



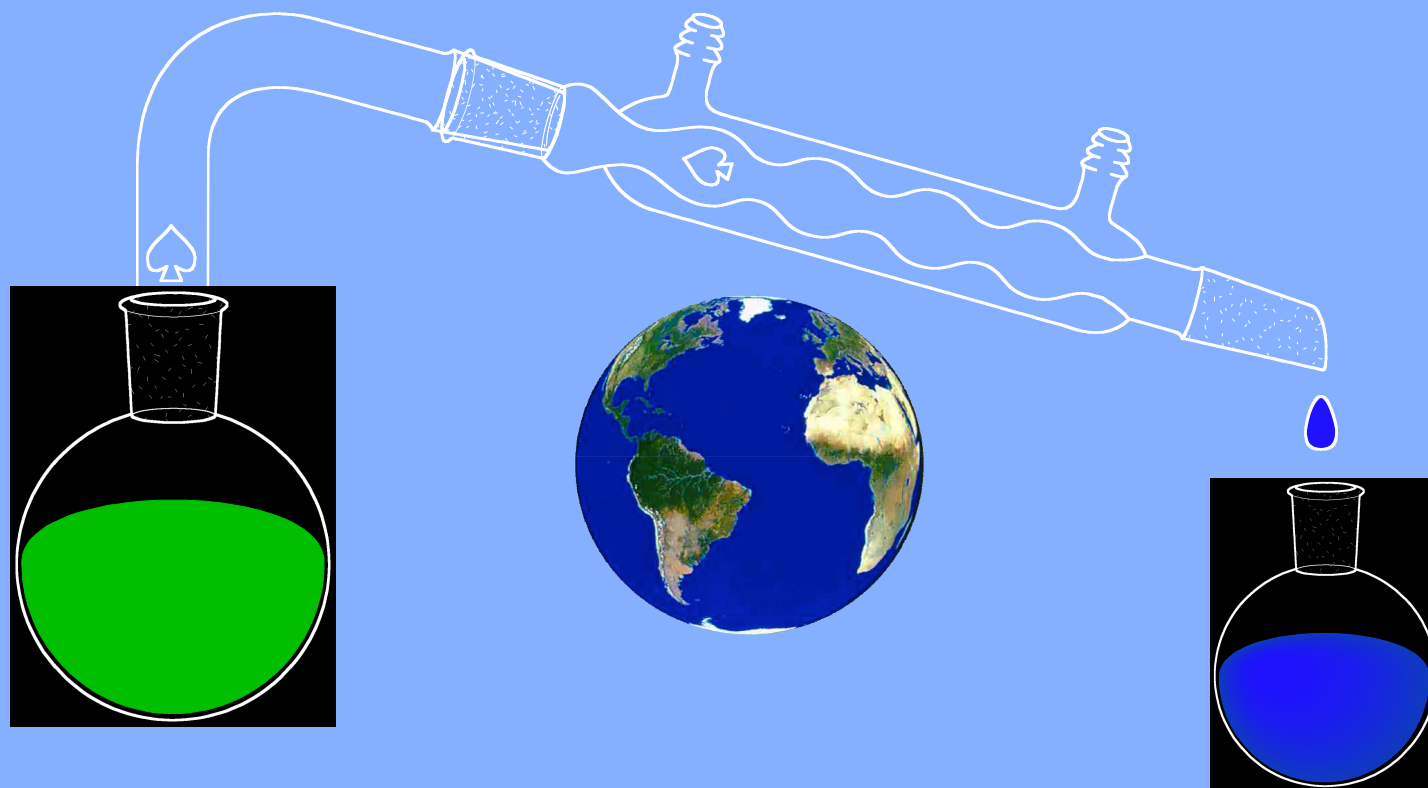
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Nordic Energy Research

# EPFB - “Efficient Production of Fuels from Biomass”

European network consisting of  
6 Countries, Coordinated by Uppsala  
2.15 million €. Started in 2010.

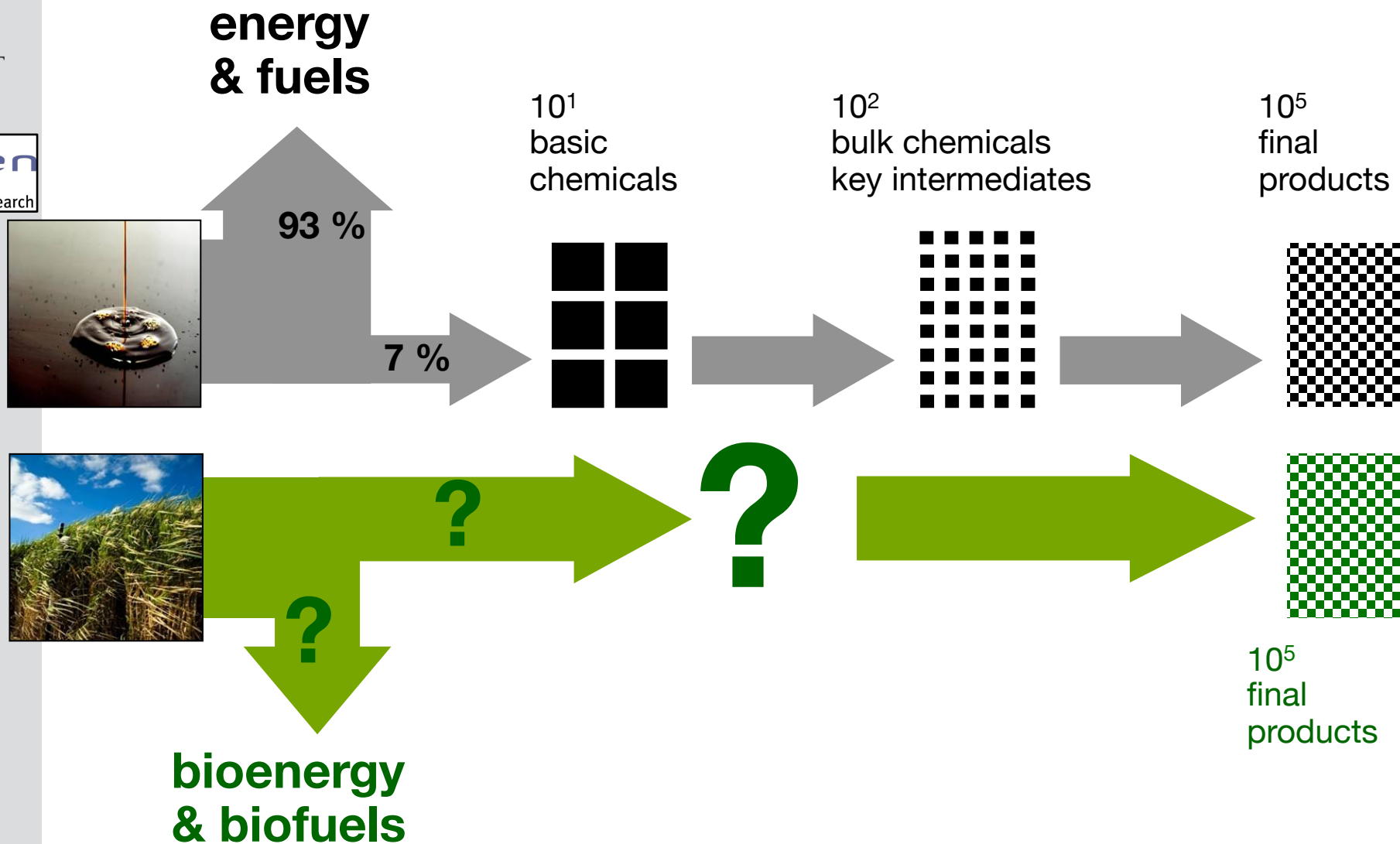




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## Building a renewable supply chain





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## *EPFB - "Efficient Production of Fuels from Biomass"*

### Participating groups

Pher G. Andersson, Uppsala University, Sweden

Robert Madsen, Technical University of Denmark, Denmark

Enn Lust, University of Tartu, Estonia

Jyri-Pekka Mikkola, Åbo Akademi, Finland

Dmitry Murzin, Åbo Akademi, Finland

Bård Helge Hoff, Norwegian Univ. of Science & Tech, Norway

Eirik Sundby, Norwegian Univ. of Science & Tech, Norway

Jürgen Klankermayer, RWTH Aachen, Germany

Walter Leitner, RWTH Aachen, Germany



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## *EPFB - "Efficient Production of Fuels from Biomass"*

PhD students enrolled in the project:



Johan Verendel, Uppsala University, Sweden

Byron Peters, Uppsala University, Sweden

Esben Olsen, Technical University of Denmark, Denmark

Kadi Tamm, University of Tartu, Estonia

Alexey Kirilin, Åbo Akademi, Finland

Aderonke Badina, Norwegian Univ. of Science & Tech, Norway

Sebastion Wanders, RWTH Aachen, Germany

Jedrzej Walkowiak, RWTH Aachen, Germany



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## *EPFB - "Efficient Production of Fuels from Biomass"*

### Areas of expertise:

Catalytic cleavage of cellulose and hemicellulose to sugars (Sweden)

Enzymatic degradation of biomass into sugars and alcohols (Norway)

Catalytic decarbonylation of alcohols into syngas (Denmark)

Aqueous Phase Reforming of biomass into liquid fuels (Finland)

Development of fuel cells for direct oxidation of alcohols (Estonia)

Optimization of synthetic, biomass derived fuels in combustion engines (Germany)



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## *EPFB - "Efficient Production of Fuels from Biomass"*

### Collaborational research:

Development and evaluation of catalysts on solid supports or ionic liquids for catalytic cleavage of cellulose into renewable H<sub>2</sub> feedstocks such as sorbitol, xylitol and mannitol.

(Sweden, Finland, Germany)

The best catalysts discovered will be evaluated for use in concert with enzymatic or microbial degradation in order to achieve even faster rates of sugar production. Upscaling to a continuous process.

(Sweden, Norway, Germany)

Low-temp conversion of sugars into liquid fuels

(Denmark, Finland)

Development of Ni-Cu-cermet anodes for direct electro-oxidation of polyols (sorbitol, xylitol and mannitol) in high power density fuel cells.

(Estonia, Finland, Denmark, Sweden)

Development of highly effective catalytic and/or enzymatic routes from biomass to well-defined small molecules.

(Norway, Germany, Sweden)



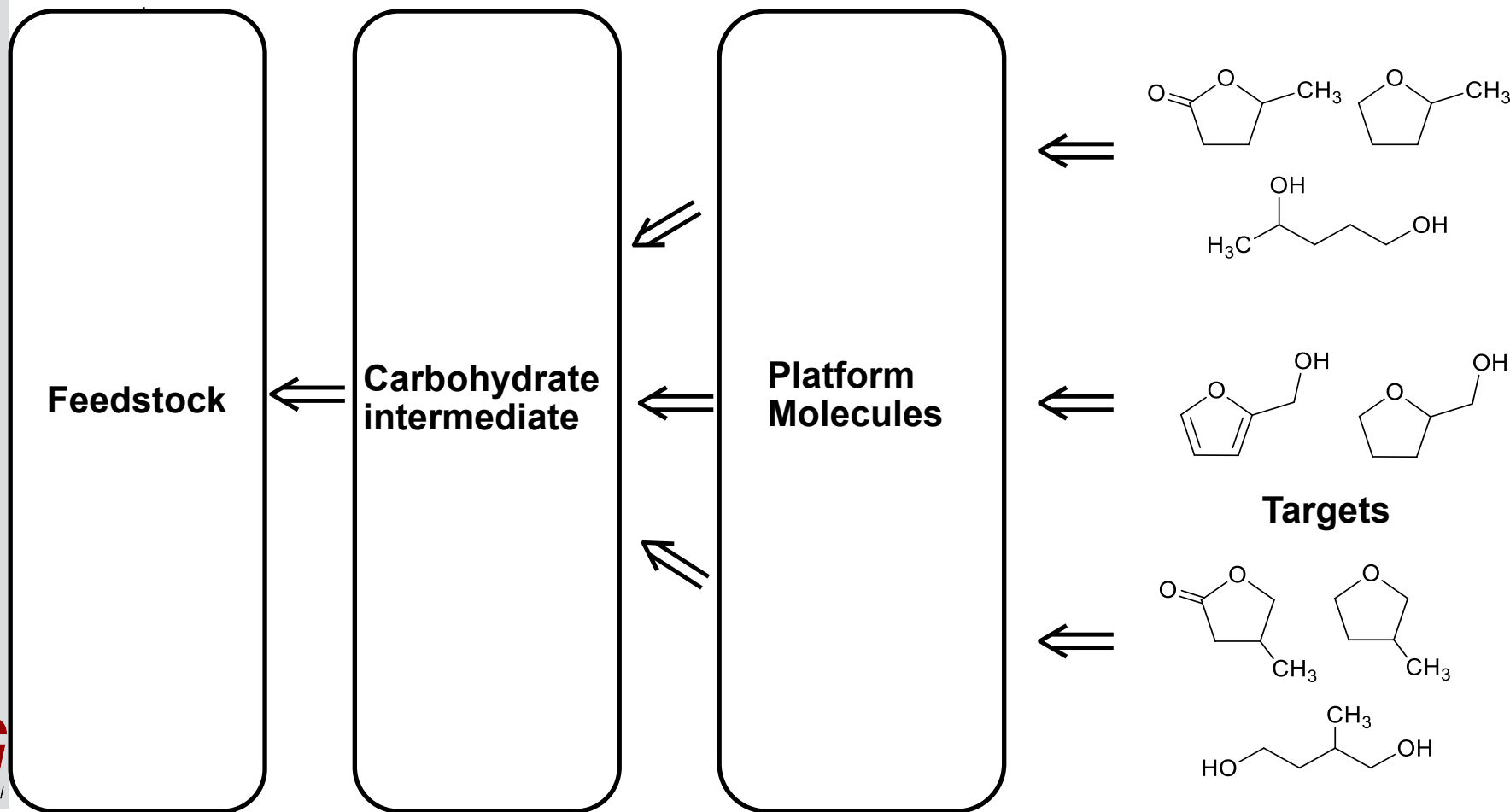
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# EPFB - "Efficient Production of Fuels from Biomass"

Germany:

## Selective Catalytic Conversion of Biogenic Platform Chemicals to Fuels



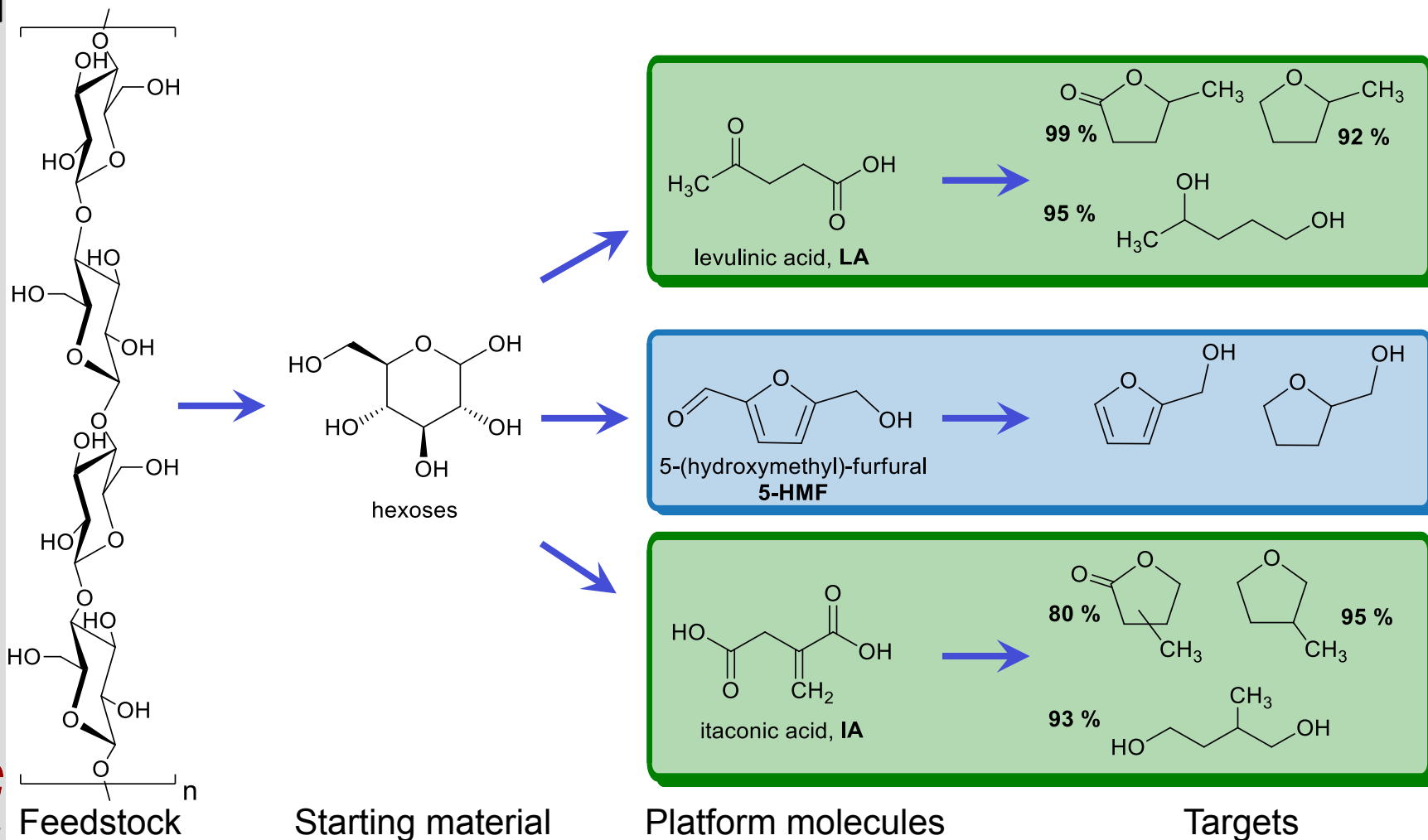


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# EPFB - "Efficient Production of Fuels from Biomass"

Germany:



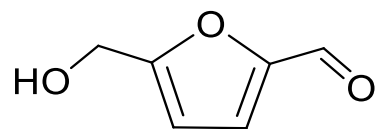
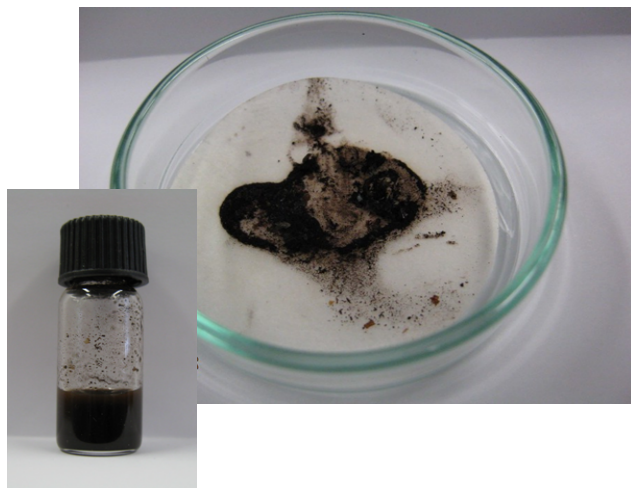




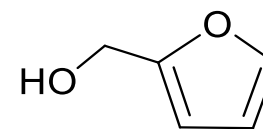
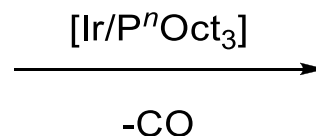
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## Catalytic Decarbonylation of 5-HMF – Influence of compressed CO<sub>2</sub>

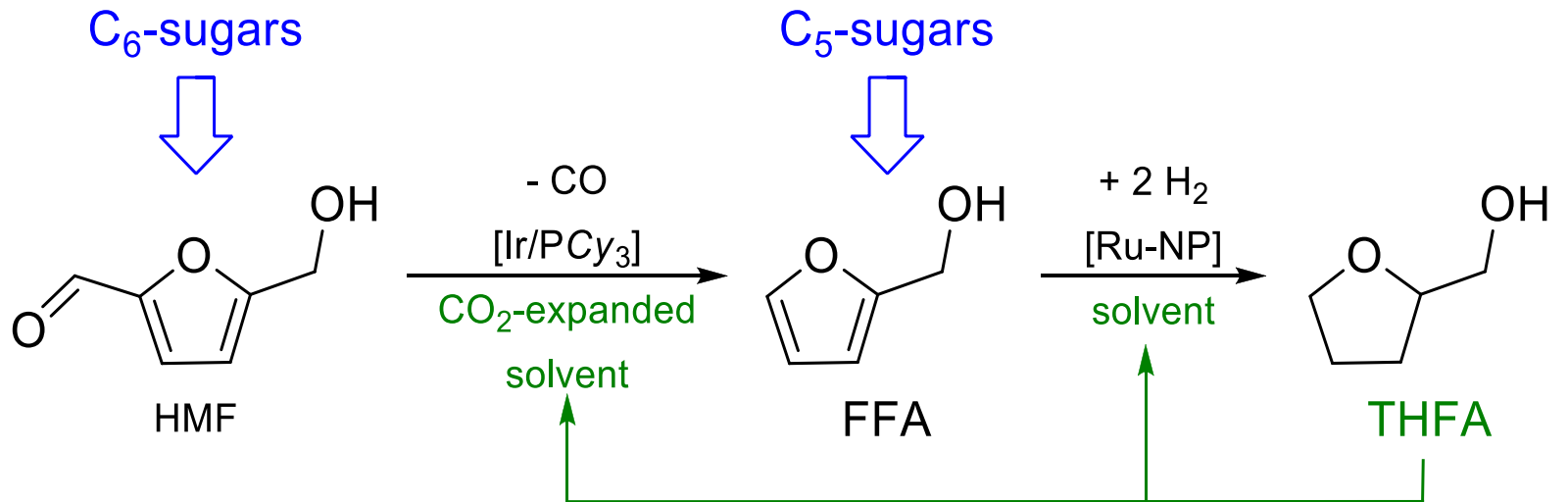


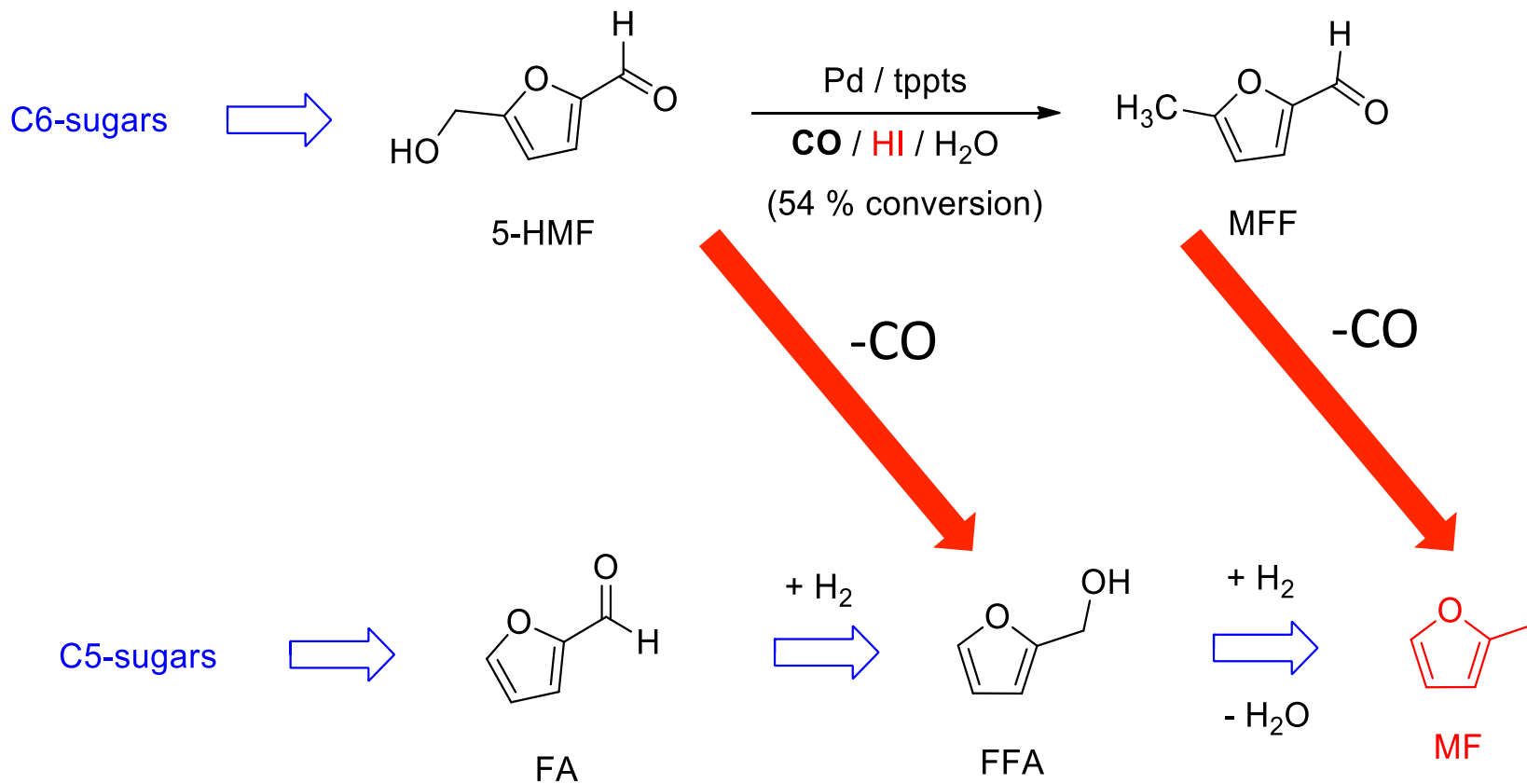
**5-HMF**



**FFA**

p(CO <sub>2</sub> ) (bar)	Conversion (%)	Selectivity FFA (%)
0	> 99	< 5







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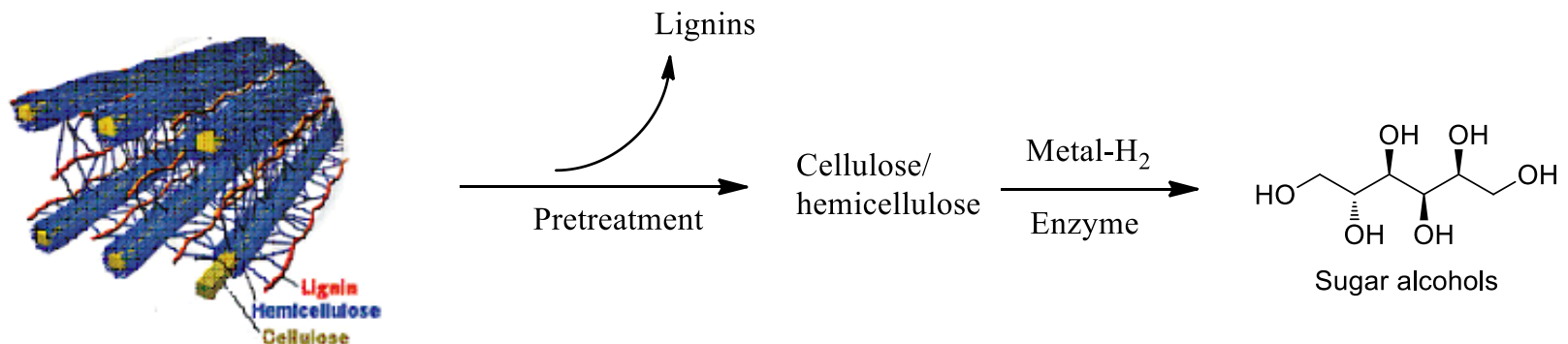


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Norway:

## Sugar alcohols from lignocellulose: MW pre-treatment and enzymatic hydrolysis

- Microwave assisted pre-treatment method
- Benefits of MW pre-treatment on enzymatic hydrolysis
- Feasibility of combining hydrolytic enzymes with metal catalysed hydrogenation





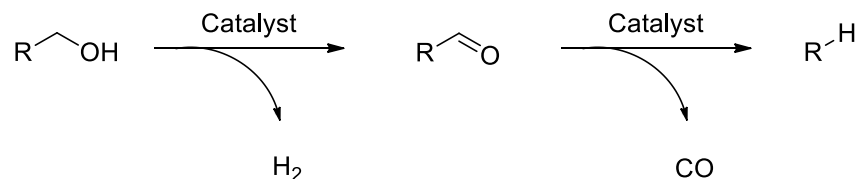
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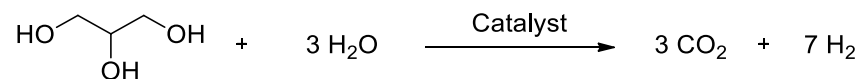
# EPFB - "Efficient Production of Fuels from Biomass"

Denmark:

Optimize a catalytic system which performs dehydrogenation and decarbonylation of primary alcohols without scavengers.



Apply homogeneous catalyst(s) for dehydrogenation and decarbonylation of C3 – C6 polyalcohols to produce hydrogen



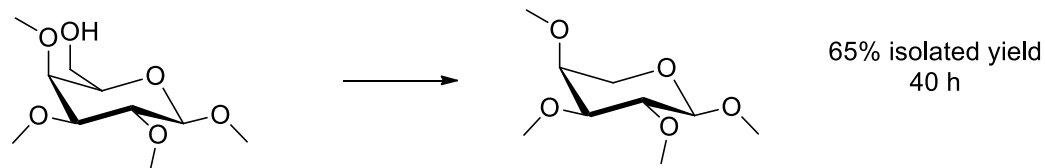
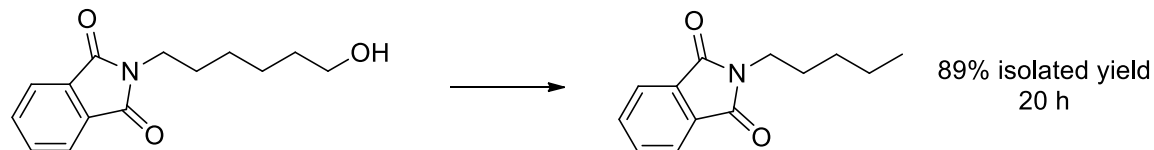
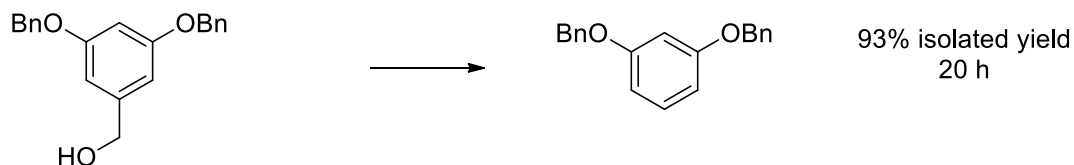
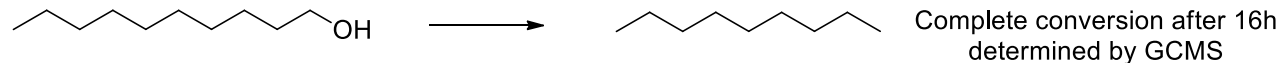
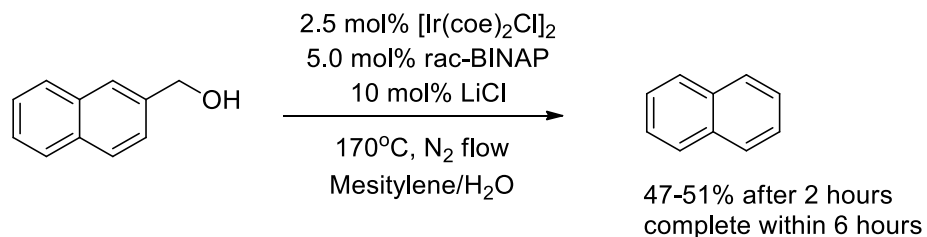


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# EPFB - "Efficient Production of Fuels from Biomass"

## Denmark:





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# EPFB - "Efficient Production of Fuels from Biomass"

## Estonia:

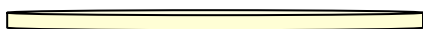
### Preparation of Solid Oxide Fuel Cell Single-Cell

5



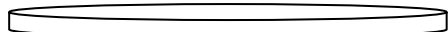
LSCO (selfmade) cathode applied by screen printing followed by sintering for 5h at 1100°C with the heating-up and down rate 2,5°C/min

4



CGO (ESL) electrolyte layer applied by screen printing followed by sintering for 3h at 1350°C with the heating-up and down rate 2,5°C/min

3



Protective ScSZ (ESL) electrolyte layer applied by screen printing followed by sintering for 3h at 1350°C with the heating-up and down rate 2,5°C/min

2



NiO-CGO (FCM) anode active layer applied by screen printing followed by sintering for 3h at 1350°C with the heating-up and down rate 2,5°C/min

1



Supportive porous NiO-CGO pellet

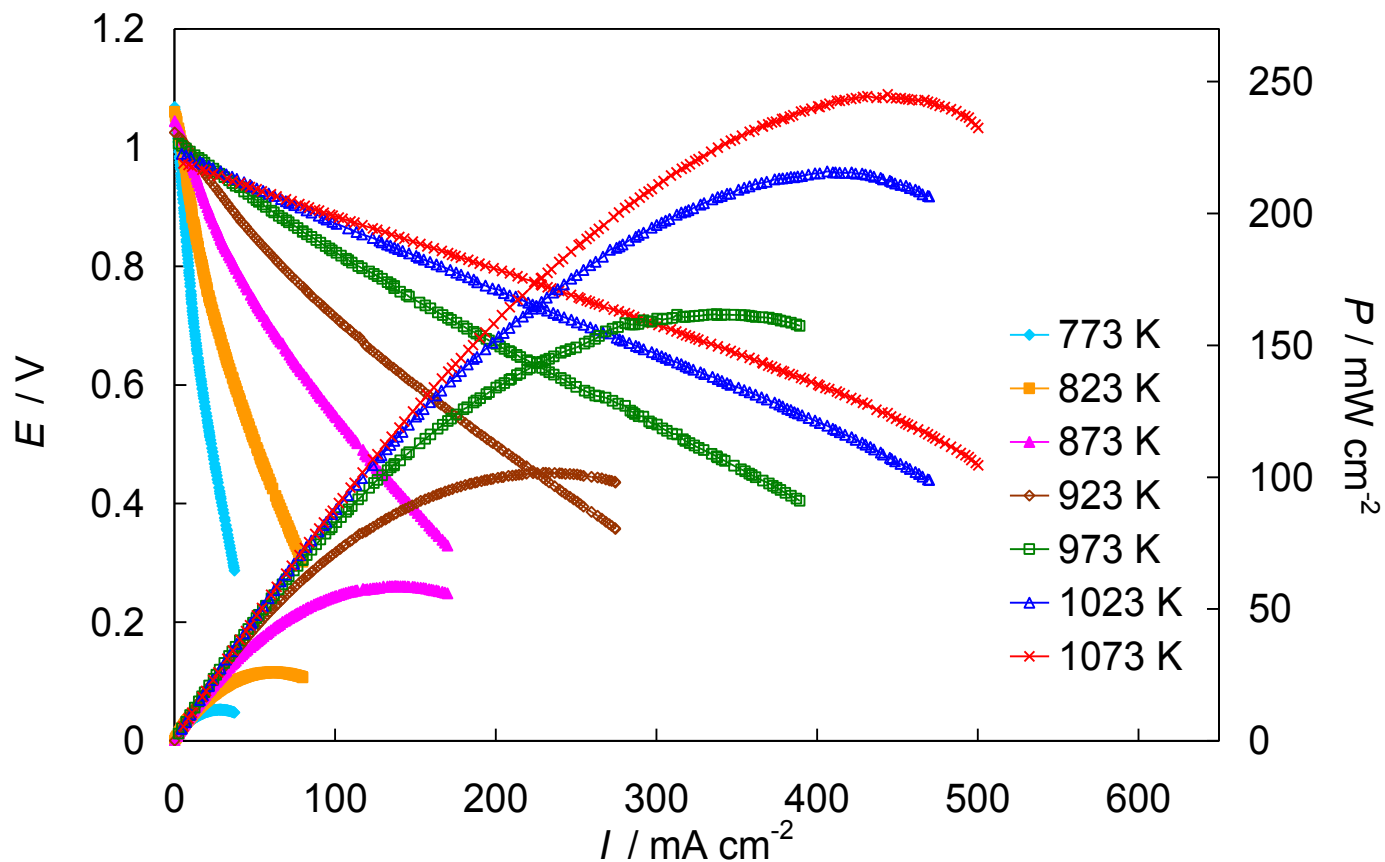
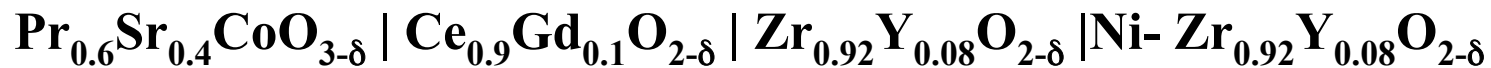


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# EPFB - "Efficient Production of Fuels from Biomass"

Estonia:







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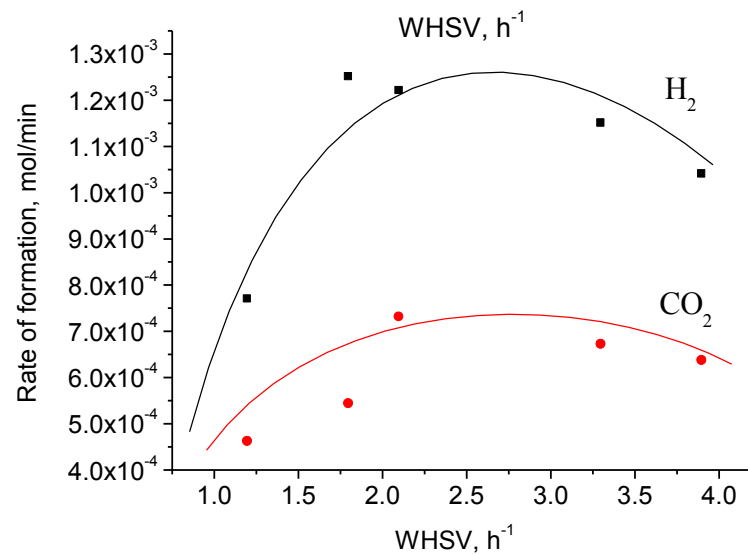
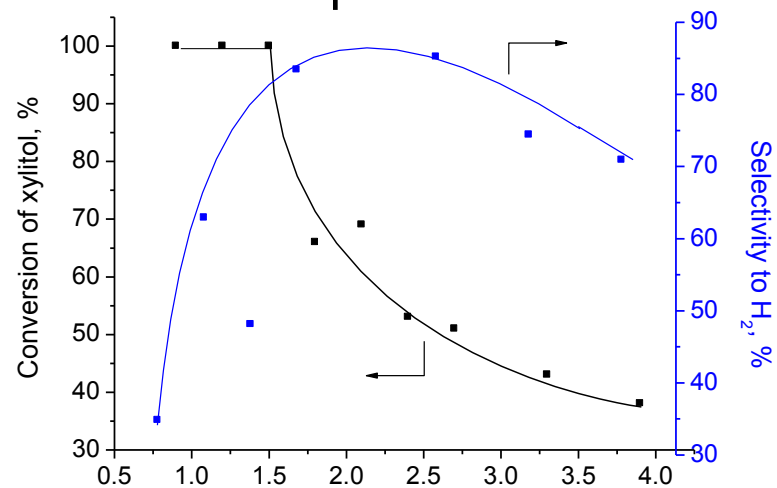
# EPFB - "Efficient Production of Fuels from Biomass"

Finland:

## Aqueous phase reforming of biomass components - **XYLITOL**



Setup – fixed bed reactor





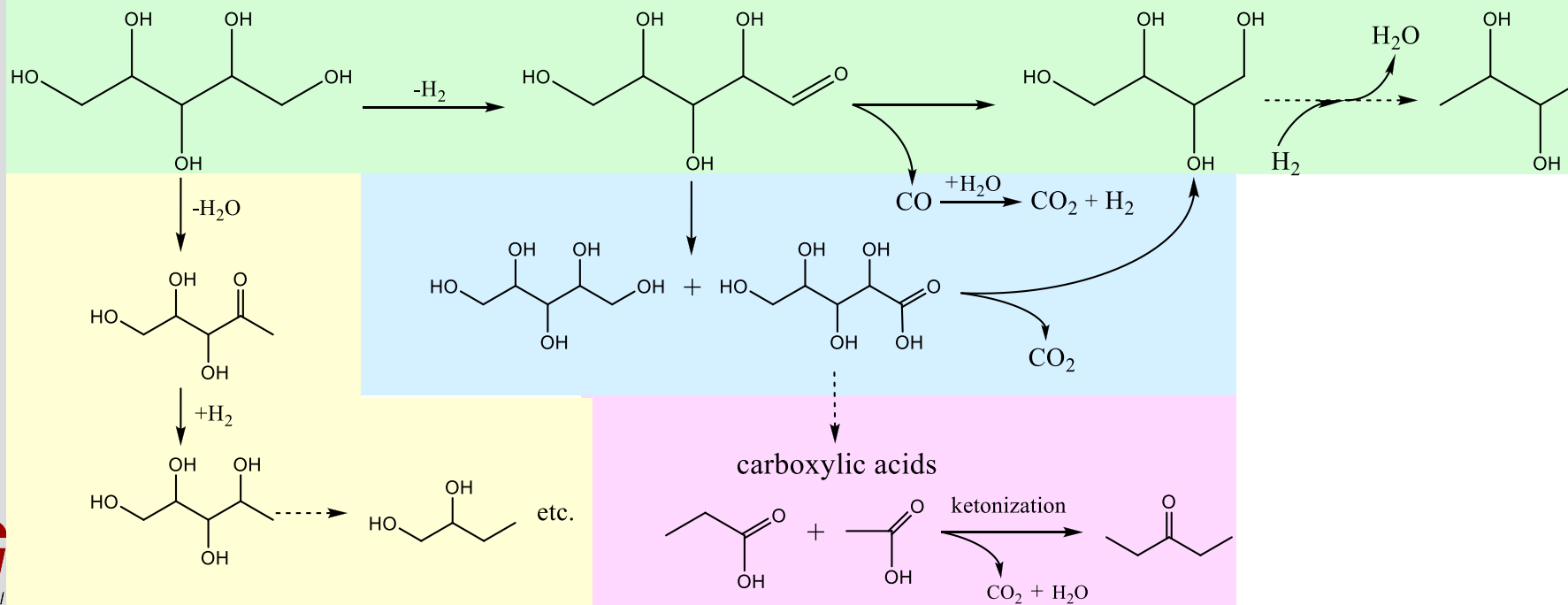
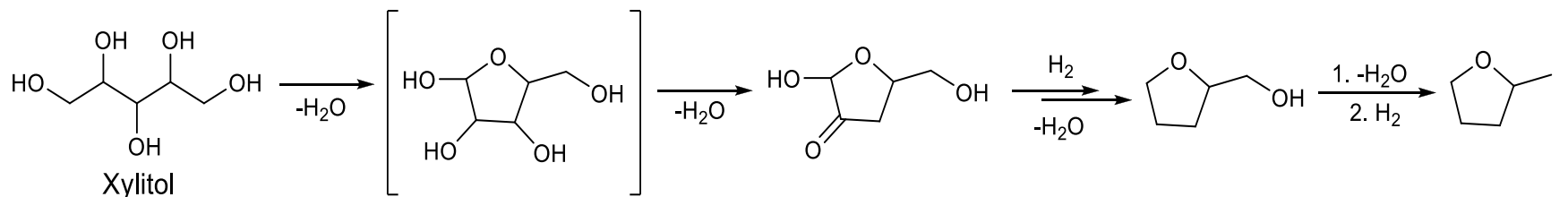
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# EPFB - "Efficient Production of Fuels from Biomass"

Finland:



## Aqueous phase reforming of biomass components - **XYLITOL**



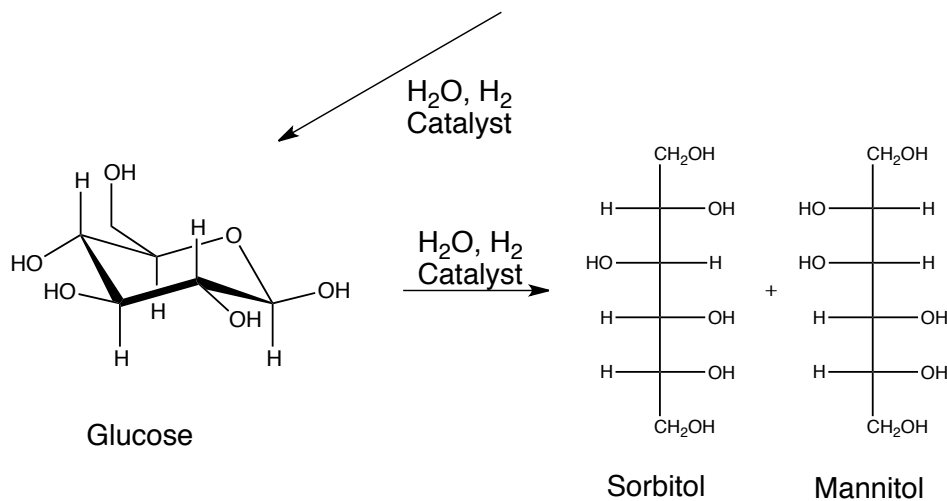
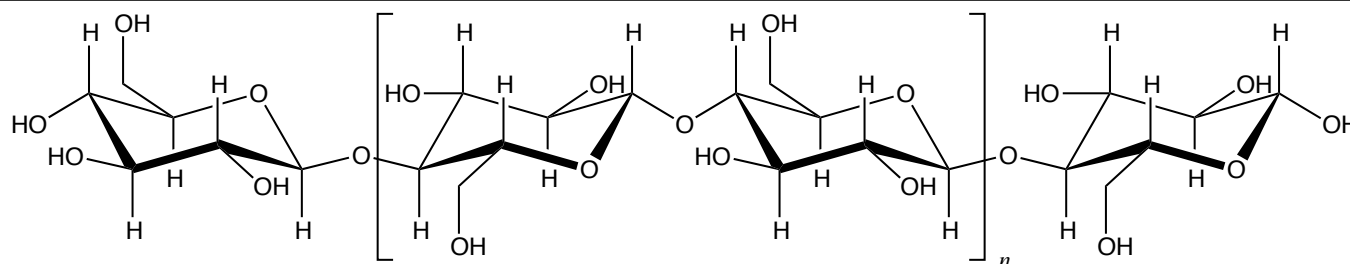


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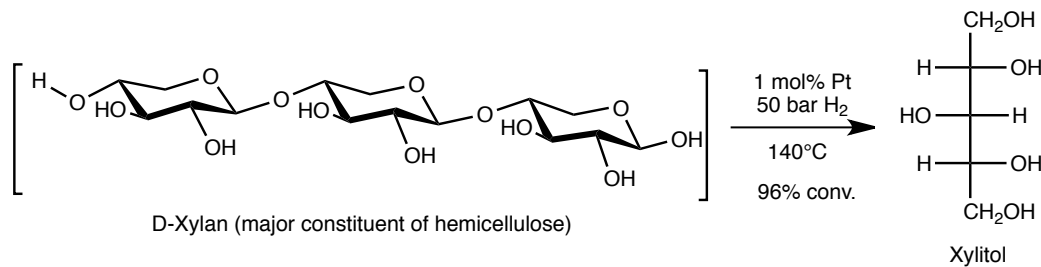
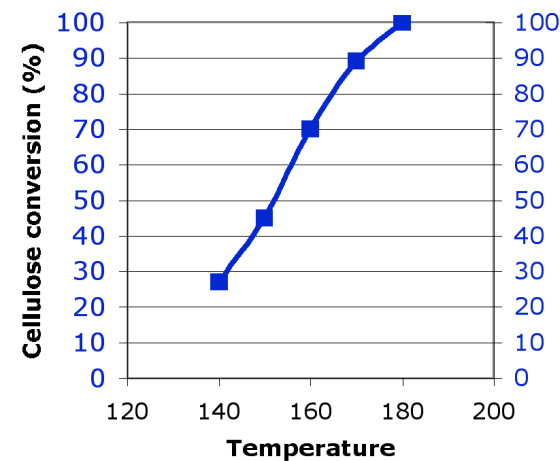


# EPFB - "Efficient Production of Fuels from Biomass"

Sweden:



Temperature dependence



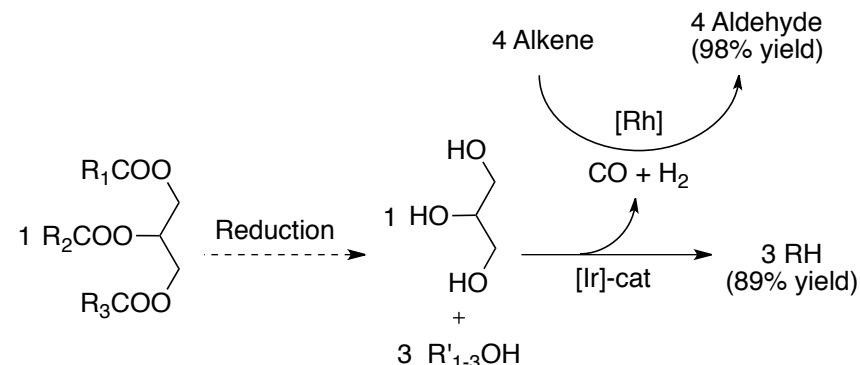
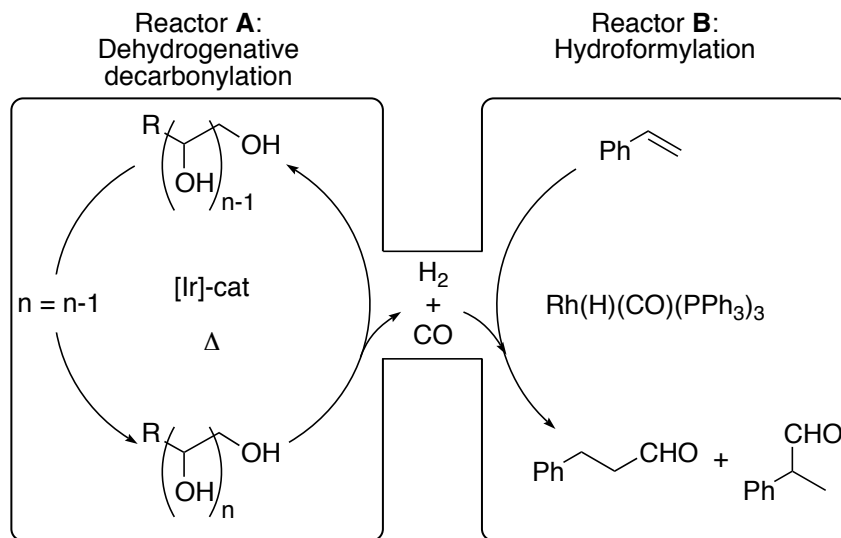
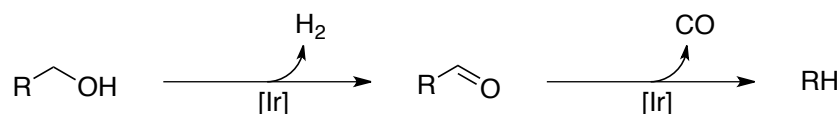
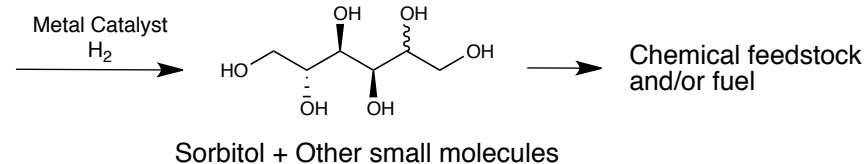
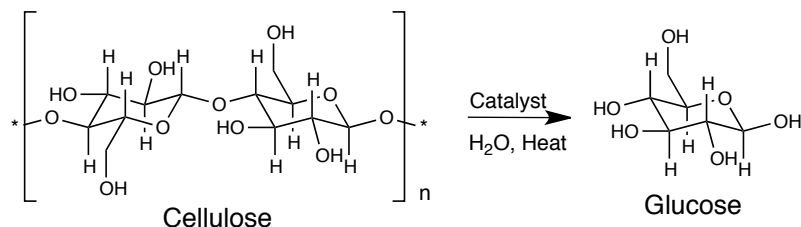


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# EPFB - "Efficient Production of Fuels from Biomass"

Sweden:



$\text{R}_{1-3} = \text{C}_{14} - \text{C}_{22}$  hydrocarbon chain

$\text{R}'_{1-3} = \text{C}_{15} - \text{C}_{23}$  hydrocarbon chain

Patent pending!



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# EPFB - "Efficient Production of Fuels from Biomass"

## Publications

### 25 Publications

1. A.V. Kirilin, A.V. Tokarev, E.V. Murzina, L.M. Kustov, J.-P. Mikkola, D.Yu. Murzin, "Reaction Products and Transformations of Intermediates in the Aqueous-Phase Reforming of Sorbitol", *ChemSusChem*, 2010, 3, 708–718.
2. A.V. Tokarev, A.V. Kirilin, E.V. Murzina, K. Eränen, L.M. Kustov, D.Yu. Murzin, J.-P. Mikkola, "The Role of Bioethanol in Aqueous Phase Reforming to Sustainable Hydrogen", *J. Hydr. En.*, 2010, 35, 12642–12649
3. A.V. Kirilin, A. Tokarev, L. Kustov, T. Salmi, J.-P. Mikkola, D.Yu. Murzin, "Aqueous Phase Reforming of Sugar Alcohols: Influence of the Substrate Structure", *Appl. Catal. A: General*, 2012, 435, 172–180.
4. Tore Aa. Gulbrandsen, Ingvild A. Johnsen, Mihaela Tanase Opedal, Kai Toven, Karin Øyaas, Andrey Pranovich, Jyri-Pekka Mikkola, Bård H. Hoff, Extracting hemicelluloses from softwood and bagasse as oligosaccharides using pure water and microwave heating, *Cell. Chem. Technol.* (submitted)
5. A.V. Tokarev, A.V. Kirilin, E.V. Murzina, K. Eränen, J.-P. Mikkola, D.Yu. Murzin, "Catalyst deactivation in aqueous phase reforming of renewables", 11th International Symposium on Catalyst Deactivation, 25–28 October 2009, Delft, The Netherlands, Books of abstracts, p. 58.
6. A.V. Kirilin, D.Yu. Murzin, J.-P. Mikkola, "Study of the aqueous phase reforming of biomass-derived components", International scientific conference of young scientists Lomonosov-2011, Moscow, Russia.
7. A.V. Kirilin, A.V. Tokarev, D.Yu. Murzin, J.-P. Mikkola, "Catalytic conversion of biomass-derived chemicals for hydrogen and liquid fuel production", COST Action CM0903 UBIOCHEM I, Utilisation of biomass for fuels and chemicals, 13–15 May 2010, University of Cordoba, Spain, Book of abstracts, p. 24.
8. A. Kirilin, A. Tokarev, T. Salmi, J.-P. Mikkola, D.Yu. Murzin, "Aqueous phase reforming of biomass derived alcohols and polyols to hydrogen and fuel components", Chemreactor-19, 5–9 September 2010, Vienna, Austria, Book of abstracts, p. 492.
9. A. V. Kirilin, A. Tokarev, L. M. Kustov, T. Salmi, J.-P. Mikkola, D.Yu. Murzin, "Aqueous phase reforming of biomass feedstocks as an approach to hydrogen production", EUROACAT X, 28 August – 2 September, Glasgow, Scotland, Book of abstracts (CD), IO21, abs. No. 1702372.
10. A. Kirilin, A. Tokarev, L. Kustov, J.-P. Mikkola, D.Yu. Murzin, "Selective hydrogen production from renewables: catalytic conversion of biomass-derived C5-C6 sugar alcohols via aqueous phase reforming", 11th International Chemical and Biological Engineering Conference, 5–7 September 2011, Lisbon, Portugal, Book of abstracts, p. 126–127.
11. A. Kirilin, A. Tokarev, L.M. Kustov, D.Yu. Murzin, J.-P. Mikkola, "Catalytic production of hydrogen via aqueous phase reforming of renewables", 1st International Congress on Catalysis for Biorefineries, 2–5 October 2011, Torremolinos – Málaga, Spain, Book of abstracts, p. 74.
12. A. Kirilin, A. Tokarev, T. Salmi, D.Yu. Murzin and J.-P. Mikkola, "Catalytic conversion of renewables via aqueous phase reforming to sustainable hydrogen", HYdrogen – POver Theoretical and Engineering Solutions International Symposium HYPOTHESIS IX, 12–15 December 2011, San José, Costa Rica, Book of abstracts, p. 15.
13. A. Kirilin, A. Tokarev, T. Salmi, D.Yu. Murzin, J.-P. Mikkola, "Aqueous phase reforming of biomass feedstocks: an approach to sustainable hydrogen and liquid fuels", 243rd American Chemical Society National Meeting, 24–29 March 2012, San Diego, California, USA, Preprints of Symposia – American Chemical Society, Division of Fuel Chemistry, 2012, 57, 614.
14. A. Kirilin, A. Tokarev, D.Yu. Murzin, J.-P. Mikkola, "Bio-hydrogen via aqueous phase reforming of sugar alcohols", International Congress on Hydrogen Production, 24–27 June 2012, Seoul, South Korea, Book of abstracts, p. 135–136.
15. A. Kirilin, A. Tokarev, T. Salmi, J.-P. Mikkola, D.Yu. Murzin, "Aqueous phase reforming of biomass feedstocks: an approach to sustainable hydrogen and liquid fuels", 15th International Congress on Catalysis, 1–6 July 2012, Munich, Germany, abs. No. 7351.
16. I. Kivi, E. Anderson, P. Möller, G. Nurk, E. Lust, Influence of Microstructural Parameters of LSC Cathodes on the Oxygen Reduction Reaction Parameters, *J. Electrochem. Soc.*, 159(11) (2012) F743-F750.
17. K. Tamm, I. Kivi, E. Anderson, A. Trikkell, P. Möller, G. Nurk, E. Lust, Influence of Graphite Pore Forming Agents on the Structural and Electrochemical Properties of Porous Ni-CGO Anode, *J. Electrochem. Soc.*, 159(12) (2012) F849-F857.
18. K. Tamm, R. Küngas, R. J. Gorte, E. Lust, SOFC anodes prepared by infiltration of Sr-doped  $\text{LaVO}_{3.5}$  into doped ceria electrolyte, (in preparation).
19. G. Nurk, T. Hauthwelker, A. Braun, C. Ludwig, E. Lust, R. Struis, Redox behaviour of sulphur at Ni/GDC SOFC anode at mid- and low-range temperatures: An operando S K-edge XANES study, *J. Power Sources* (submitted).
20. Aslan M. Esmurziev, Arne Reimers, Trygve Andreassen, Nebojsa Simic, Eirik Sundby, and Bard Helge Hoff. Benzoylated uronic Acid building blocks and synthesis of N-uronate conjugates of lamotrigine. *Molecules* 17:820-835, 2012.
21. Tore Aa. Gulbrandsen<sup>1</sup>, Ingvild A. Johnsen<sup>2</sup>, Mihaela Tanase Opedal<sup>2</sup>, Kai Toven<sup>2</sup>, Karin Øyaas<sup>2</sup>, Andrey Pranovich<sup>3</sup>, Jyri-Pekka Mikkola<sup>3,4</sup>, Bård H. Hoff<sup>1</sup> Extracting hemicelluloses from softwood and bagasse as oligosaccharides using pure water and microwave heating. Submitted to *Cellulose Chemistry and Technology*.
22. Verendel, J. Johan; Church, Tamara L.; Andersson, Pher G. Catalytic One-Pot Production of Small Organics from Polysaccharides. *Synthesis* (2011); (2011), 1649-1677
23. Verendel, J. Johan; Nordlund, M.; Andersson, Pher G. Selective, metal-catalyzed transfer of H<sub>2</sub> and CO from polyols to alkenes. *ChemSusChem* (2013) In print.
24. Catalytic Dehydrogenative Amide and Ester Formation with Rhenium-Triphos Complexes, P. P. M. Schleker, R. Honeker, J. Klankermayer, W. Leitner, *ChemCatChem* 2013, accepted.
25. Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain, M. Peters, B. Koehler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Mueller, *ChemSusChem* 2011, 4, 1216-1240.



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# *EPFB - "Efficient Production of Fuels from Biomass"*

## Collaborations and exchanges

Collaboration with the partners from other EU countries was very successful. We had a possibility to collaborate with the groups dealing with homogeneous catalysis, electrochemistry and biomass transformations.

Several researcher visits were carried out from and to Finland: a doctoral student (A.Kirilin) visited both Haldor Topsoe company in, Lyngby, Denmark (1 month) and Wisconsin University in USA (2 months) as well as Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow (4 months). In addition Ms. Dilek Boka from Utrecht University, the Netherlands (1 month) and Tore Aarhus Gulbrandsen, NTNU Trondheim, Norway visited Åbo Akademi (2 months).





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# EPFB - "Efficient Production of Fuels from Biomass"

## Educational Outcome



Nordic Energy Research

### Ph.D. Theses related with project

- (1) K. Tamm: Optimization of anode porosity for medium-temperature solid oxide fuel cells (under progress)
- (2) M. Vestli: New materials for bi-layered electrolytes for medium-temperature solid oxide fuel cells (under progress)
- (3) One PhD student has been educated in the framework of the project. Alexey Kirilin has got PhD degree in Chemistry on 18<sup>th</sup> of December 2012 (Zelinsky Institute of Organic Chemistry, Russian Academy of Science) and corresponding defense will take place at Åbo Akademi during the year 2013
- (4) J. Verendel: Transition Metal Catalysis for Selective Synthesis and Sustainable Chemistry. PhD degree at Uppsala University 1212-11-30
- (5) B. Peters: Biofuels via catalytic degradation of biomass. Planned PhD degree at Stockholm University 2014.
- (6) A. Badina: Title not decided yet. Planned PhD degree from NTNU, Trondheim 2016 (delayed due to 2 maternity leaves).
- (7) One PhD student is being educated in the framework of the project. Esben Paul Krogh Olsen will be handling in his PhD thesis in Chemistry on 30<sup>th</sup> of September 2013 (Department of Chemistry, Technical University of Denmark) and corresponding defense will take place in the end of year 2013. One PhD student has been educated in the framework of the project.
- (8) Sebastian Wanders will finish his PhD in 2013 at the Institut für Technische und Makromolekulare Chemie at RWTH Aachen University.

### 7 Masters theses related to the project:

Masters Thesis: "*Iridium Catalysed Degradation of Alcohols and Polyols to Synthesis Gas*" Kristoff Jess, Uppsala, **2011**.

Masters Thesis: "*Iridium-Catalysed Production of Synthesis Gas from Alcohols and Polyols*" Michael Nordlund, Uppsala **2012**.

One bachelor student has gotten his bachelor degree on the basis of the project. Samuel Gilbert Elliott defended his bachelor thesis on 4<sup>th</sup> of July 2012 (Department of Chemistry, Technical University of Denmark).

T. A. Gulbransen. Master thesis: Hot water extraction of hemicellulose from spruce and bagasse by use of microwave heating, NTNU, Trondheim, Norway. June 2012.

M. Seljenes Bøe. Master thesis: Organosolv pretreatment of biomass for biofuel and biorefinery applications. NTNU, Trondheim Norway, 2012.

Two bachelor students have been getting their bachelor degree on the basis of the project. Andreas Falkenberg and Jascha Rosenbaum defended their bachelor theses on 5<sup>th</sup> of July 2011 (Department of Chemistry, Technical University of Denmark).



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# EPFB - "Efficient Production of Fuels from Biomass"

## Budget

Year:	2010	2011	2012	2013
Salary (one swedish PhD-student)	65'	67'	70'	continues
Salary (10% administrator)	5'	5'	5'	
Chemicals and consumables	10'	10'	10'	
Salary (one Danish PhD-student)	66	68	70	continues
PhD tuition	15	16	17	
Salary (two German PhD-students)	60'	60'	60'	continues
Chemicals and consumables	15'	15'	15'	
Salary (one Norwegian PhD student)	73	73	75	continues
Chemicals and consumables	10	10	9	
Direct salaries (one Finnish PhD stud.)	31'	31'	31'	
Indirect salary costs (55%)	17'	17'	17'	
General overhead costs (84%)	40'	40'	40'	
Chemicals and consumables	2'	2'	2'	
COSTS, total	90'	90'	90'	
Travel:	50'	100'	100'	
Workshops:	50'	50'	50'	
TOTAL:	509'	514'	521'	





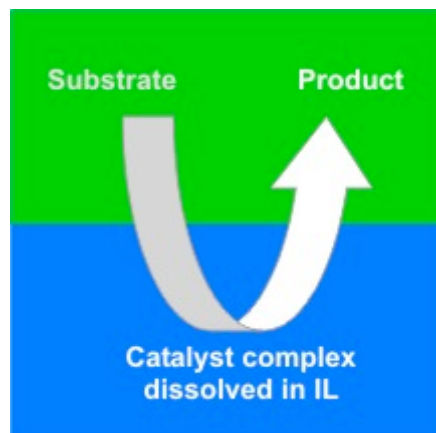
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“SYNFLOW” a European FP7 project  
involving 18 research partners, Coord: Aachen  
11.5 million €. Started in 2010.

Innovative Synthesis in Continuous-Flow Processes for Sustainable Chemical Production.



Principle of biphasic catalysis using  
ionic liquids for catalyst immobilization

Uppsala contributes with catalysts having  
wide-scope for asymmetric hydrogenation.

Opens up for:

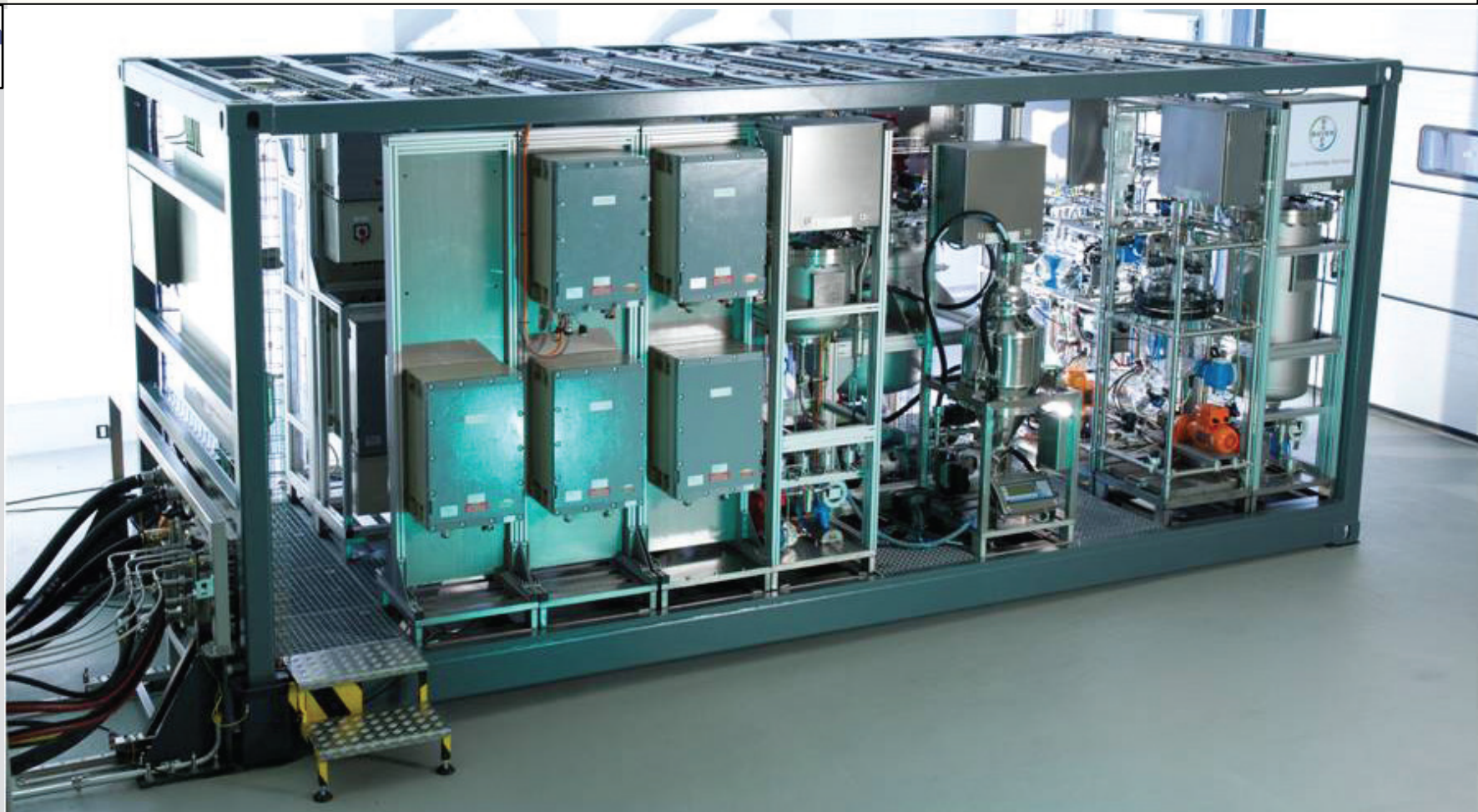
- Small footprint reactors for large production
- Cascade catalysis
- Synergy with Biomass & Nordic Synthesis projects



UPPSALA  
UNIVERSITET



“SYNFLOW” a European FP7 project  
involving 18 research partners, Coord: Aachen  
11.5 million €. Started in 2010.



The F<sup>3</sup> Factory project at INVITE Research Centre in Leverkusen.