Photocatalytic bioethanol production as future green energy solution

Aakash Welgamage Don

Nathan Skillen

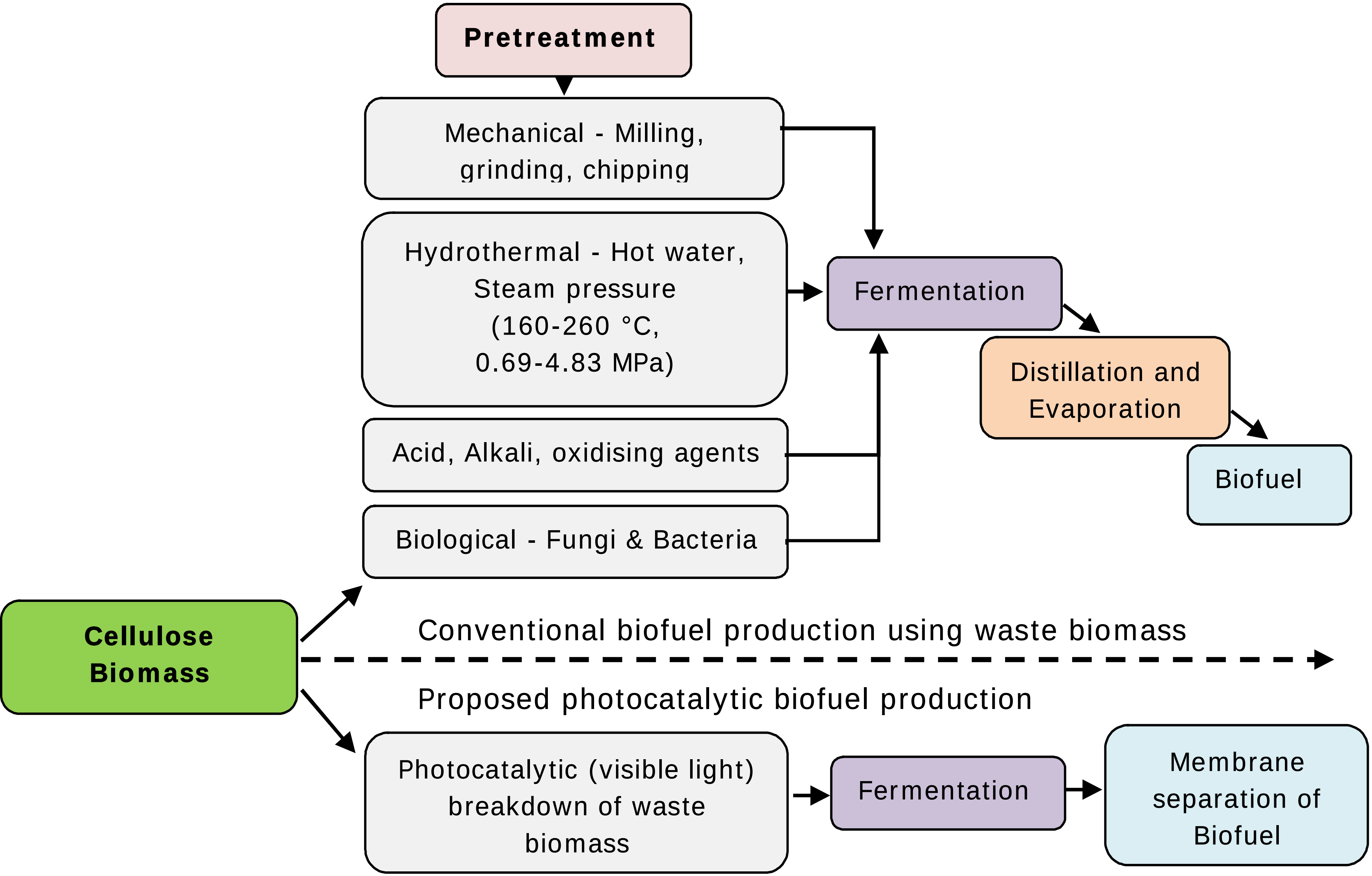
Peter Robertson and Linda Lawton

Guan Zhang

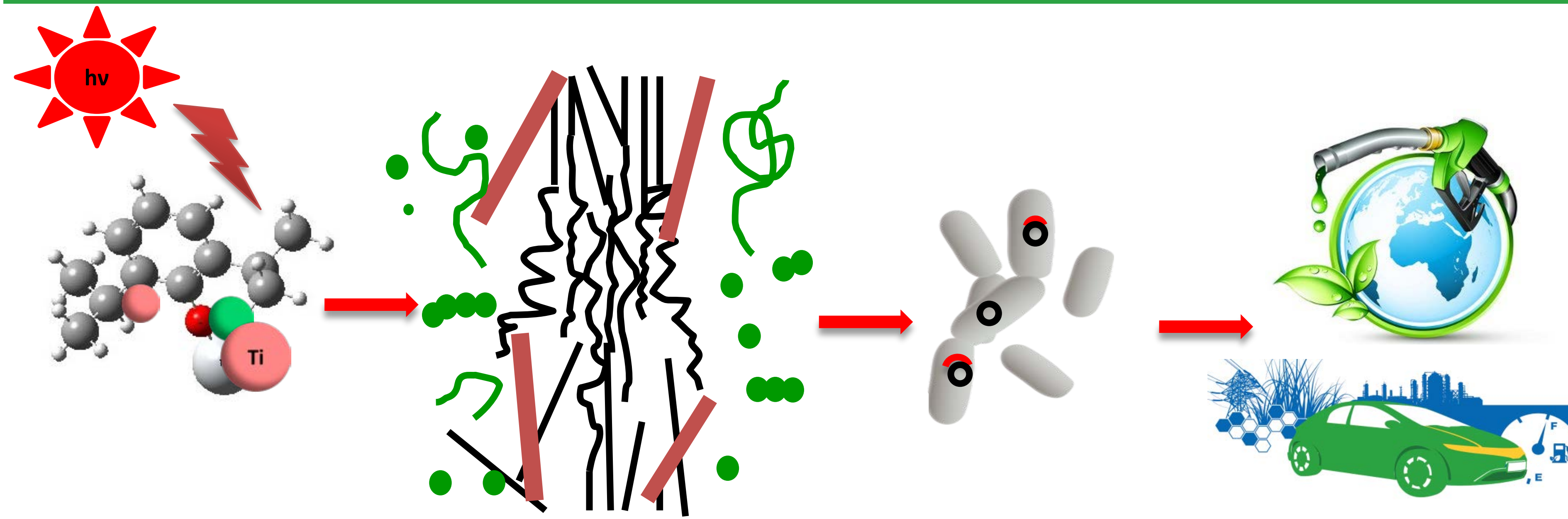
Federica Fina

Paraskevi Efstathiou and John Irvine

Photocatalytic bioethanol vs conventional bioethanol



Photocatalytic Bioethanol Production
Project overview



Natural irradiation or low power illumination | Release of fermentable sugars | Microbial Fermentation | Energy demand - EtOH Supply

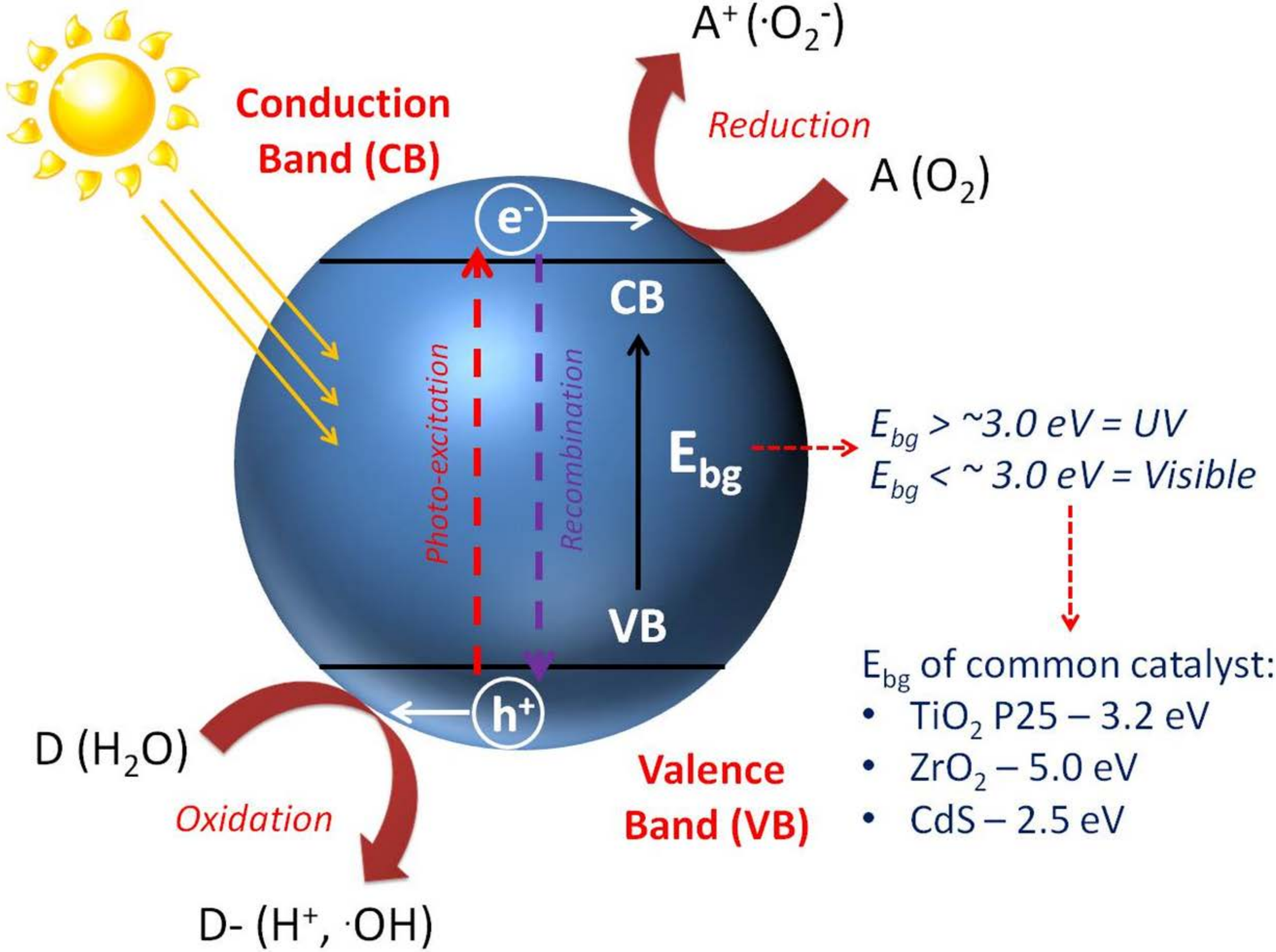
- Visible light nanoparticulate catalyst to release of fermentable sugars from waste biomass.
- Engineer cost and energy efficient cellulosic photocatalytic saccharification reactor
- Select or manipulate microorganism(s) those ferments the photocatalytic by-products

Content of cellulose in common agricultural residue and wastes

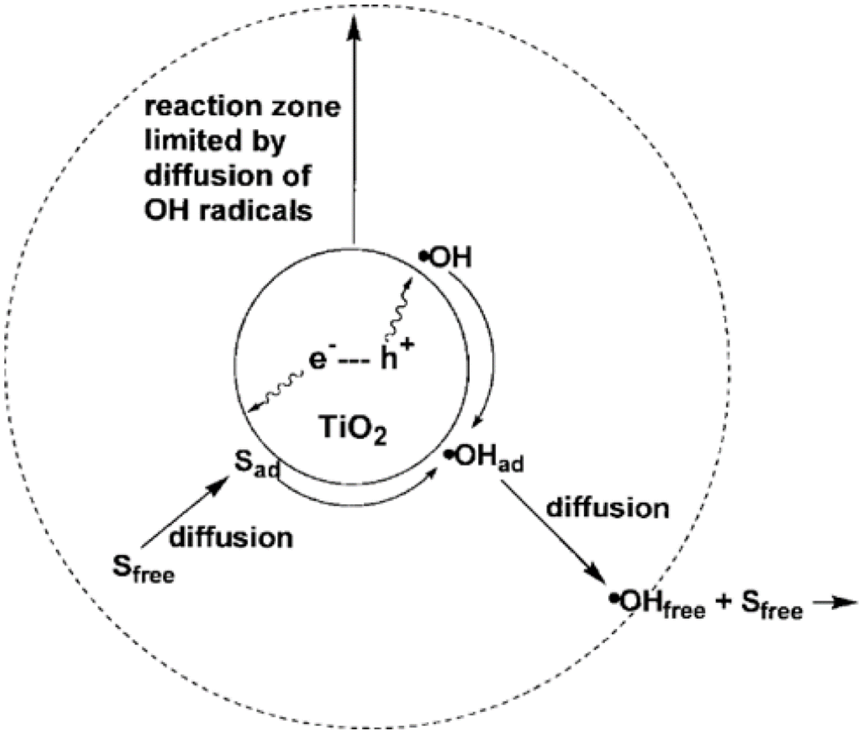
Lignocellulosicbiomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	45-50	24-40	18-25
Softwood stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper →	85-99	0	0-15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspapers	40-55	25-40	18-30
Waste papers from chemical pulps	60-70	10-20	5-10
Primary waste water solid	8-15	NAb	24-29
Swine waste	6.0	28	NAb
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12.0

Prasetyo and Park, 2013

Photocatalysis



The importance of hydroxyl radicals ($OH^{\cdot}$)



Scheme 1. Photocatalytic oxidation of substrates (S) initiated by the surface OH radicals or the diffusing OH radicals in the bulk medium.

Choi, W.; Kim, S.; Cho, S.; Yoo, H.-I. & Kim, M.-H.
Korean J. Chem. Eng., **2001**, *18*, 898-902

Cellulose photodegradation is a

Solid-Solid photocatalysis

Cellulose will not adsorb, so:

- very close contact with catalyst
- Or migrating $OH^{\bullet}$

radius of diffusion will dictate the reaction zone.

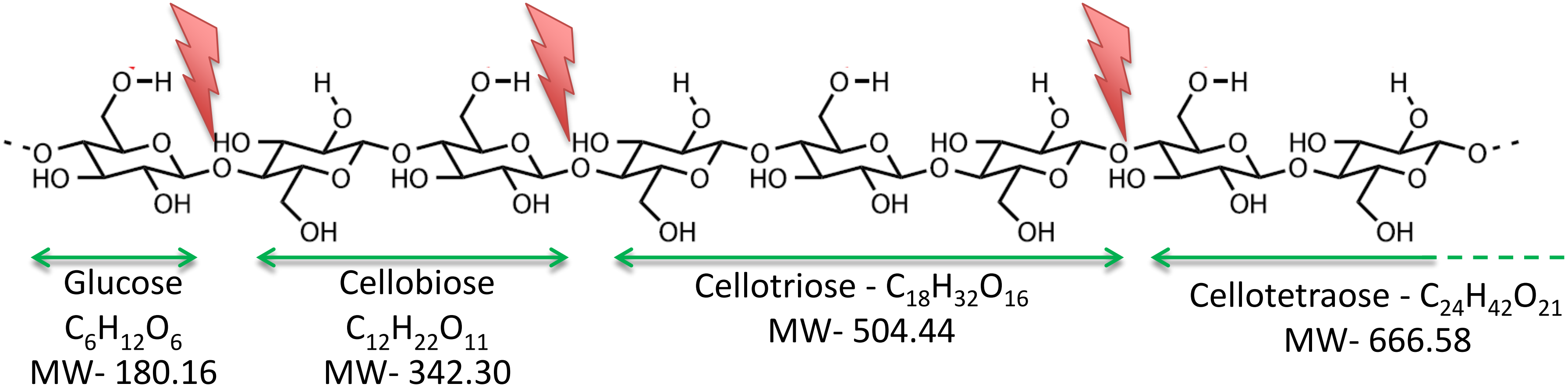
From ~ 1 μm to ~2 mm:

J. Phys. Chem. B, **2002**, *106*, 11818

J. Phys. Chem. B, **2001**, *105*, 6987

Cellulose photodegradation

cleave hydrogen and glycosidic bonds



Organism	Characteristics	Advantages	Reference
Saccharomyces cerevisiae	Facultative anaerobic yeast	Naturally adapted, High alcohol yield, High alcohol tolerance, genetic modification	Girio et al., 2010,
Zymomonas mobilis	Ethanologenic Gram-neg bacteria	High ethanol productivity (five-fold more than *S. cerevisiae*)	Balat & Balat, 2008
Esherichia coli	Mesophilic Gram-neg bacteria.	Ferments pentoses & hexoses, Amenability for genetic modifications	Zayed et al., 1996
Thermoanaerobacterium Saccharolyticum, Thermoanaerobacter ethanolicus, Clostridium thermocellum	Extreme anaerobic bacteria	Resistance to an extremely high temperature of 70 °C Ferment a variety of sugars Amenability to genetic modification	Georgieva et al., 2008 Kumar et al., 2009

HPLC-ELSD analysis of cellodextrins

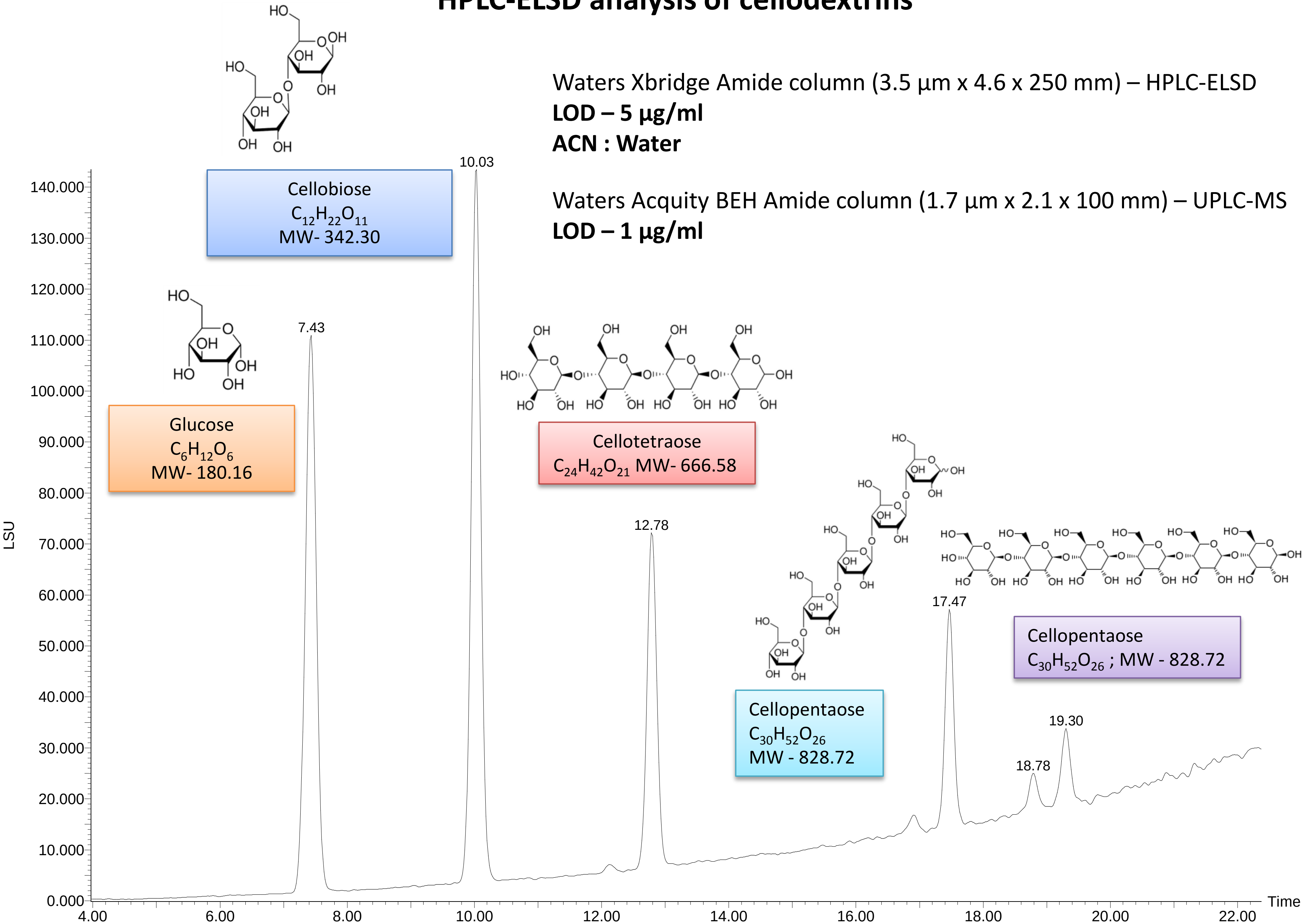
Waters Xbridge Amide column (3.5 µm x 4.6 x 250 mm) – HPLC-ELSD

LOD – 5 µg/ml

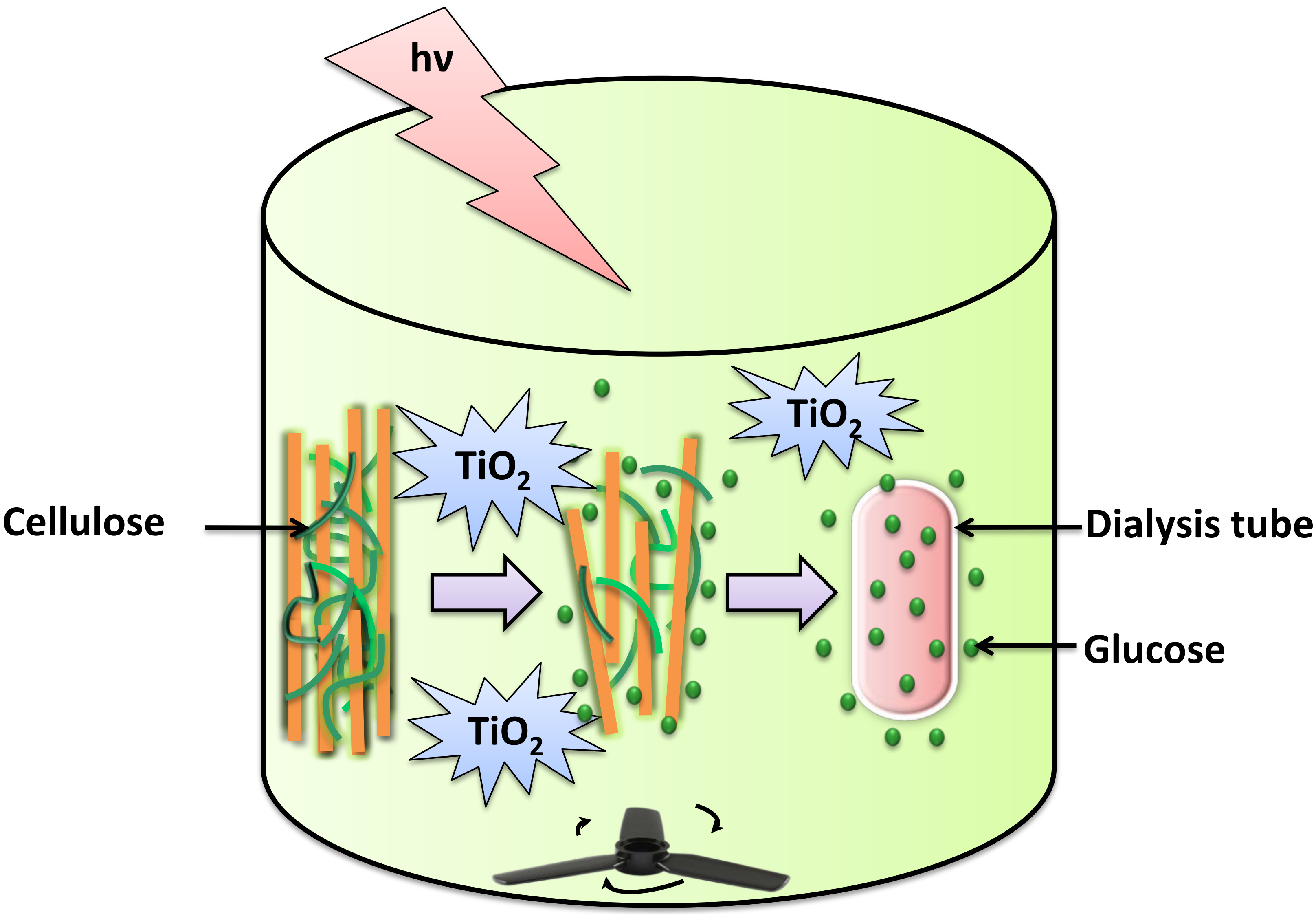
ACN : Water

Waters Acquity BEH Amide column (1.7 µm x 2.1 x 100 mm) – UPLC-MS

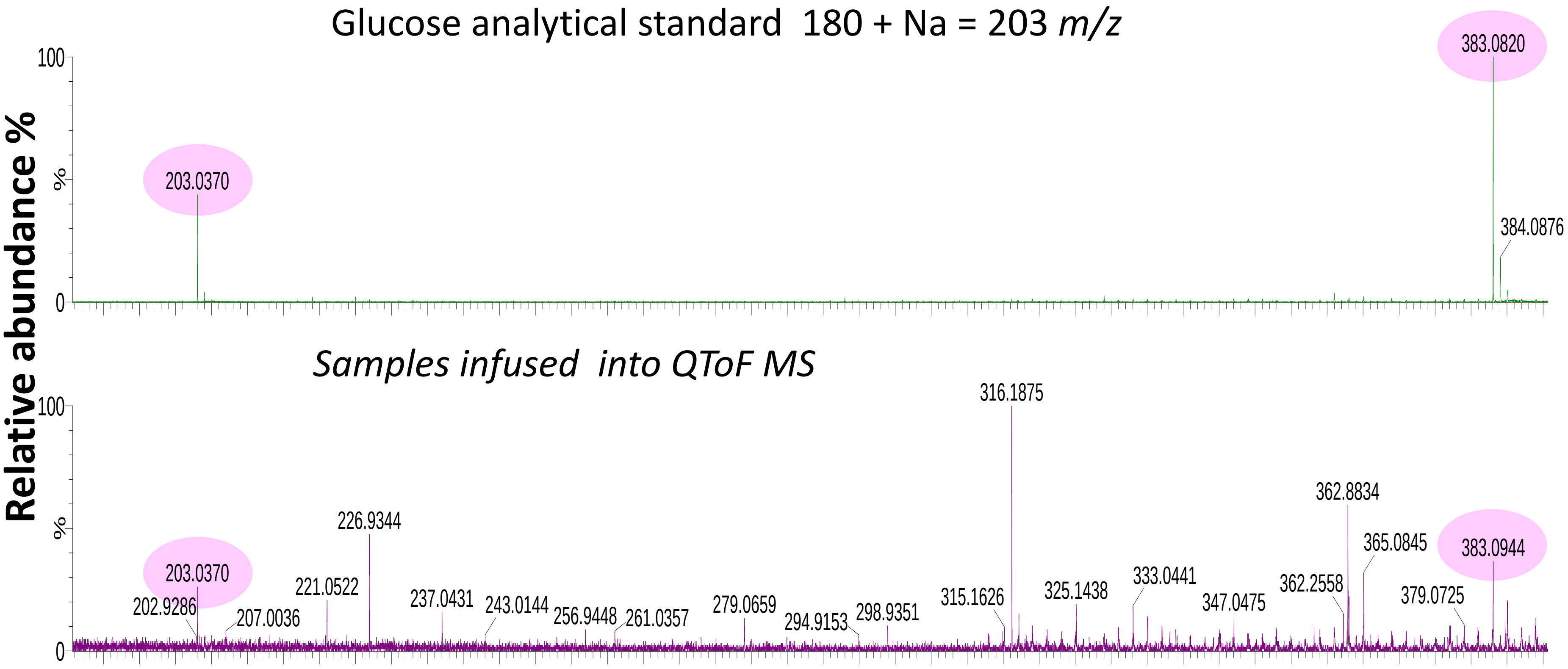
LOD – 1 µg/ml



Proof of Principle

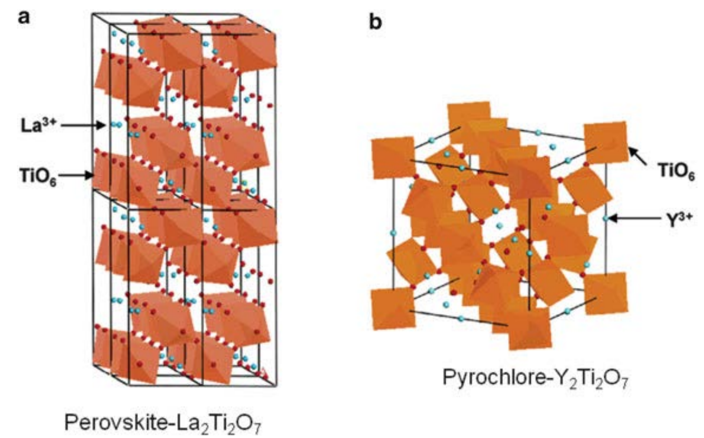


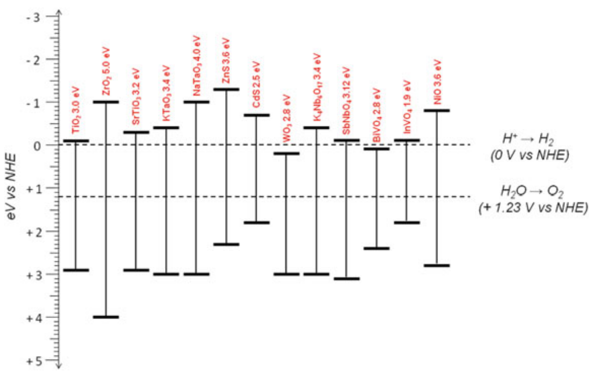
UPLC-MS analysis of cellulose breakdown products

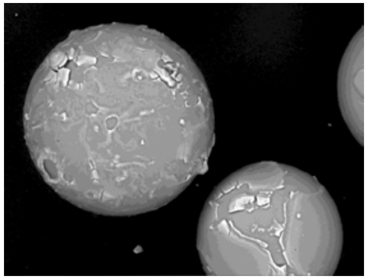


Catalyst development

- Key features for catalysts
  - **<u>Visible light activation</u>**
  - Structure
    - Increases e^- and h^+ mobility and separation
  - Band gap energy
    - For solar photon absorption
  - Surface Area
    - Increases catalyst-reactant surface reaction
  - Particle size
    - Critical for catalyst interaction with cellulose chains – catalyst needs to 'penetrate' cellulose chains
  - Recyclability
  - Cost
  - **<u>Hydroxyl radical formation</u>**







Catalyst development

initial work by St. Andrews

- In-situ growth of CdS QDs on cellulose
  - Coupling CdS quantum dots with cellulose increases the stability of CdS and can prevent photo corrosion.
- Irradiation under visible light for 24 hrs (420 nm cut-off filter)
  - CdS E_{bg} = ~2.5 eV which corresponds to excitation at ~495 nm
- Analysis by HPLC-RI
- Small sugars or organic acids from cellulose decomposition were found out – further detection and identification is currently ongoing.

Reactor Development

- The effectiveness of any photocatalytic treatment processes depends on:
  - Distribution of target molecule and photocatalyst
  - Reaction kinetics
  - Irradiation characteristics
  - **<u>Mass transfer of target molecule and photocatalyst</u>**
    - Maximise interaction between cellulose and $OH^{\cdot}$ in order to cleave hydrogen and glycosidic bonds

The conversion of target species (cellulose) is controlled by the rate of mass transfer

↓

Mass transfer of a reactor is capable of supplying target species to the catalyst surface

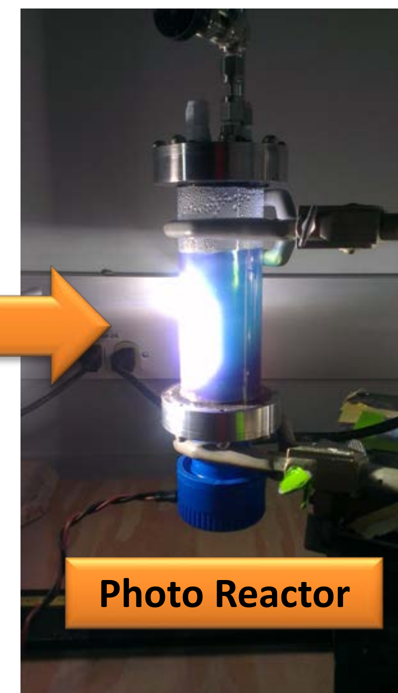
↓

In a mass controlled reactor, increasing mixing properties will increase level of conversion

Solar Light Utilisation

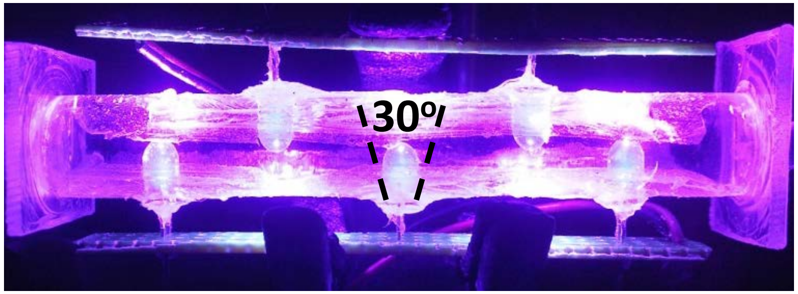
- Solar light is potentially a huge source of energy
  - **120 000 TW year^{-1}** solar irradiation reaching Earths surface
  - Capturing and harvesting light is a major limitation
  - Photocatalysis has ability to harness solar light and convert into renewable energy products – Bioethanol production
- Concentration of solar light is essential
  - Parabolic mirrors and solar concentrators
  - Light guiding mirrors can concentrate and direct a focused photon beam towards a target reactor
  - Under diffuse weather conditions concentrating solar irradiation is key to drive the photocatalytic release of glucose from cellulose

Concentrated light from a solar telescope

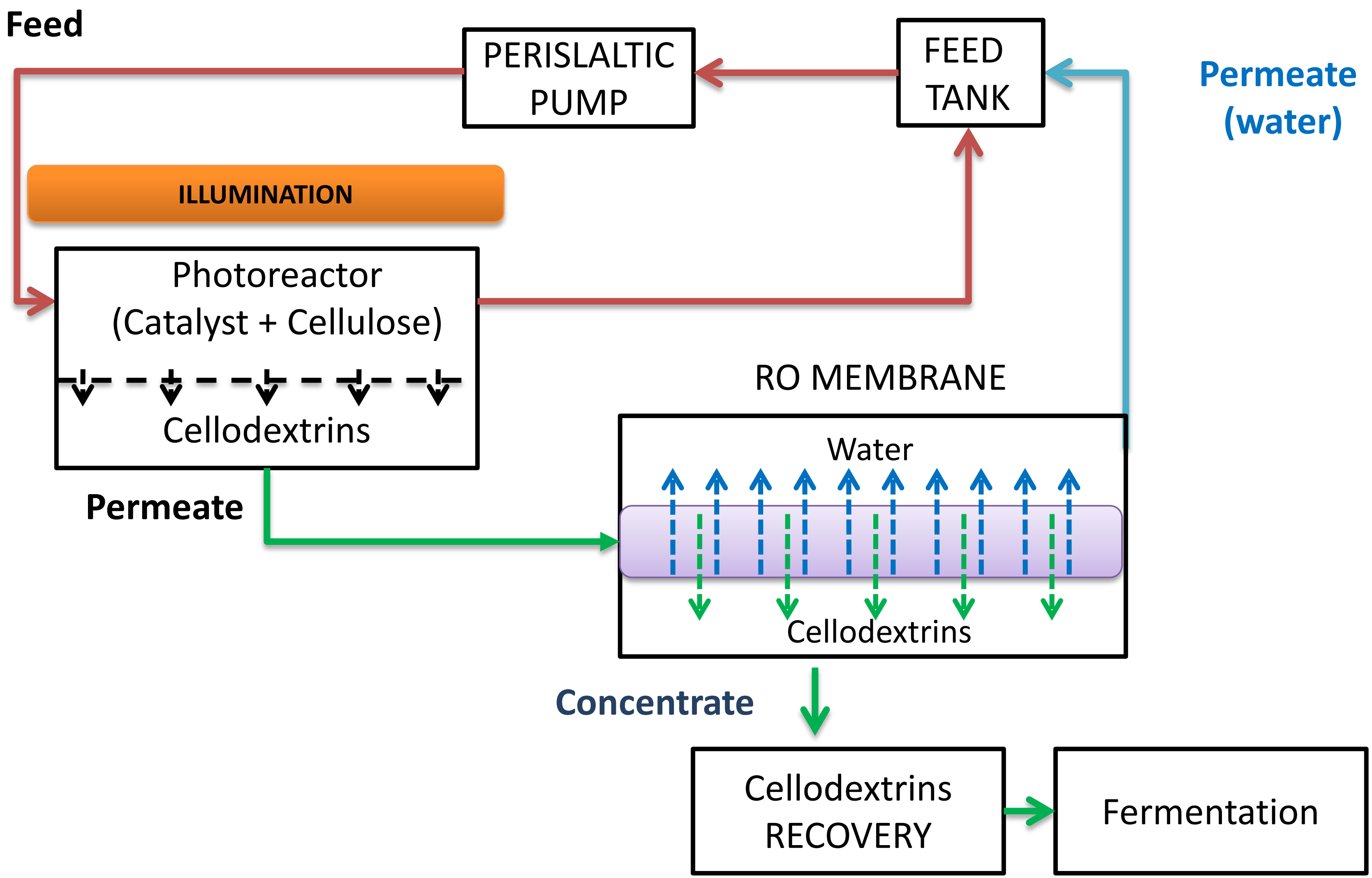


Simulated Light

- LED illumination is a low power lab scale alternative to solar irradiation
  - Temporary approach for evaluation of catalysts and systems
  - Currently in use are 3.8 V LEDs that provide a 30^{o} viewing angle
  - Ideal for use in submerged systems to maximise light penetration and flow characteristics
  - Range of LEDs can be used to mimic solar irradiation
  - Choice of LED is dictated by catalyst development
    - Incorporation of co-catalysts and dopants will change the electronic configuration of the catalyst which can shift the E_{bg} and absorption region



Multistage reactor development



Yields of bioethanol by photocatalytic release of glucose from paper mill waste (% dry weight)

• Dry paper mill waste	- 1 tonne (1000 kg)
• Cellulose content in paper mill waste (85%)	- 850 kg (Prasetyo and Park, 2013)
• Photocatalytic efficiency (90%)	- x 0.90
• Efficiency of glucose harvest (90% RO)	- x 0.90
• Ethanol stoichiometric yield	- x 0.51 (Badger, 2002)
• Glucose fermentation efficiency (75%)	- x 0.75 (Badger, 2002)
• EtOH harvest – membrane separation (80%)	- x 0.80
• **Yield of EtOH from glucose**	**= 210 kg (267 L) per tonne**

• Annual paper mill waste produced	= ~6000 tonnes
• Dry annual paper mill waste (40%)	= 2400 tonnes
• Potential annual EtOH production	= 267 L x 2400 = **640,000 L**



Acknowledgments

RGU
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