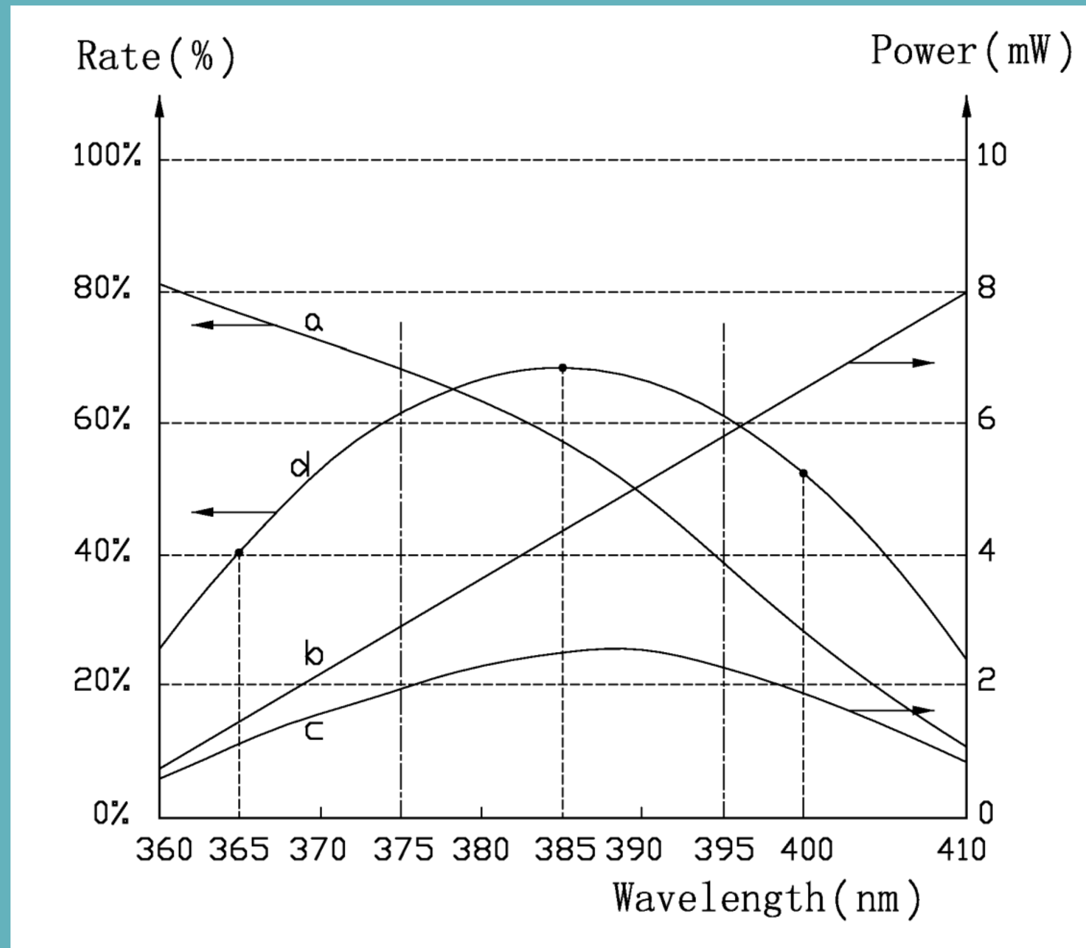
Photolysis: higher quantum yield with shorter wavelength
Photocatalysis: higher quantum yield with medium wavelength

C. C. Wang, W. Chu, Chemosphere 50 (2003) 981 – 987

Optimal wavelength?

<u>Decomposition of NO_x</u>

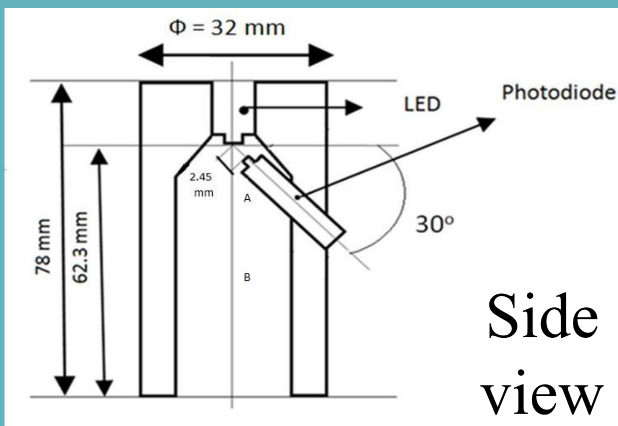
Highest decomposition rate (curve d) was observed at 385 nm

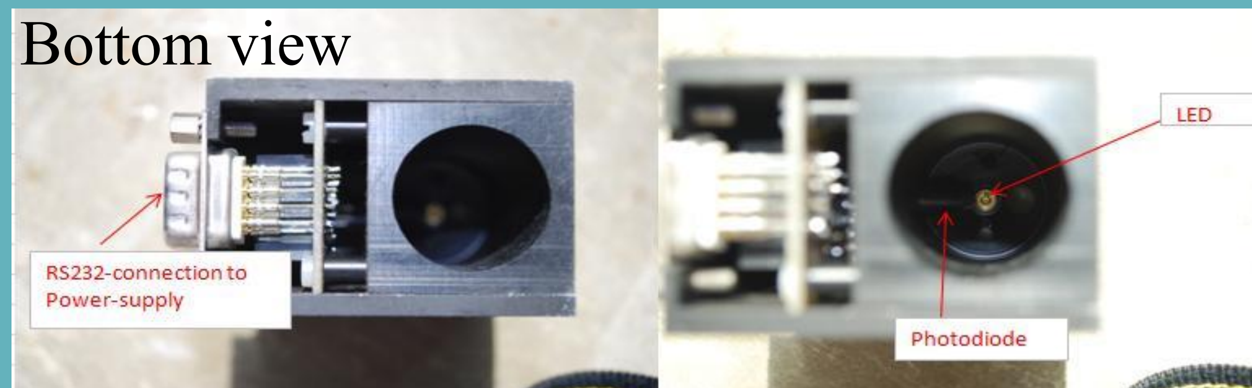


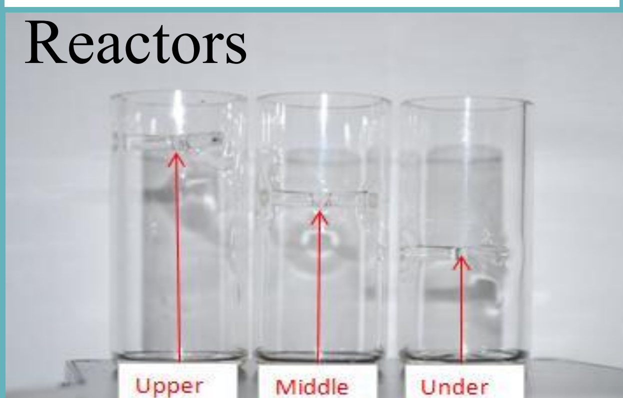
Hsu et al, United States Patent Application publication, 2009 US2009/0263298 A1

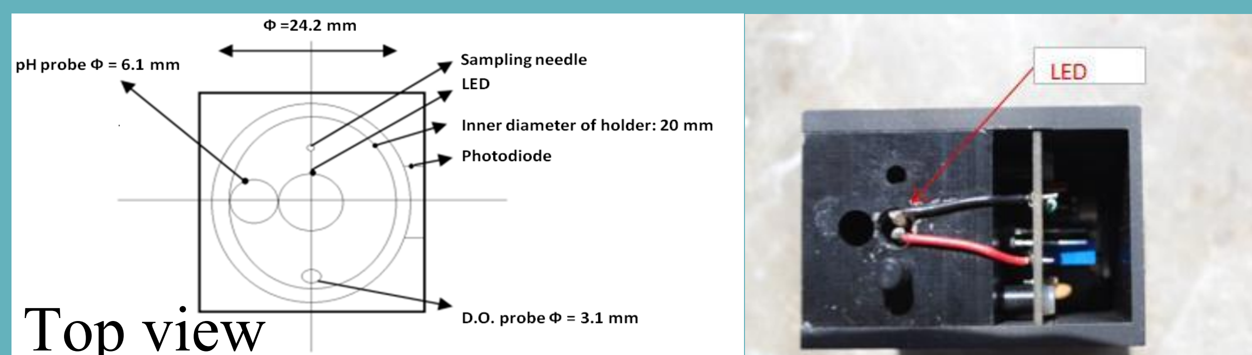
Set-up @ KU Leuven

Batch mono-LED reactor









Uniformity of light immission?

Dionysiou et al., 2000

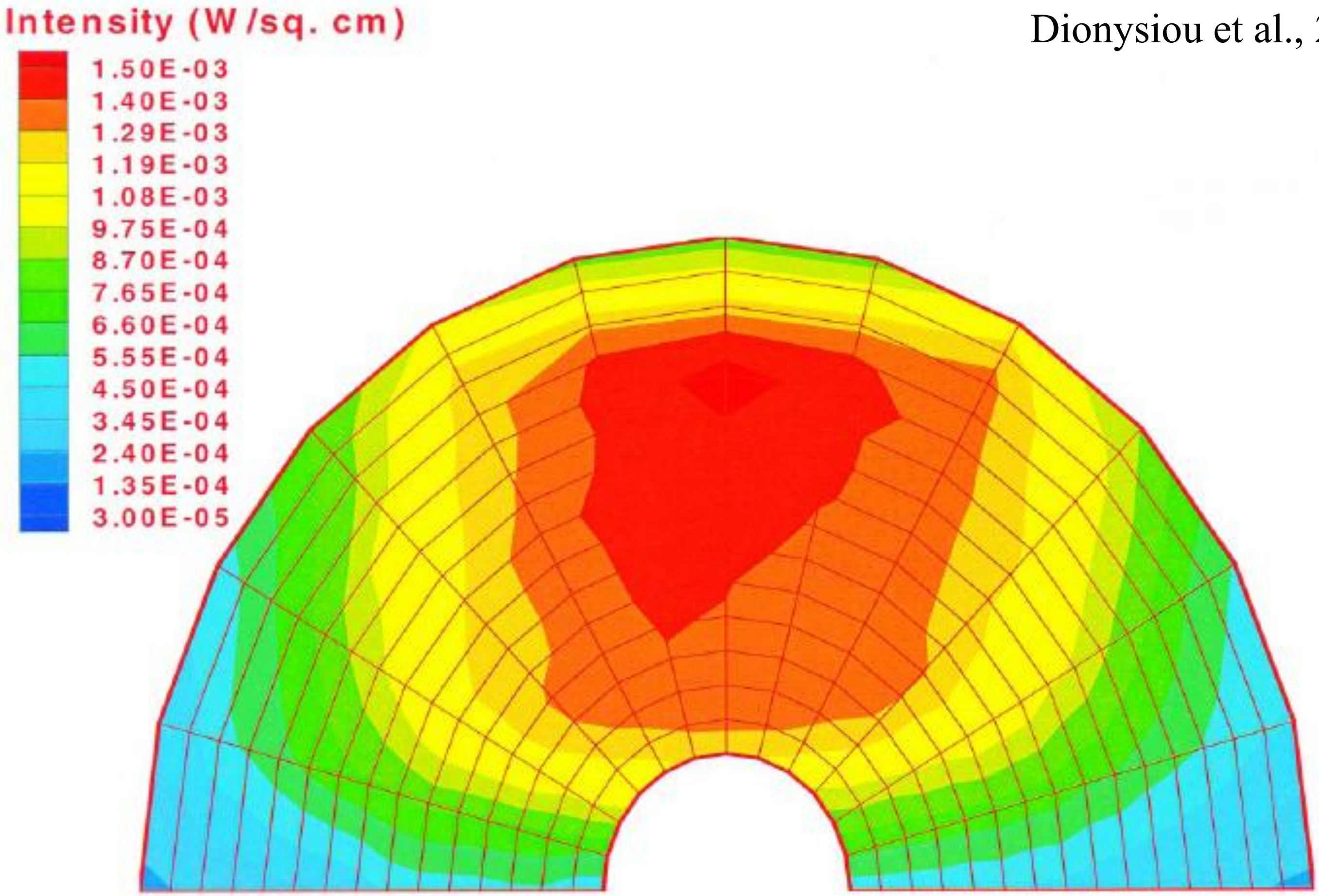
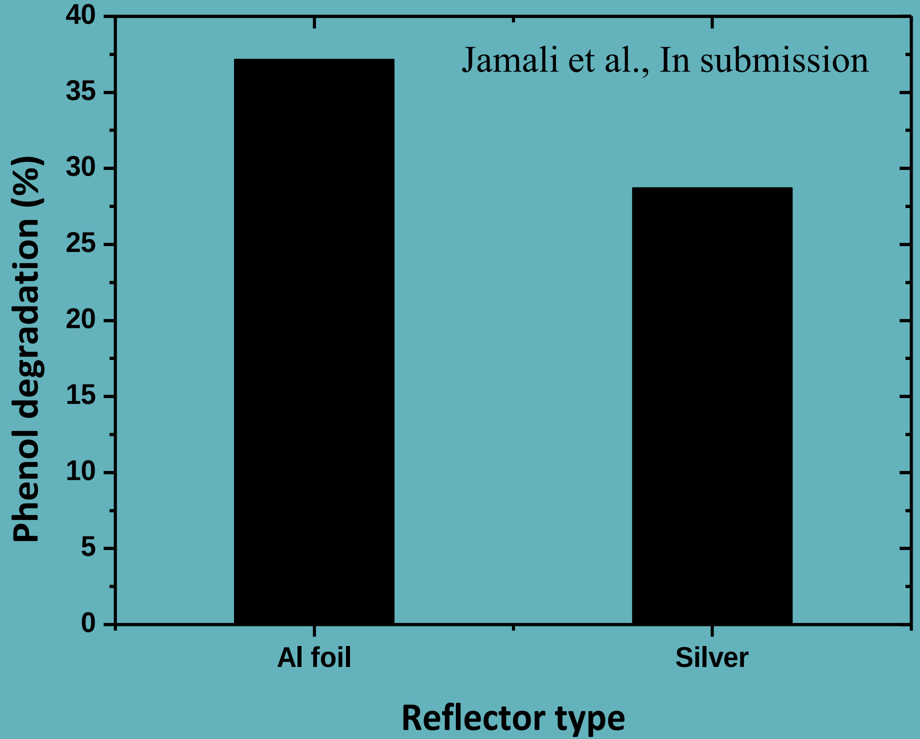
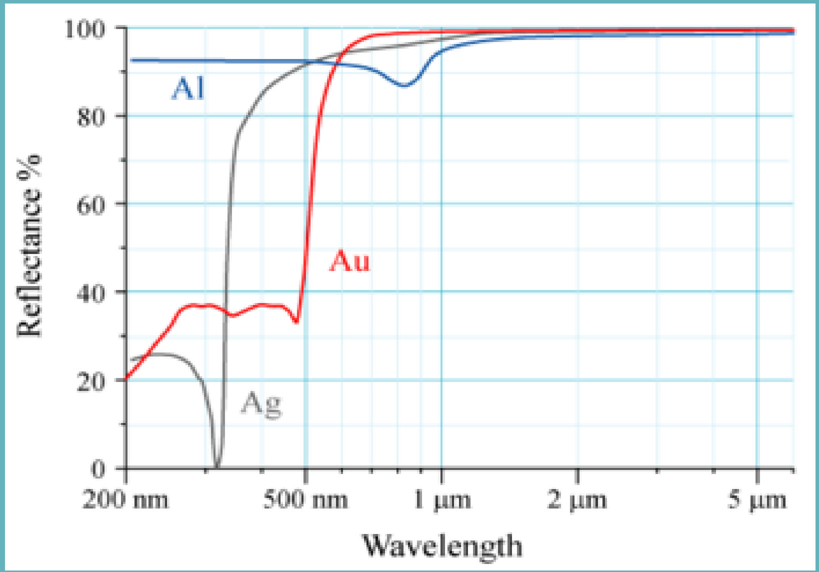


Fig. 5. Light (UV 365 nm) intensity distribution on the rotating disk.

Use of reflectors

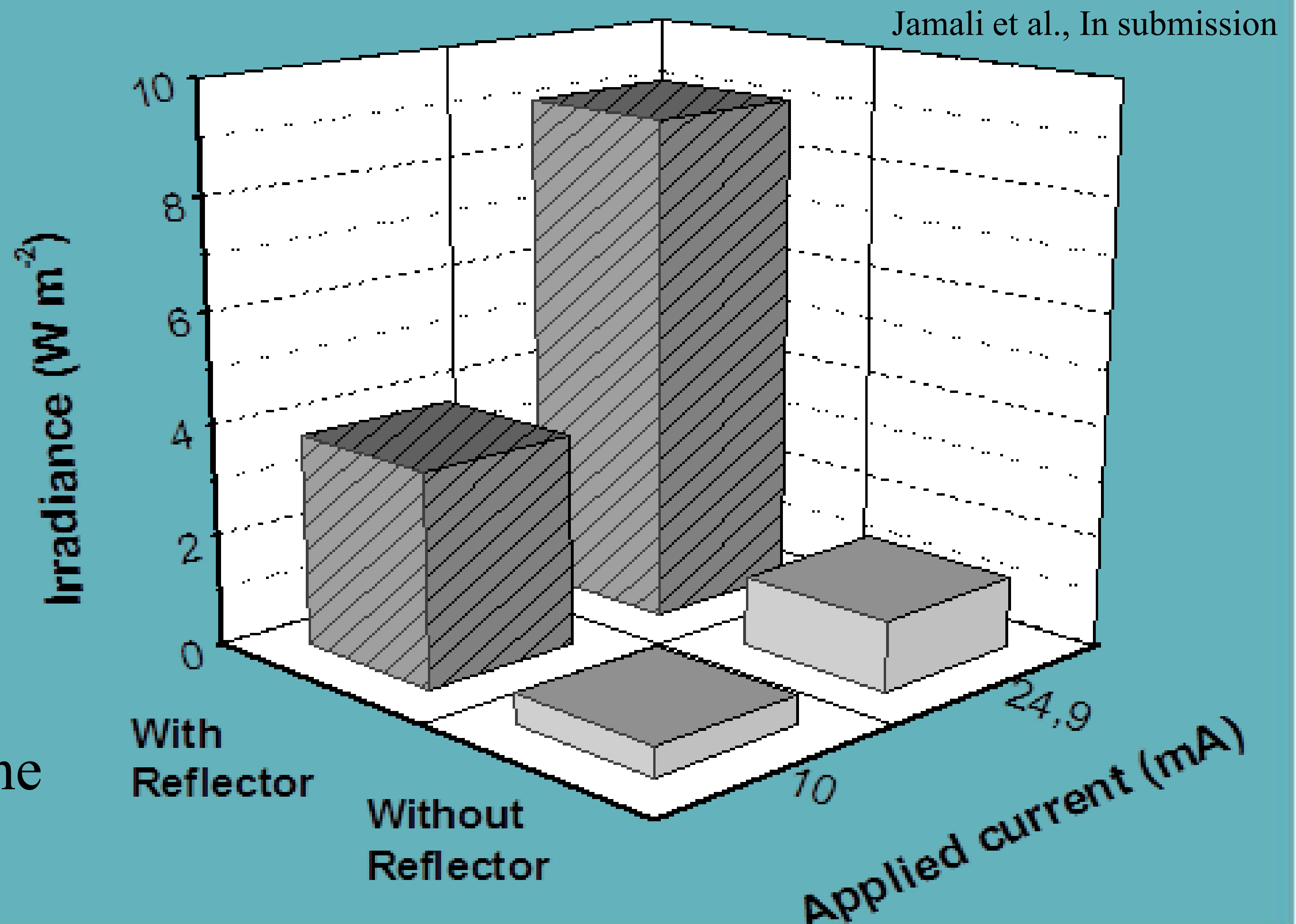




M. Bass, E. W. Van Stryland, Handbook of Optics vol. 2 (2nd ed.), McGraw-Hill (1994)

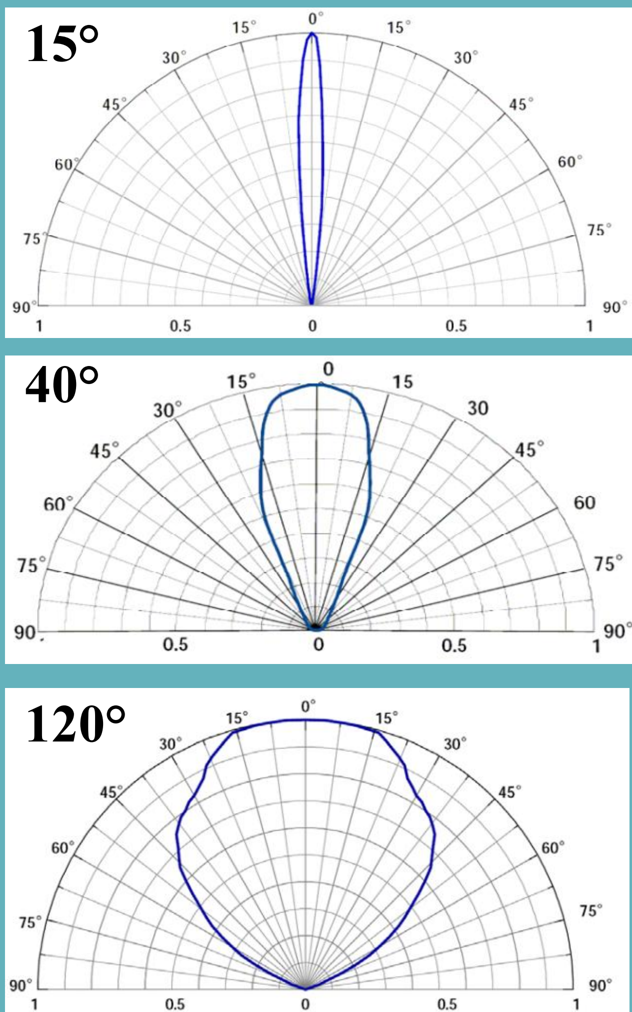
Use of reflectors

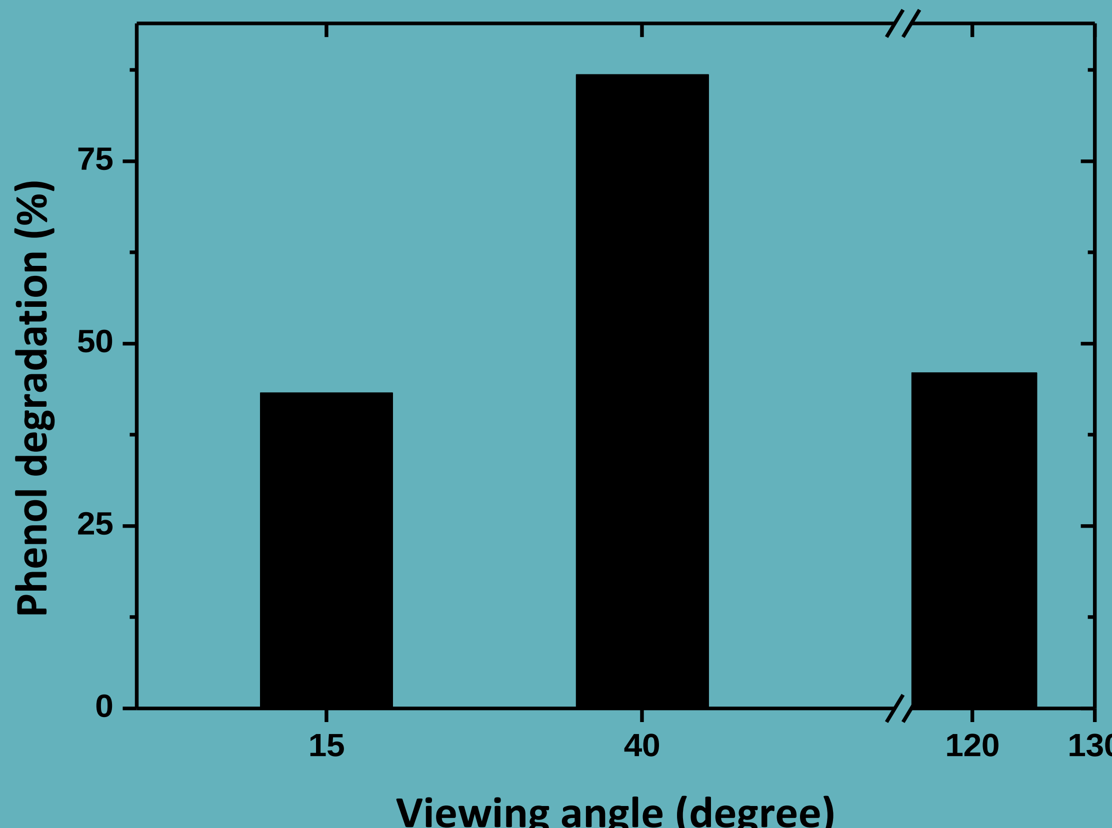
Comparison of Al foil reflector with no reflector



Irradiance measured in the centre of the reactor

Optimise LED viewing angle





Jamali et al., In submission

Comparison

UV light source	irradiance (W/m²)	Pollutant	I.C (ppm)	Reaction time (h)	Reaction rate ($mol.l^{-1}.s^{-1}$)	Degradation (%)
1 LED (our results)[1]	9.055	Phenol	10	4	6.41×10^{-9}	87
7 UVA lamps[2]	70.6	Phenol	20	3.5	1.45×10^{-8}	86

The reaction rate in Vezzoli et al. is 2.2 times faster compared to our test. However, the irradiance used in our experiments was 7.8 times less.

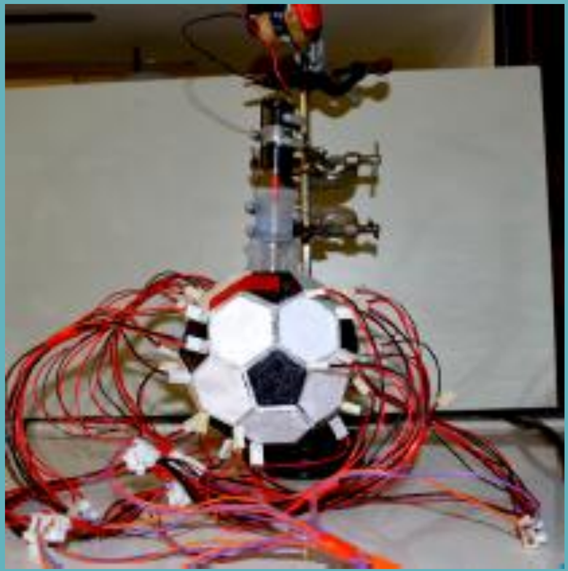
[1] Jamali et al., In submission

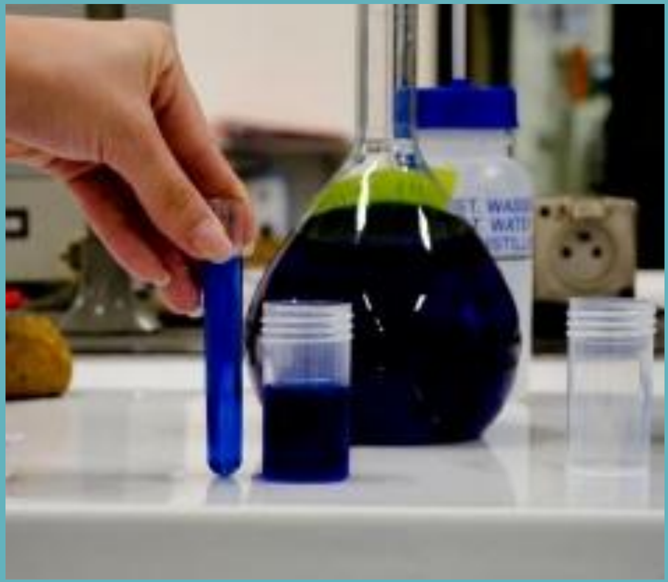
1. Vezzoli et al. Applied Catalysis A: General 404 (2011) 155-163

Optimal design?

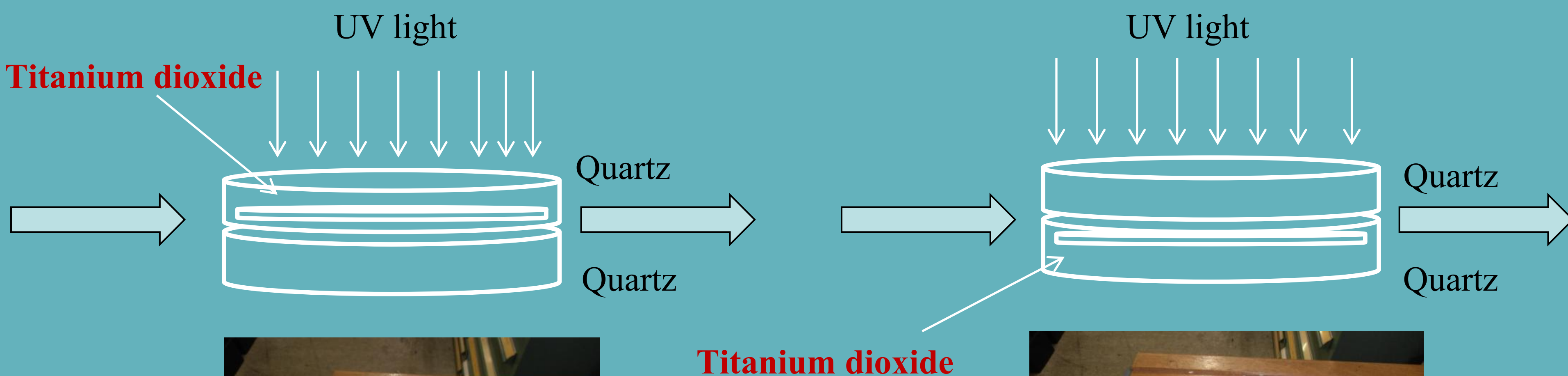
Bucky Ball Batch Reactor

- 20 hexagons and 12 pentagons
- LED on each corner





From batch to flow



Optimal design

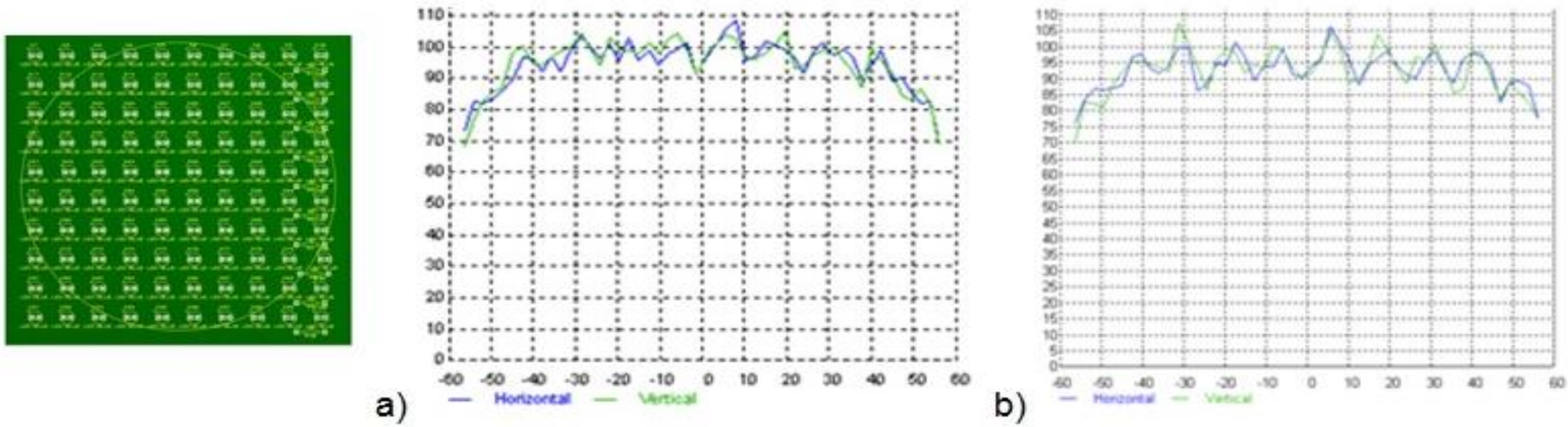


Figure 1. Irradiance distribution Wm^{-2} when the LED distance: 12mm; distance between LED array and catalyst surface a) 10 mm b) 8 mm

Optimal design

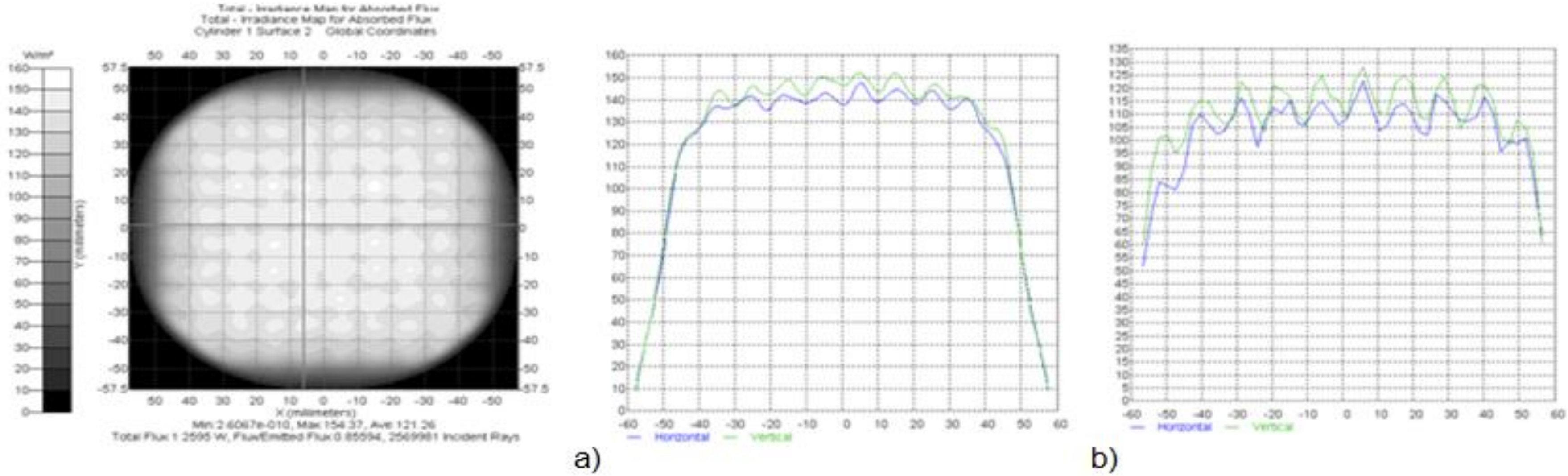
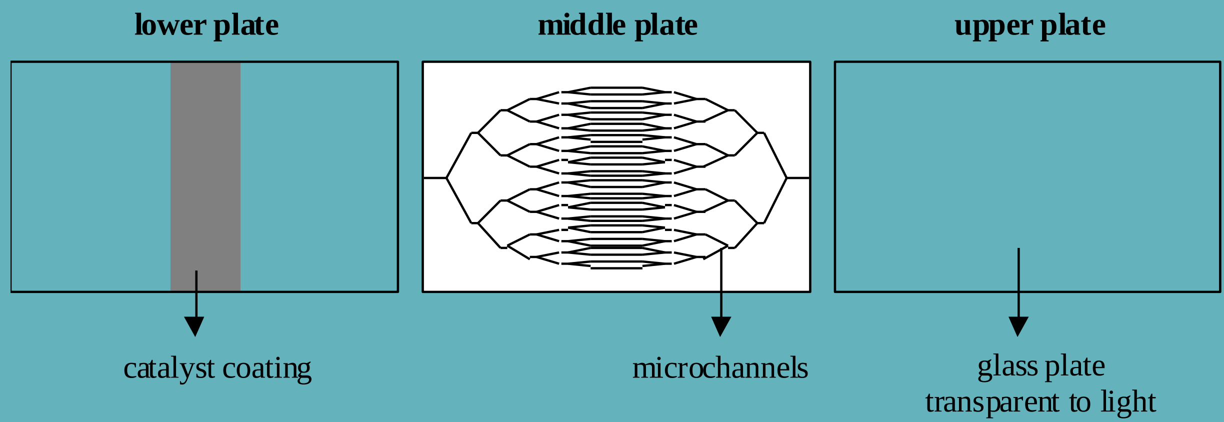


Figure 3. Irradiance distribution Wm^{-2} when the distance between LED array and catalyst surface: 8 mm; LED distance a) 10 mm b) 11.5 mm

Improving mass transfer

- Microreactors



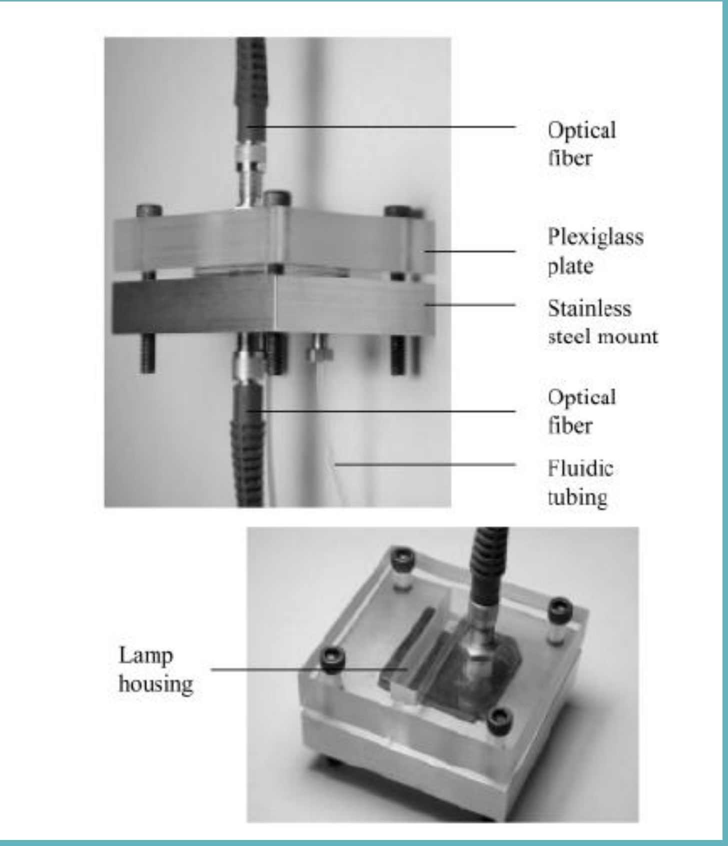
Advantages

- excellent temperature control
- excellent flow rate control

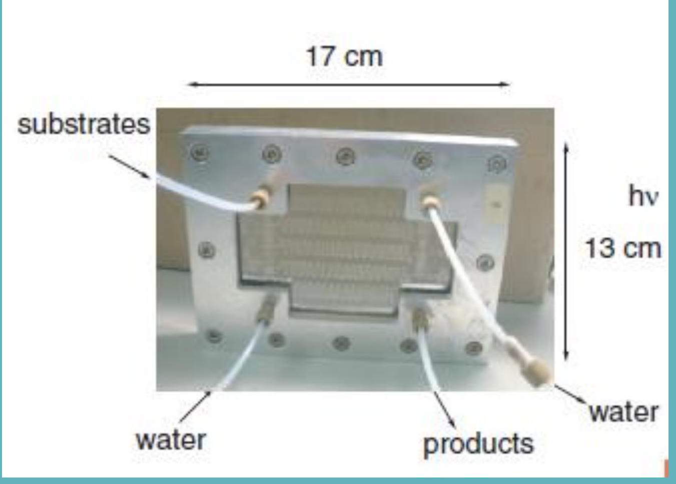
Disadvantages

- high pressure drop
- small throughput

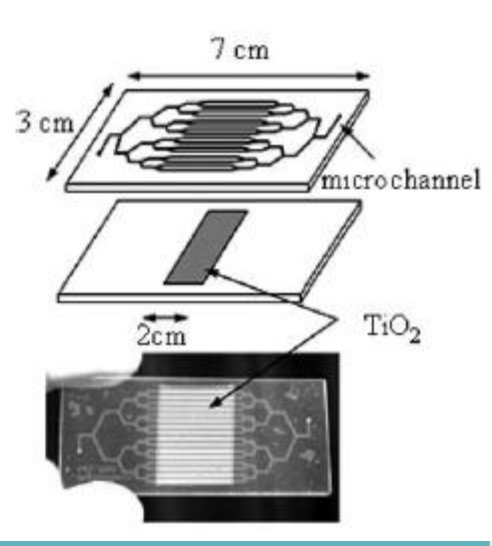
Photo(cata)lytic microreactors



Lu et al., 2004



Fukuyama et al., 2004



Takei et al., 2005

(Van Gerven, Mul, Moulijn, Stankiewicz)

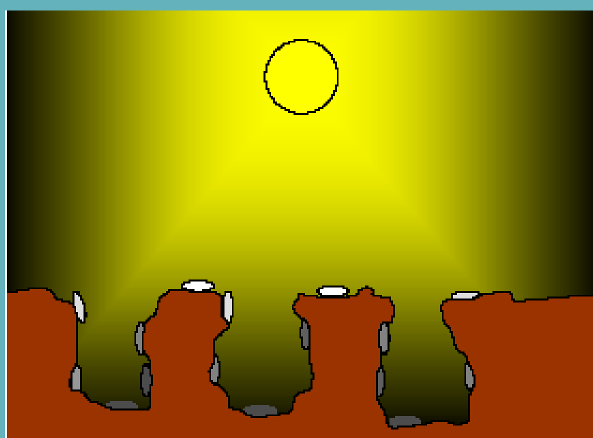
Research evolution

external HID

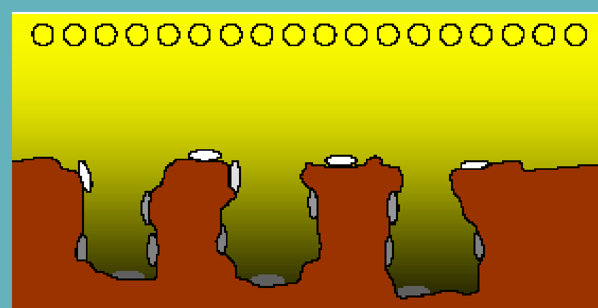
external LED, OF

internal LED

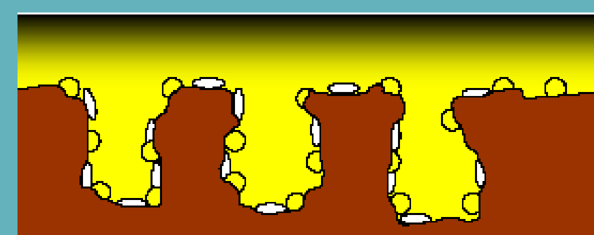
PAST APPROACH



CURRENT APPROACH



PROPOSED APPROACH

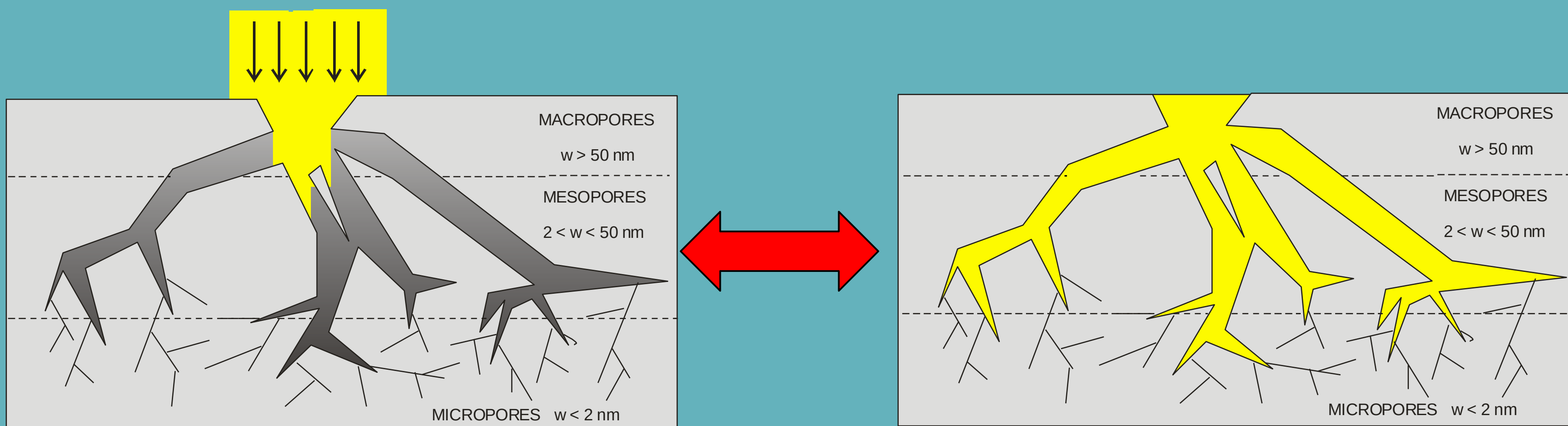


(Van Gerven, Mul, Moulijn, Stankiewicz)

Improving energy/catalyst efficiency

External light

Internal light



Proof of concept still required!

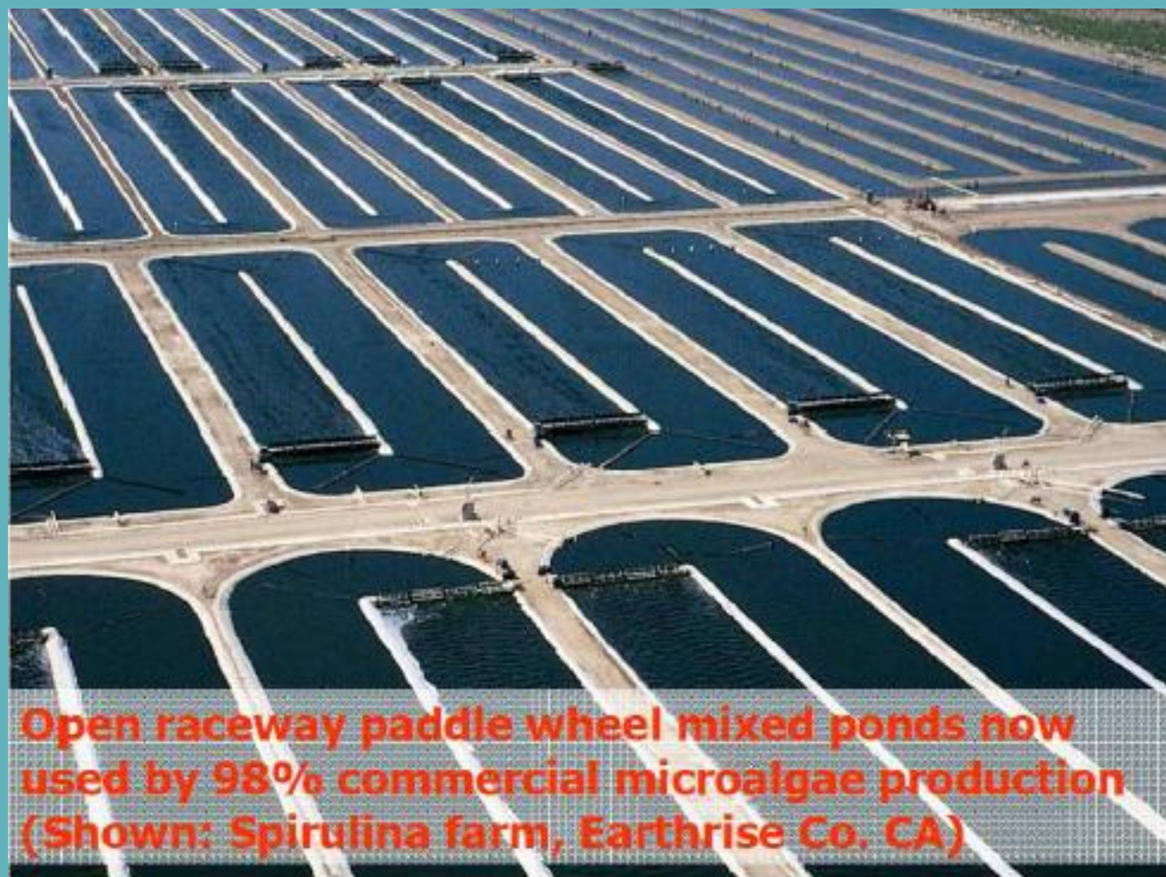
Photosynthesis

Photosynthetic cell culturing (algae biotechnology)

closed photobioreactors (option 1)

Photosynthesis

Photosynthetic cell culturing (algae biotechnology)



outdoor

open

ponds

(option 2)

Photosynthesis

Open Ponds vs. Closed Photobioreactors

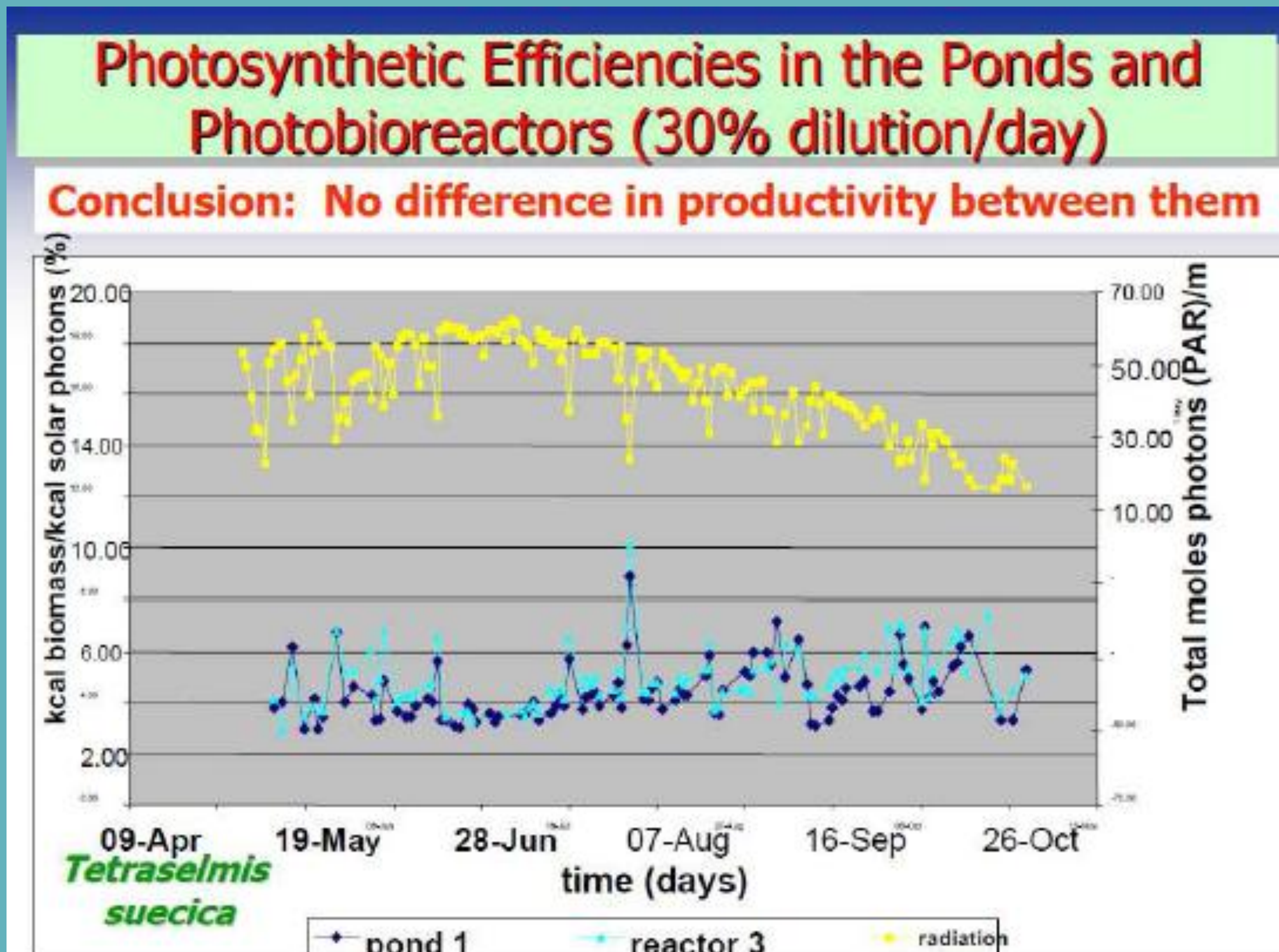
Parameter	Relative advantage	Note
Contamination risk	Ponds < PBRs	Just a matter of time for either
Productivity	Ponds ~ PBRs	NO substantial difference*
Space required	Ponds ~ PBRs	A matter of productivity
Water losses	Ponds ~ PBRs	Evaporative cooling needed
CO2 losses	Ponds ~ PBRs	Depends on pH, alkalinity, etc.
O2 Inhibition	Ponds > PBRs	O2 major problem in PBRs
Process Control	Ponds ~ PBRs	no major differences (weather)
Biomass Concentration	Ponds < PBRs	function of depth, 2 -10 fold
Capital/Operating Costs	Ponds << PBRs	Ponds >10 x lower cost!

*Productivity can be higher if PBRs are vertical or in cold conditions.

CONCLUSION: Are PBRs better than ponds? Sometimes (e.g. in cold climate), sometimes not. Advantages greatly overstated. For biofuels can't afford PBRs, except for inoculum production

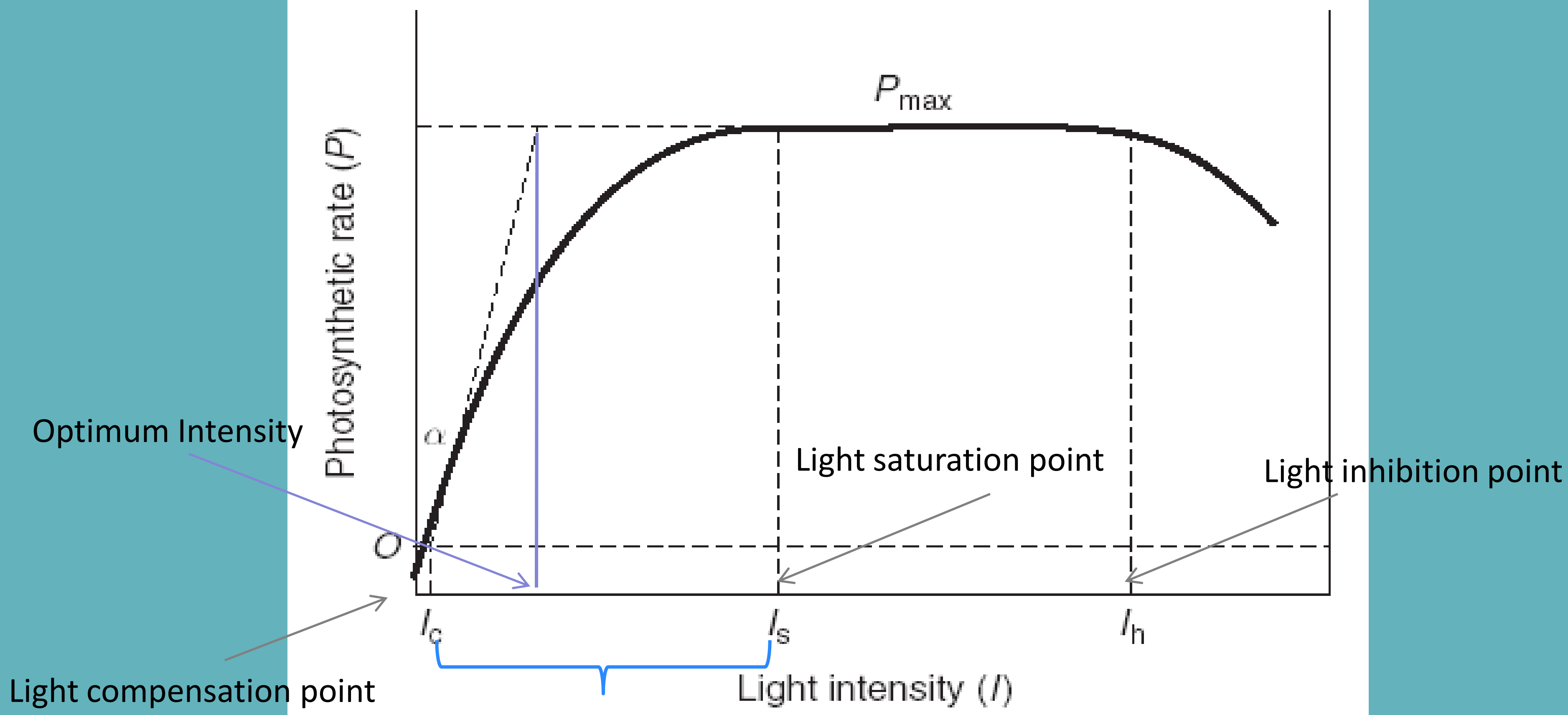
J. Benemann, 5th Annual World Congress on Industrial Biotechnology, Chicago, April 30, 2008

Photosynthesis



Photosynthesis

Light-response curve of photosynthesis (P-I curve)

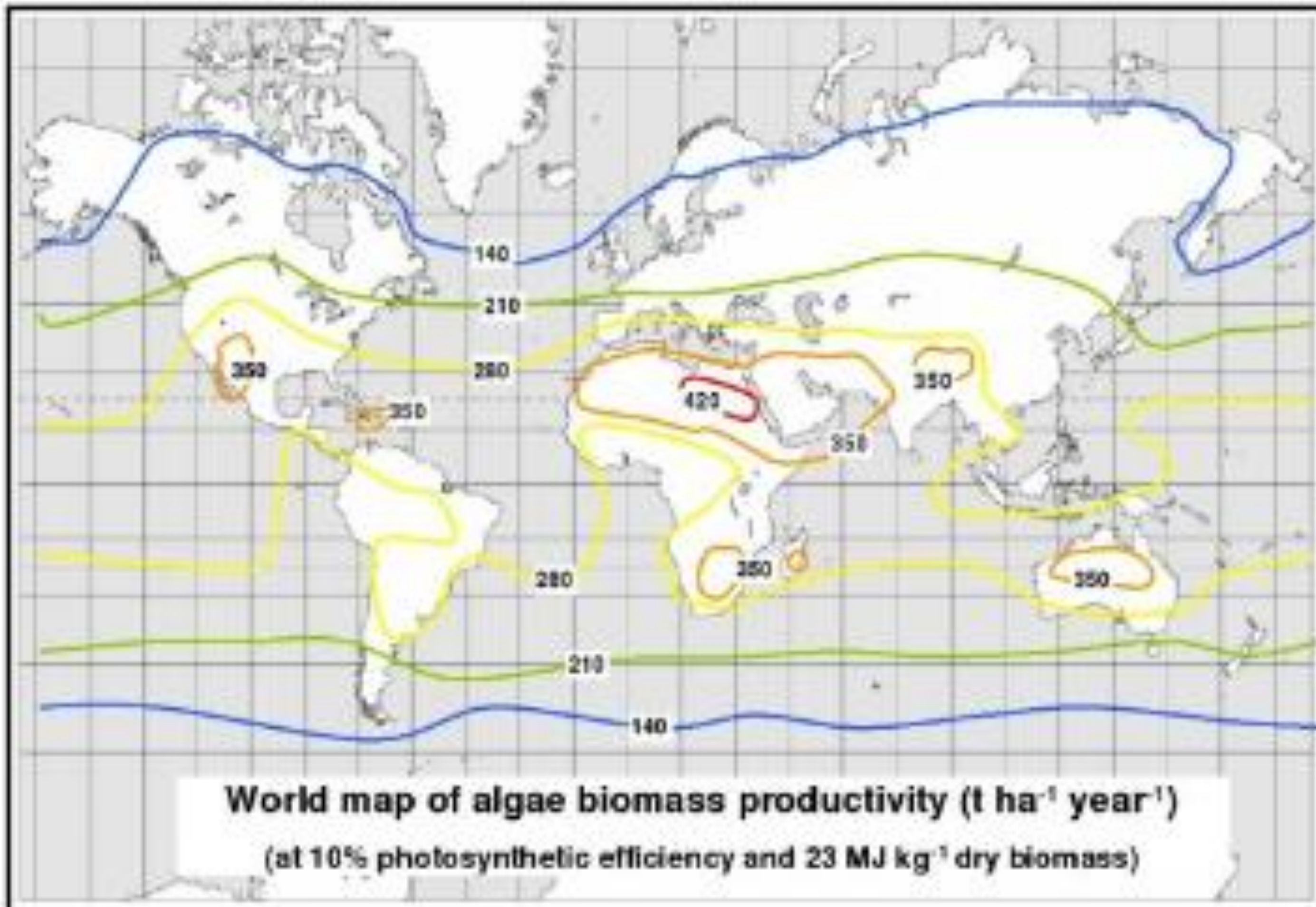


Proper intensity range

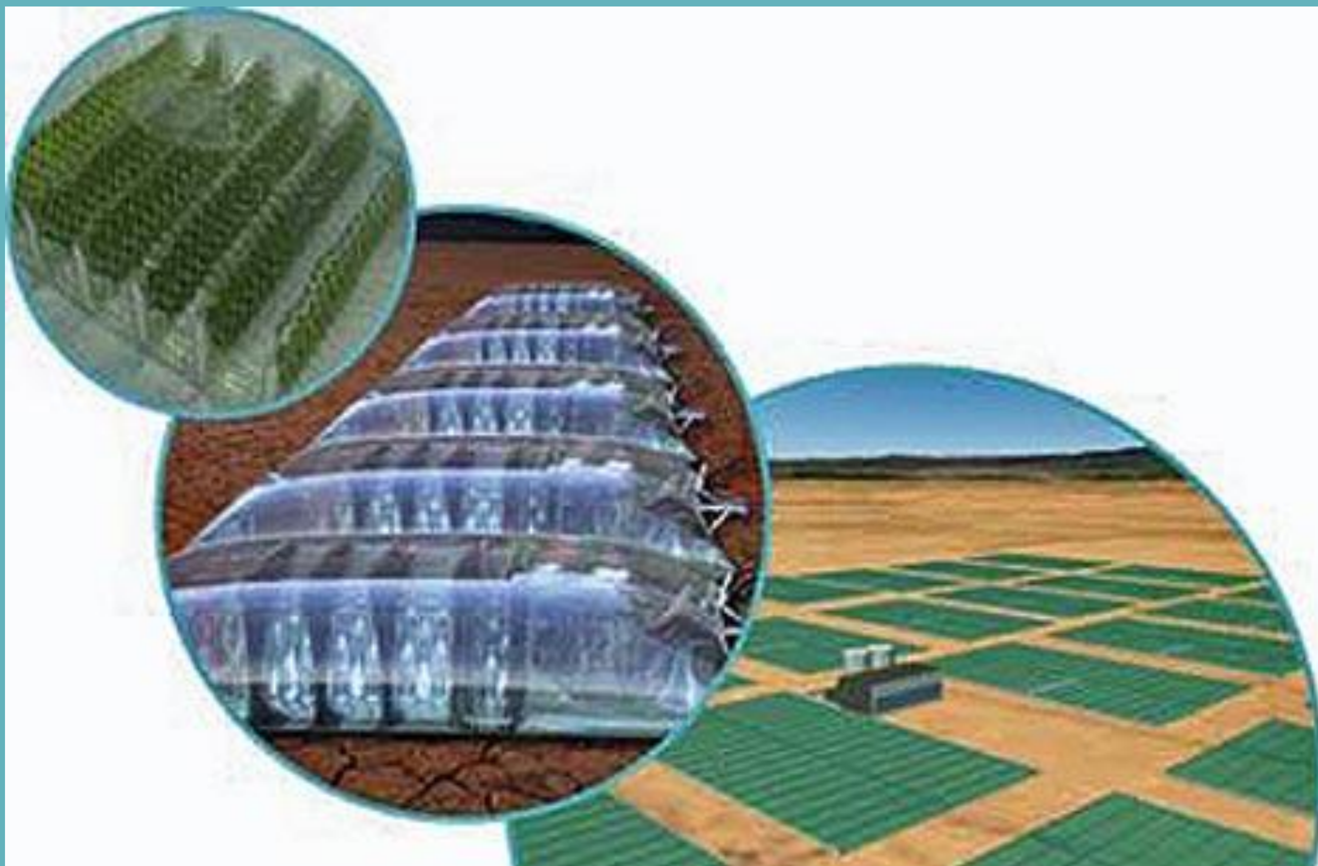
The curve is strain dependent

Photosynthesis

Theoretical maximum for open ponds based on useful solar light intensity and photosynthetic conversion efficiency



Photosynthesis



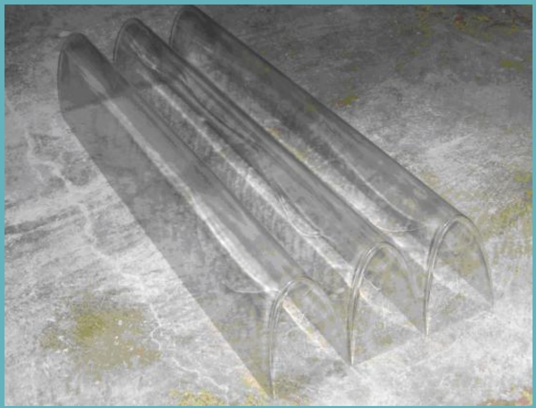
Quest for optimal combination between open ponds and closed photobioreactors

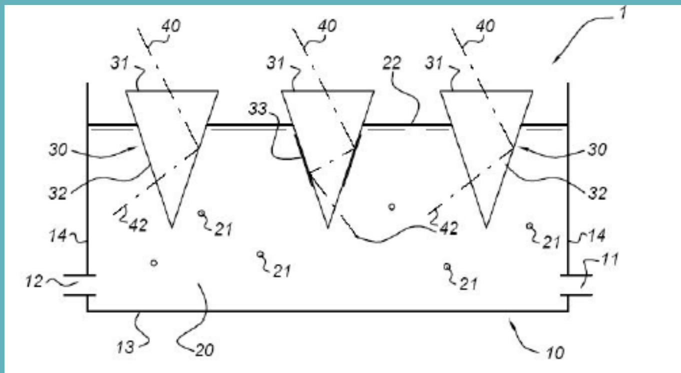
e.g. Proviron, Belgium

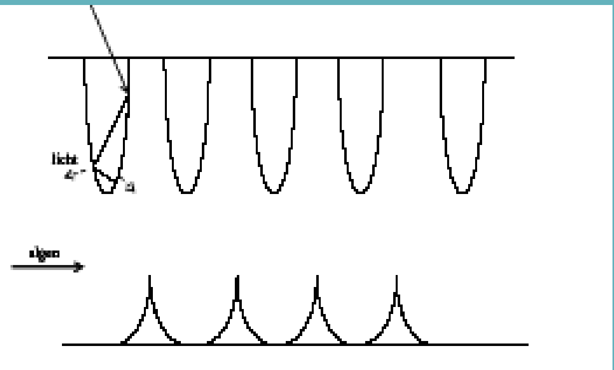
(Ranjbar,Van Gerven, Stankiewicz)

Case 3: LEF

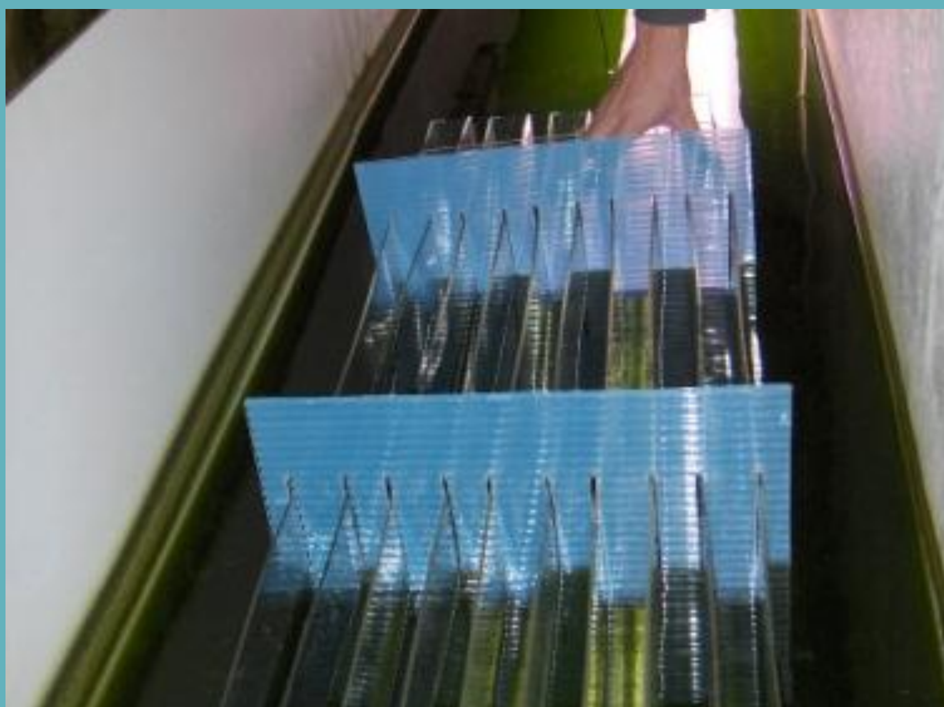
Improved sunlight distribution in algae ponds





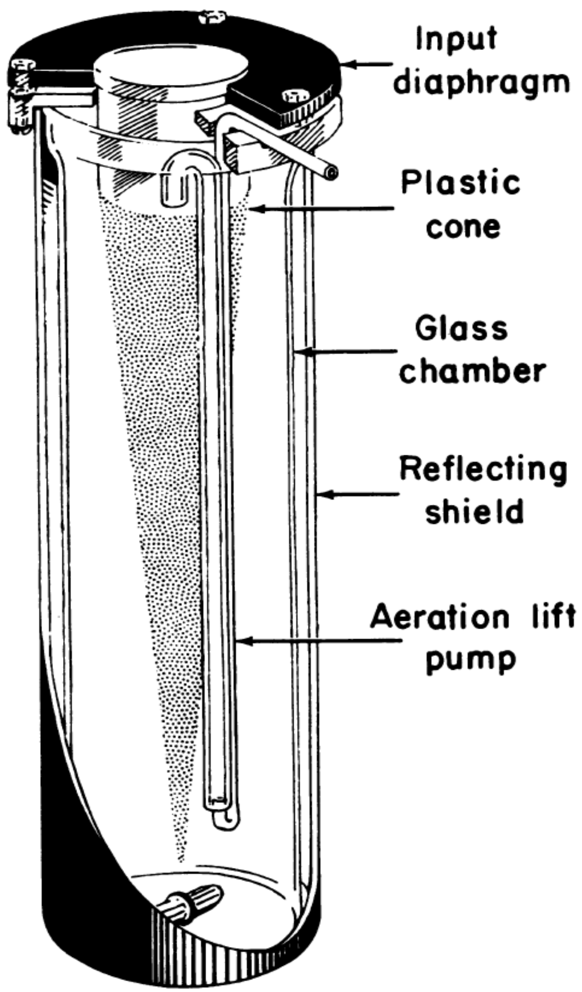


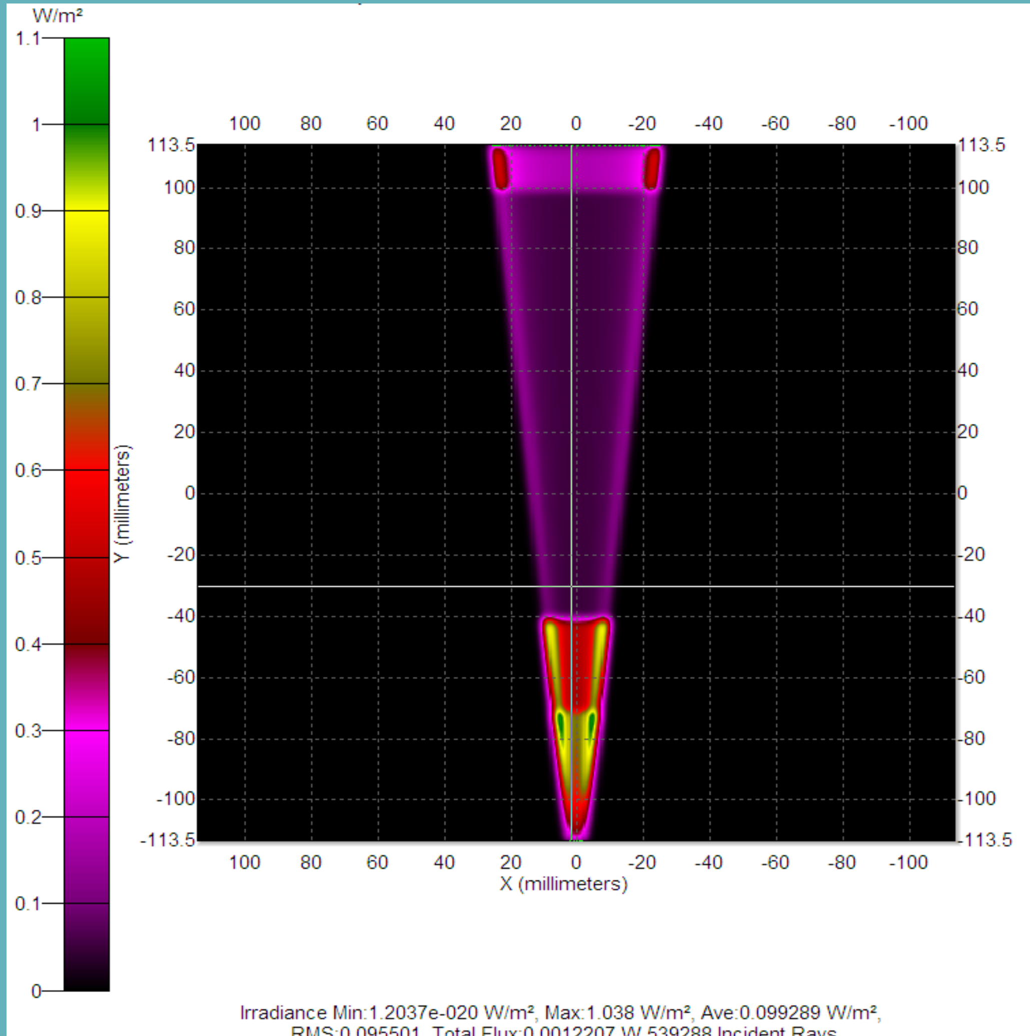
Improving light ingress in pond



(Ranjbar,Van Gerven, Stankiewicz)

LEF design by modeling





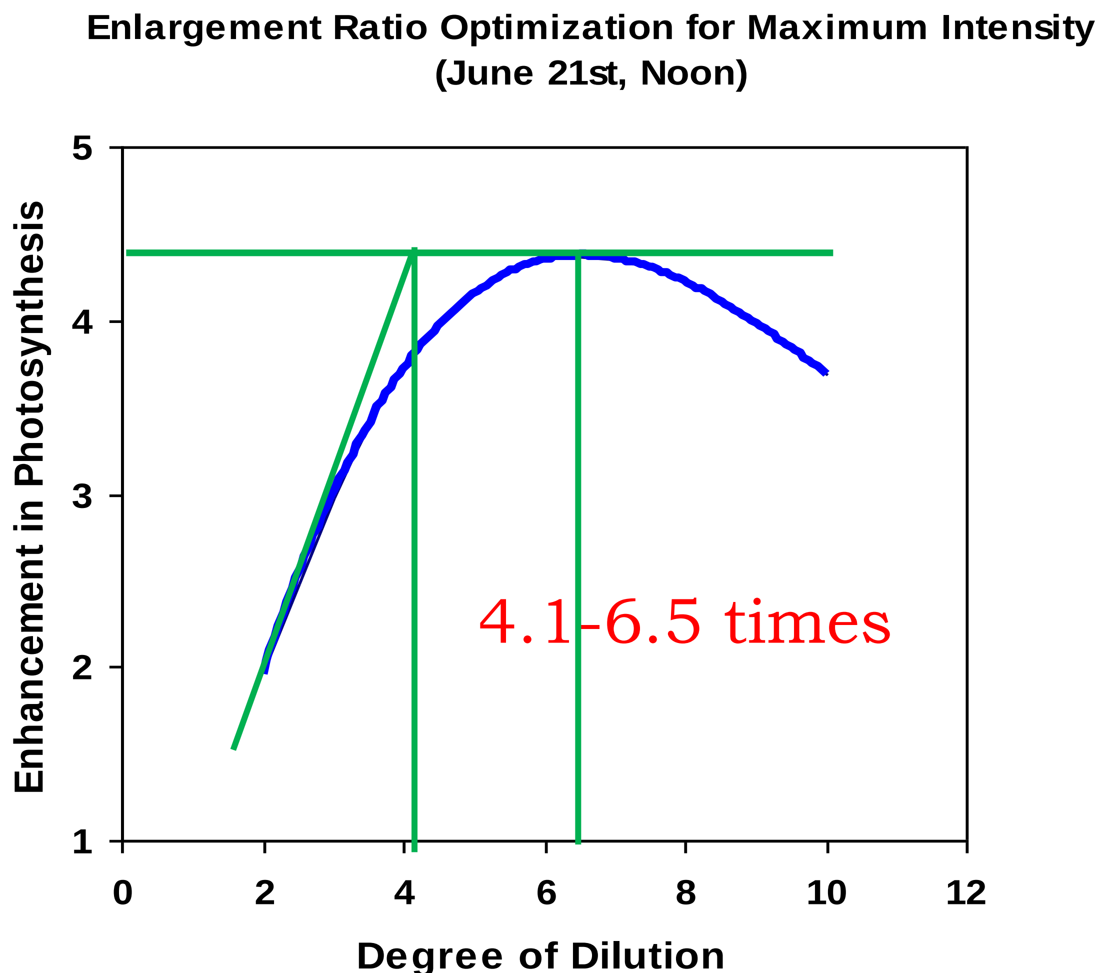
- Ray tracing technique
- Validation of model with literature and experimental data

(Ranjbar,Van Gerven, Stankiewicz)

Indoor application

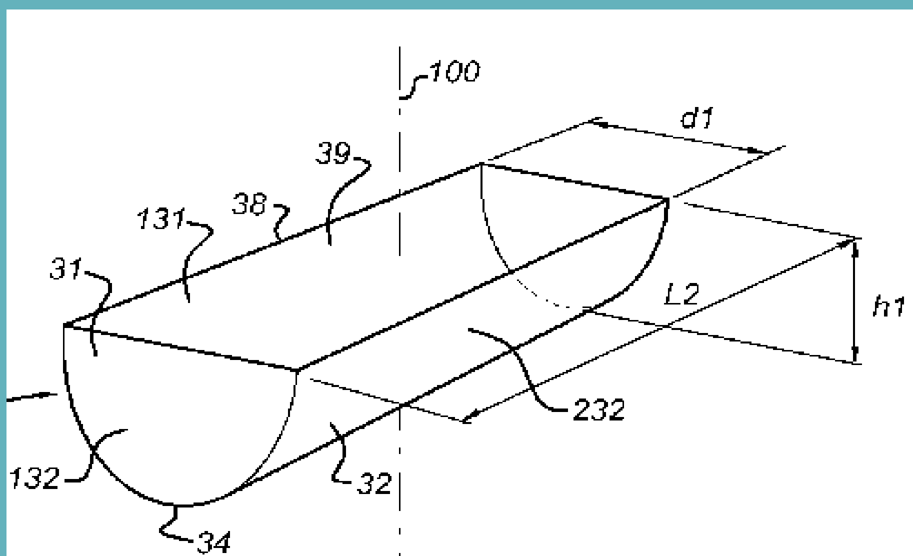
1-Optimum Degree of Dilution

The maximum intensity of sunlight is a factor of geographic latitude. For Gran Canaries the relation between degree of dilution and expected enhancement in productivity is shown in this graph (for maximum light intensity at noon June 21st)

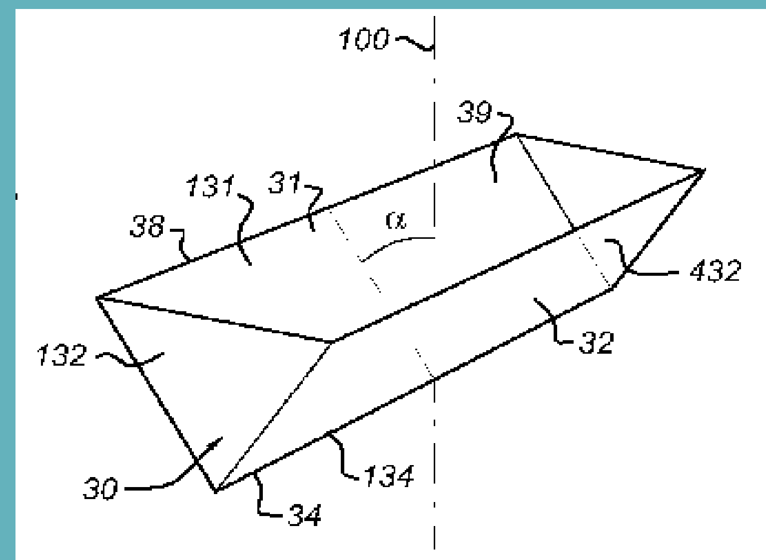


Indoor application

2- Shape and Geometry



‘parabola’

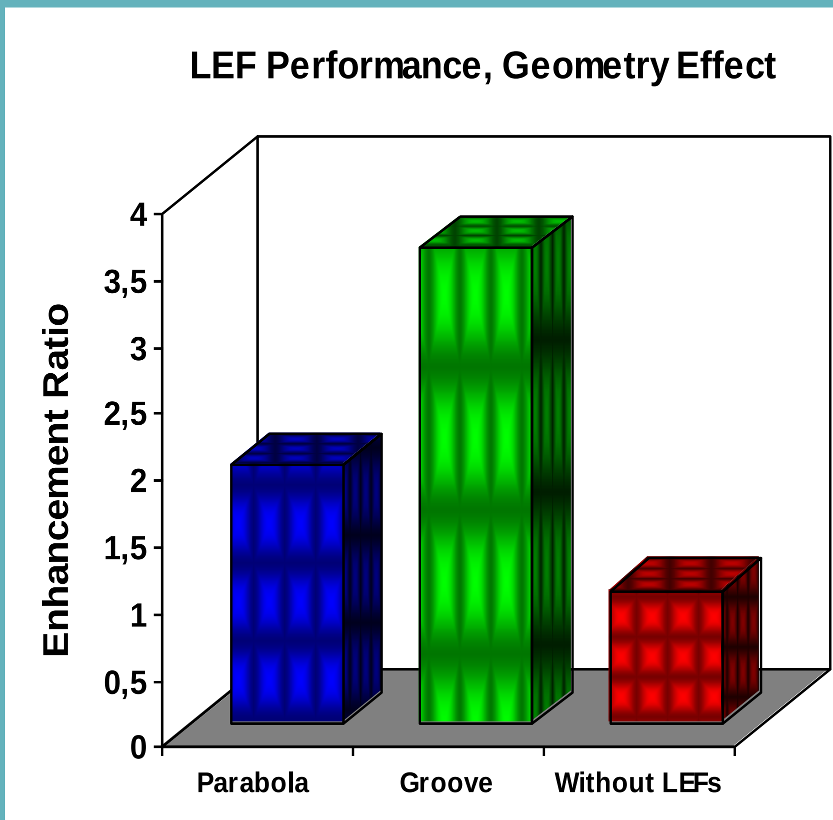


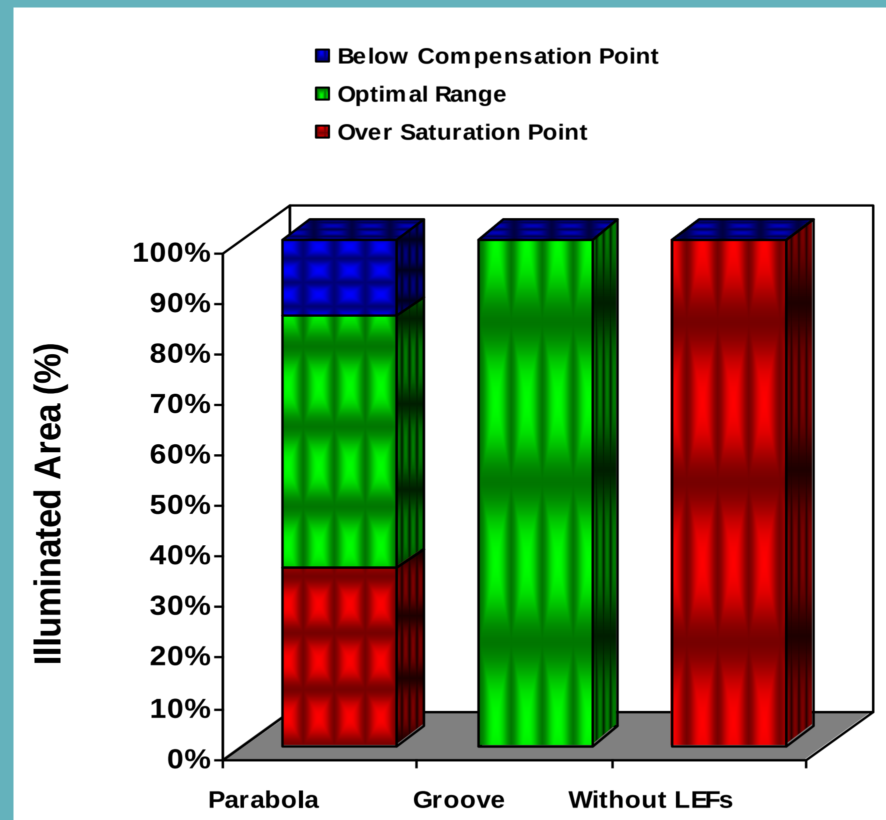
‘groove’

(Ranjbar,Van Gerven, Stankiewicz)

Indoor application

2-Effect of Shape on Productivity





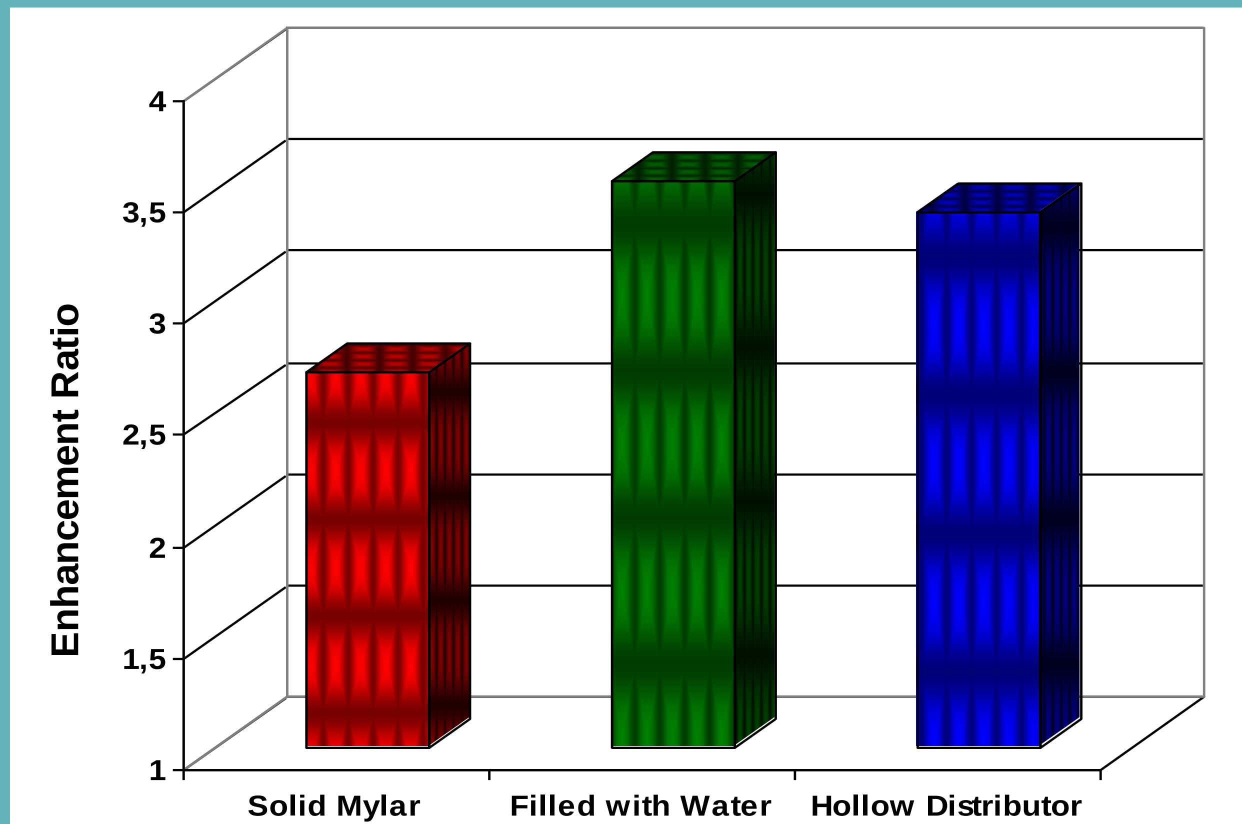
Indoor application

3- Material

The material should have
1-Good optical properties
2-UV durable
3-Not brittle
4-Cheap and easy to form

The candidates are

1-PVC (food grade, UV durable)
2-PET
3-Mylar
4-PC

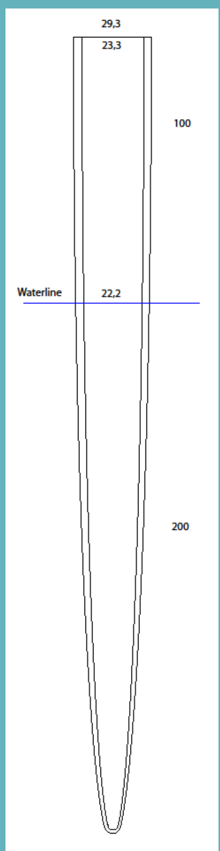


Since the size of distributor and amount of polymer is a considerable cost, it is preferred to reduce the amount of polymer. A hollow distributor filled with water is easier to implement.

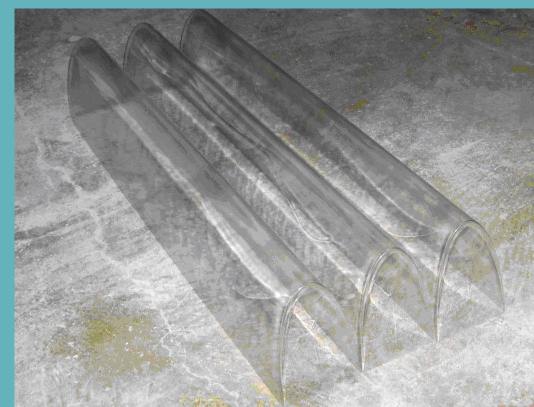
(Ranjbar,Van Gerven, Stankiewicz)

Indoor application

3- Material



polycarbonate

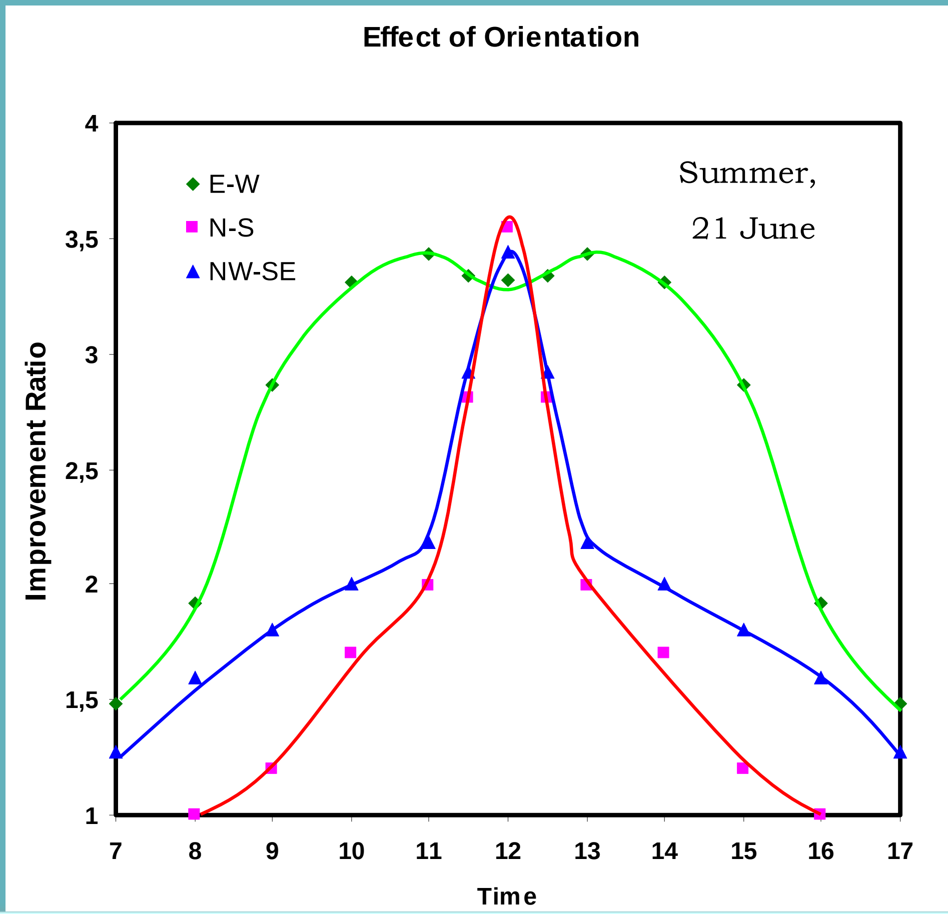


acrylic

mylar

Outdoor application

1- Effect of orientation and daily variation



Average daily improvement

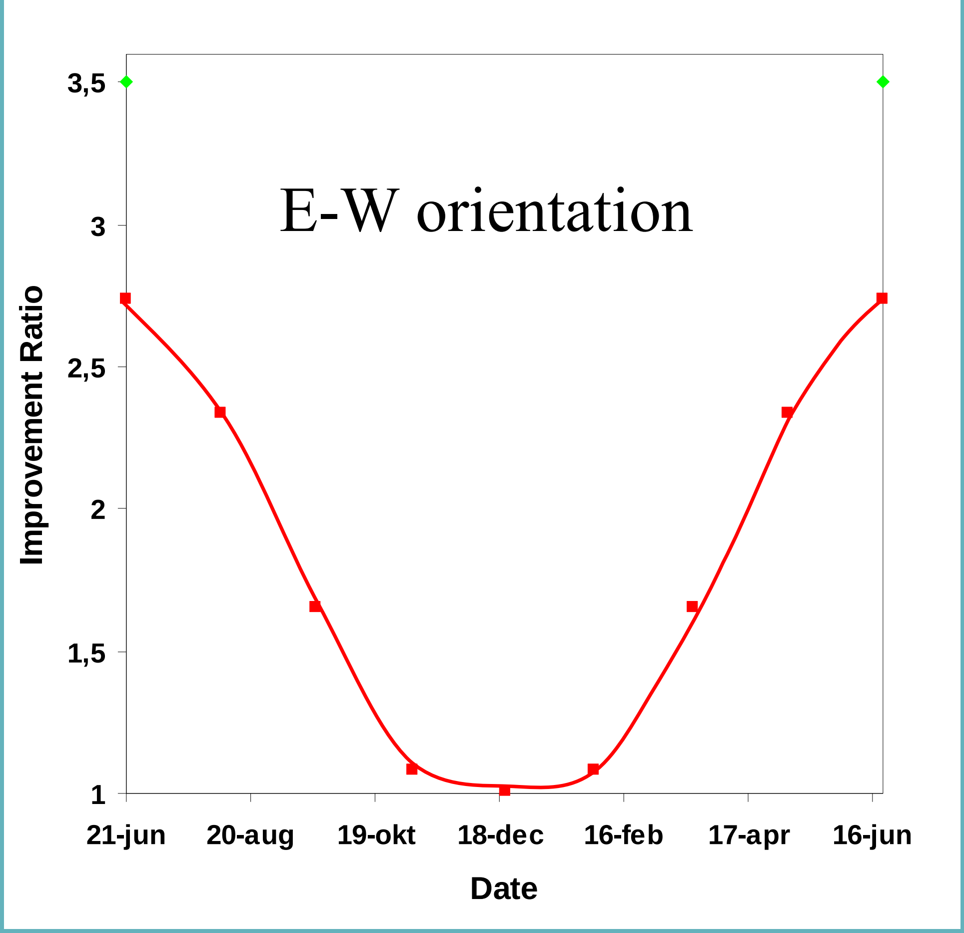
- **N-S = 1.750**
- **NW-SE = 2.077**
- **E-W = 2.766**

Outdoor application

2- Effect of annual variation

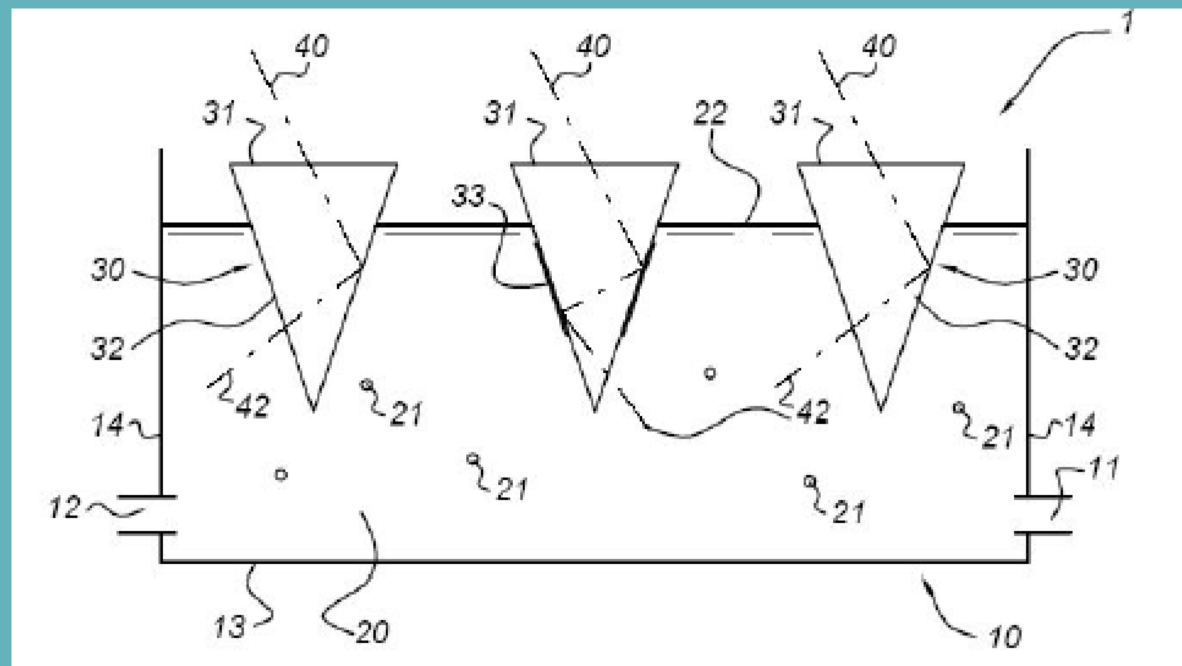
Average annual improvement

Ordinary LEFs=1.831



LEFs in practice

- Concept is proven
- More experimental validation under way
- Current dilution ratio = 1.8, however ideal ratio = 4.1-6.5
- Further optimisation needed
- Pilot scale, cost-benefit calculation still to come



Conclusion

- Light energy is still under-utilised
- Advances require collaboration between chemical engineers and mechanical engineers/physicists
- Due to the energy crises and the advances in light technology, interest is growing again
- Process intensification required to increase efficiency/productivity