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 = the main form of energy for plants
• **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

- Gamma rays
- X-rays
- Ultraviolet rays
- Infrared rays
- Radar
- FM
- TV
- Shortwave
- AM

Wavelength (meters):
- $10^{-14}$
- $10^{-12}$
- $10^{-10}$
- $10^{-8}$
- $10^{-6}$
- $10^{-4}$
- $10^{-2}$
- 1
- $10^2$
- $10^4$

Visible Light

Wavelength (nanometers):
- 400
- 500
- 600
- 700

= Solar Energy
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

- 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)

Ullmann’s Encyclopedia, 2006
Photochemistry is already implemented in industry, although limited.

Some examples:

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

60-100 ton/y, main process route

Monnerie & Ortner, 2001
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

- **Commercial**
  - **Air purification**
    - Decomposition of aldehyde
    - Removal of NOx
  - **Water purification**
    - Decomposition of organics
    - Municipal water sterilization
    - Decomposition of virus
  - **Self-cleaning**
    - Anti-fogging
    - Anti-contamination
    - Decomposition of oil
    - Superhydrophilic effect
  - **Energy conversion**
    - Hydrogen production
    - Artificial synthesis
  - **Organic synthesis**
    - Production of monomers
    - Selective oxidation

*Lab scale*

Source: Guido Mul
Air Purification

NO + O₂ → NO₂ → NO₃⁻

Source: Guido Mul
Water Purification

\[ H_2O_2 + \text{`CH'} \rightarrow CO_2 + H_2O \]

No catalyst

Andijk

\[ O_2 + \text{`CH'} \rightarrow CO_2 + H_2O \]

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

- Efficient conversion of input energy into light

- Adsorption

- Mass transfer

- Desorption

- Reactor design

- Photon transfer

- Catalyst design

- Catalyst recovery
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
- Spinning disc reactors
- Microreactors

Improvement of mass transfer
Optical fibers

Improvement of light transfer
LED
Comparison of reactor configurations

<table>
<thead>
<tr>
<th>Photocatalytic reactor</th>
<th>catalyst coated surface per reaction liquid volume (m²/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>slurry reactor</td>
<td>2631</td>
</tr>
<tr>
<td></td>
<td>8500-170000</td>
</tr>
<tr>
<td>(multi)annular/immersion reactor</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>2667</td>
</tr>
<tr>
<td>optical fiber/hollow tube reactor</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>1087</td>
</tr>
<tr>
<td></td>
<td>1920</td>
</tr>
<tr>
<td></td>
<td>2000</td>
</tr>
<tr>
<td>monolith reactor</td>
<td>943</td>
</tr>
<tr>
<td></td>
<td>1333</td>
</tr>
<tr>
<td>spinning disc reactor</td>
<td>50-130</td>
</tr>
<tr>
<td></td>
<td>20000-66000</td>
</tr>
<tr>
<td>microreactor</td>
<td>7300</td>
</tr>
<tr>
<td></td>
<td>12000</td>
</tr>
<tr>
<td></td>
<td>14000</td>
</tr>
<tr>
<td></td>
<td>250000</td>
</tr>
</tbody>
</table>

- Comparison based on catalyst coated surface per reaction liquid volume (m²/m³)
- 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)

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

Optical Fiber Reactor

Optical Fiber Reactor (Carneiro, Mul, Moulijn)
Optical Fiber Monolith Reactor

- wastewater treatment
- monolith merely distributor of optical fibers
- **Not exploited:** excellent mass transfer characteristics for gas/liquid systems

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Optical fiber monolith reactor 1.0

1 coating

3 coatings

9 coatings

Choi et al. 2001
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
Advantages:

- light propagation process in the fiber
- Is NOT DEPENDENT on physical properties of the catalytic layer

Monolith multiphase advantages considered

Monolith: catalyst support
Operating conditions:
V = 800 mL
Film flow regime
Φ_{air} = 15 dm^3/min
Φ_{Liq} = 0.5 dm^3/min
16.7g TiO₂
Air presaturated with Chexane

Monolith:
Cordierite
25 cpsi
L = 25 cm
Side Light Fibers (OFMR 2.1)
Side Light Fibers

Light intensity homogeneous throughout the length

Relative intensity \([I/I_0]\)

Distance from fiber entrance [cm]

Bare fibers
Tip-coated fibers

(Carneiro, Mul, Moulijn)
Top Illumination Reactor (slurry)
Side Light Fiber Reactor (slurry)
Annular Reactor (slurry)
OFMR a) Fiber Optic
b) Liquid
c) Catalyst layer
d) Monolith

Reactor comparison (Carneiro, Mul, Moulijn)

1g/L catalyst
### Results

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$R^\text{in}$ [mol.s$^{-1}$]</th>
<th>$\rho_p$ [Einst.s$^{-1}$]</th>
<th>$\xi$ [mol.Einst$^{-1}$]</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annular reactor</td>
<td>$1.59 \times 10^{-6}$</td>
<td>$1.96 \times 10^{-4}$</td>
<td>$0.008$</td>
<td>Low efficiency of light utilization</td>
</tr>
<tr>
<td>Side light fiber reactor</td>
<td>$7.68 \times 10^{-10}$</td>
<td>$3.69 \times 10^{-7}$</td>
<td>$0.002$</td>
<td>Low exposure of catalyst to light</td>
</tr>
<tr>
<td>OFMR</td>
<td>$2.28 \times 10^{-8}$</td>
<td>$3.69 \times 10^{-7}$</td>
<td>$0.062$</td>
<td>Bad desorption from catalyst</td>
</tr>
<tr>
<td>Top illumination reactor</td>
<td>$1.20 \times 10^{-7}$</td>
<td>$7.95 \times 10^{-7}$</td>
<td>$0.151$</td>
<td>... but slurry reactor, requiring post-separation of catalyst</td>
</tr>
</tbody>
</table>

$$\xi = \frac{\text{reaction rate (mol/s)}}{\text{photon flow (Einstein/s)}} = \text{photonic efficiency}$$
Further work needs to be done

Present results

Petroleum geochemistry

Biochemical processes

Industrial catalysis

Reactivity (mol / (m_3.s))

10^{-9} 10^{-6} 10^{-3} 1

(Carneiro, Mul, Moulijn)
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

Output Spectrum Medium Pressure Mercury Lamp versus UV LED 395nm

Spectral Intensity vs. Wavelength (nm)
Advantages of LED 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

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

White LED 152 lm/W small chips (UCSB SSLEC)

Luminous Efficiency (lm/W)

- Fluorescent
- Compact Fluorescent
- AllInGaP/GaP (red, orange)
- Incandescent bulb
- GaAsP:N
- InGaN (green)
- InGaN (blue)
- SiC (blue)
- Thomas Edison's first bulb

Time (years)

Optimal wavelength?

Alachlor degradation by UV with/without TiO2

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Total power consumption (W)</th>
<th>Photointensity (Einstein l⁻¹ min⁻¹)</th>
<th>Direct photolysis quantum yield</th>
<th>Photocatalysis quantum yield</th>
<th>Photolysis rate constant (min⁻¹)</th>
<th>Photocatalysis rate constant (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>70</td>
<td>1.80 x 10⁻⁴</td>
<td>0.095</td>
<td>0.12</td>
<td>0.088</td>
<td>0.112</td>
</tr>
<tr>
<td>300</td>
<td>210</td>
<td>6.64 x 10⁻³</td>
<td>0.051</td>
<td>0.54</td>
<td>0.012</td>
<td>0.128</td>
</tr>
<tr>
<td>350</td>
<td>240</td>
<td>3.24 x 10⁻²</td>
<td>0.008</td>
<td>0.21</td>
<td>0.005</td>
<td>0.129</td>
</tr>
</tbody>
</table>

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

Optimal wavelength?

Decomposition of NO\textsubscript{x}

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

Set-up @ KU Leuven

Batch mono-LED reactor

Reactors

Side view

Bottom view

Top view
Uniformity of light immission?

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

- Al foil
- Silver

Phenol degradation (%)

Jamali et al., In submission

Use of reflectors

Comparison of Al foil reflector with no reflector

Irradiance measured in the centre of the reactor

Jamali et al., In submission
Optimise LED viewing angle

Phenol degradation (%) vs. Viewing angle (degree)

Jamali et al., In submission
### Comparison

<table>
<thead>
<tr>
<th>UV light source</th>
<th>irradiance (W/m²)</th>
<th>Pollutant</th>
<th>I.C (ppm)</th>
<th>Reaction time (h)</th>
<th>Reaction rate (mol.l⁻¹.s⁻¹)</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LED (our results)¹</td>
<td>9.055</td>
<td>Phenol</td>
<td>10</td>
<td>4</td>
<td>6.41 x 10⁻⁹</td>
<td>87</td>
</tr>
<tr>
<td>7 UVA lamps²</td>
<td>70.6</td>
<td>Phenol</td>
<td>20</td>
<td>3.5</td>
<td>1.45 x 10⁻⁸</td>
<td>86</td>
</tr>
</tbody>
</table>

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

Optimal design?

Bucky Ball Batch Reactor
• 20 hexagons and 12 pentagons
• LED on each corner
From batch to flow

Titanium dioxide

UV light

Quartz

Quartz

UV light

Quartz

Quartz

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

  ![Diagram of microreactor components](image)

  - **Advantages**
    - excellent temperature control
    - excellent flow rate control
  
  - **Disadvantages**
    - high pressure drop
    - small throughput

(Van Gerven, Mul, Moulijn, Stankiewicz)
Photo(catalytic)ytic microreactors

Lu et al., 2004

Fukuyama et al., 2004

Takei et al., 2005
Research evolution

PAST APPROACH
external HID

CURRENT APPROACH
external LED, OF

PROPOSED APPROACH
internal LED

(Van Gerven, Mul, Moulijn, Stankiewicz)
Improving energy/catalyst efficiency

Proof of concept still required!

External light

Internal light

(Macro pores $w > 50$ nm)
(Mesopores $2 < w < 50$ nm)
(Micro pores $w < 2$ nm)
Photosynthesis

Photosynthetic cell culturing (algae biotechnology)

closed photobioreactors (option 1)
Photosynthesis

Photosynthetic cell culturing (algae biotechnology)

Open raceway paddle wheel mixed ponds now used by 98% commercial microalgae production (Shown: Spirulina farm, Earthrise Co. CA)
**Photosynthesis**

### Open Ponds vs. Closed Photobioreactors

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

*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.
Photosynthesis

Photosynthetic Efficiencies in the Ponds and Photobioreactors (30% dilution/day)

Conclusion: No difference in productivity between them

- kcal biomass/kcal solar photons (%)
- Total moles photons (PAR/m)

Graph showing data over time (days) with labels for pond 1, reactor 3, and radiation.
Photosynthesis

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

- Optimum Intensity
- Light compensation point
- Light saturation point
- Light inhibition point
- 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
Case 3: LEF

Improved sunlight distribution in algae ponds

(Ranjbar, Van Gerven, Stankiewicz)
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)
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’
Indoor application

2-Effect of Shape on Productivity

LEF Performance, Geometry Effect

Enhancement Ratio

Parabola | Groove | Without LEFs

Illuminated Area (%)

Below Compensation Point
Optimal Range
Over Saturation Point

Enhancement Ratio

Parabola | Groove | Without LEFs

(Ranjbar, Van Gerven, Stankiewicz)
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.
Indoor application

3- Material

- Polycarbonate
- Acrylic
- Mylar

(Ranjbar, Van Gerven, Stankiewicz)
1- Effect of orientation and daily variation

Average daily improvement

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

(Ranjbar, Van Gerven, Stankiewicz)
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