OPEN DAYS, European Week of Regions and Cities Brussels, October 5-8, 2009 Growth and Competitiveness through Renewable Energy Resources

#### Sustainable Energy – Biofuels and Biorefinery Concept

Prof., Vice-rector Riitta Keiski University of Oulu, Department of Process and Environmental Engineering; POB 4300, 90014 University of Oulu riitta.keiski@oulu.fi, http://www.oulu.fi/pyolam/





Prof. Riitta Keiski 06.10.2009



#### CONTENTS

University of Oulu and Its New Structure Spearhead Sectors in the Environmental Engineering Research at the University of Oulu Catalysis Research Biorefinery Concept Sustainable Energy Research - Examples • Renewable Energy – Biofuels • Energy-efficient Products and Processes Mitigating the Environmental Impacts of Energy Generation • CO<sub>2</sub> Related Research and Fuels Production SkyPro Oulu – Science into Products and Processes Education in Sustainable Energy - Examples Contact Information







Founded in 1958 6 faculties 16 000 students 3 000 employees **Total funding EUR 208** million in 2008 Among the largest universities in Finland with an exceptionally wide scientific base

## **University of Oulu 2008**

- First degrees 1340 ٠
- **Doctoral degrees 134** .
- **Publications 3640** .
  - Scientific publications 2254
- 63 invention disclosures, 6 patent applications

#### New University law in 2009:

The University of Oulu will be developed as an international science university in collabortion with research institutes and companies.









#### Structure for the New Collaboration at the University of Oulu

High quality, interdisciplinary, international, focused research and educational activities



## Environmental Engineering Research at the University of Oulu -**Spearhead Sectors**



- **Resource efficiency** 
  - Waste minimization and resources use optimization
  - Process control and automation
  - Recycling technologies

#### Water



- Air
  - Catalytic air purification technologies

Drinking and industrial water purification

CO<sub>2</sub> utilization



- Energy
  - **Biorefineries**
  - Biofuels, biogas, bio-H<sub>2</sub>, fuel cells
  - Power plant automation
  - **Energy efficiency**







# Sustainable Energy Research at the University of Oulu



#### Energy generation and renewable energy sources

- Modelling and Control of a Solar Thermal Power Plant
- Hydrogen Fuel Cell Electrochemical Model
- Hydrogen Production by Bio-ethanol Reforming
- Anaerobic Bioreactor for Biobutanol Production
- Bio-ethanol Production from Potatoes



#### Environmental impacts of energy production

- Control of Biomass Combustion for Emission Reduction
- · Health impacts of particulates originating from engines
- Wood Ash a Potential Forest Fertilizer
- · Chemical utilization of carbon dioxide
- Socio-ecological impacts of energy generation (hydropower) in the North



#### Energy-efficient products and processes

- Piezoelectric Energy Harvesting, Low Power Electronics
- Study of fouling on heat exchanger surfaces, effect on energy-efficiency
- Improved control of the cooking process in Kraft pulping
- Energy-efficiency in steel manufacture
- Improved measurement technologies



# **Catalysis Research by the Oulu Group - Pollution** control, Sustainable energy and production, **Fuels, Chemicals, Catalysts for biorefineries**

- Catalytic oxidation of VOCs, CVOCs, malodorous compounds ٠
- Catalytic oxidation and reduction of flue and exhaust gases ٠

Formaldehyde production from contaminated methanol

Catalytic materials and their characterization

Abatement and health effects of fine particulates

best features e.g. in bio-fuels production

**Catalytic routes in CO<sub>2</sub> utilization (methanol, DMC, carbonic esters)** ٠

Catalytic wet oxidation and Photocatalysis (oxidation, non-fouling

Heterogeneous, homogeneous and biocatalysis - Combining the

**Reforming (CO<sub>2</sub>) and Water gas shift reaction (H<sub>2</sub> production)** ٠



**Catalytic converters** in exhaust gas purification



#### **Biomass to biogas** and synthetic fuels

Deactivation of catalysts, Control of the surface poisoning phenomena Catalytic nanotubes and membranes in e.g. bio-fuels production Catalysis in supercritical CO<sub>2</sub>, microwave and plasma activation

surfaces, H<sub>2</sub> production)

ethanol, biobutanol, biopentanol)

•

•

٠

٠

٠

٠

٠

٠

•





**Department of Process and Environmental Engineering** 

UNIVERSITY of OUL OULUN YLIOPISTO



# **Renewable Energy - Biofuels**

#### **Bioethanol reforming to H<sub>2</sub> for e.g. fuel cells**

- Focuses on developing new technologies for bioethanol ethanol produced from lignocellulose materials - to be used effectively in smallscale fuel cell systems of electric power output between 0.5 to 10 kW.
- The technologies will cover low temperature bioethanol reforming in hydrogen selective membrane reactors and cleaning methods as well as their combinations with any type of low-temperature fuel cells (200-390°C)
- In addition, the bioethanol driven fuel cells could be an intermediate step towards **glucose driven fuel cells**.
- Catalytic microreactor concept, catalytic membranes
- CNTs as catalyst supports for fuel cells and reforming units
- Bio-ethanol reforming is potential technology for hydrogen
  production
  - Ethanol is non-toxic, easily deliverable substance with relatively high H<sub>2</sub> content
  - Can be produced from renewable sources, e.g. biomass
  - Group VIII metals (Ni, Co, Pt, Rh) are found effective reforming catalysts

Contact: Prof. Riitta Keiski, riitta.keiski@oulu.fi Department of Process and Environmental Engineering









UNIVERSI

### Photocatalysis, sustainability and hydrogen production

#### Our research approach: Microreactor concept, H<sub>2</sub>-selective membranes, CNTs



Contact: Prof. Riitta Keiski, riitta.keiski@oulu.fi Department of Process and Environmental Engineering 

# **Renewable Energy - Biofuels**

#### **Biobutanol and biopentanol**

- Microbiological production of biobutanol, higher alcohols and oxygenates as fuel substitutes (efficient processes)
- An anaerobic reactor system with temperature control and pH monitoring, cell immobilization unit, and circulation of fermentation medium was developed.
- Butanol was produced from whey supplemented with yeast extract
- Involves developing and optimize catalytic materials and chemical (catalytic) reaction pathways in the production of bioalcohols and other bio-derived compounds







- Anaerobic reactor system
- A: Reactor
- B: Three-way valve
- C: Pre-filter
- D: Cell immobilization unit,
- E: Filter used with gas-inlet and water lock tubings
- F: Water lock

Contact: Prof. Ulla Lassi, ulla.lassi@oulu.fi Department of Chemistry



# **Renewable Energy - Biobutanol and biopentanol**



#### Technological challenges and opportunities in bio-alcohols production

- **Digestion of the raw material** (e.g., by-products of food or paper/pulp industry) to fermentable sugars
- Inhibition caused by high solvent content, decomposition of solvent and the loss in microbiological activity
- **Separation of butanol** is a challenge due to its water solubility (Butanol forms a separate phase only after the concentration exceeds 7%)
- Novel catalysts and catalytic processes for chemical synthesis (from glycerol)
- Several species of anaerobic, spore-forming *Clostridia* are capable of metabolizing different carbon sources to **butanol**, **ethanol** and **acetone** (ABE-fermentation)
- Butanol yield can be increased with genetic manipulation of the micro-organisms, continuous fermentation process, bacterial cell immobilization and in-situ product recovery
- Opportunities:

These technologies are expected to be applicable for the conversion of glycerol (a higher alcohol) and lower (bio)alcohols into high-value liquid fuels.



# **Energy-efficient products and processes**

#### **Piezoelectric energy harvesting for powering low power electronics**

- Wireless data transmission techniques need wires for the power supply or batteries
- The development of energy harvesters would reduce the need for batteries and wires costeffective solutions for
  - autonomous wireless sensor networks
  - powering portable electronics
  - maintenance-free systems
- One of the most promising techniques is mechanical energy harvesting e.g. by piezoelectric components
  - deformations produced by different means is directly converted to electrical charge via direct piezoelectric effect
- The obtained results prove that piezoelectric energy harvesters are a viable option when powering low power electronics in vibrating environments.



Schematics of (a) unimorph type piezo structure (b) energy harvester system with the harvester and accompanying electronics

Contact: Prof. Heli Jantunen, hali.jantunen@ee.oulu.fi Department of Electrical Engineering



# **Energy-efficient products and processes**

#### Improved control of the cooking process in Kraft pulping

- The control of the impregnation vessel and digester in a cooking . process of the chemical pulping plant has a great influence on energy and raw material savings
- If the quality control variations can be eliminated in the cooking . process, the energy and raw material saving are significant
- The quality change in cooking process affects the fibre line's • energy consumption e.g. in oxygen delignification and raw material consumption e.g. bleaching chemicals.

#### Managing the energy efficiency of a process sensor network

- Energy consumption is the main limitation of wireless sensor networks • (WSN) and Deployment of WSNs in difficult environments or at high great White Liquer. A data transfer speeds is especially challenging
- In this research the possibilities of saving energy & producing energy of a • wireless process measurement system is studied
- The main focus areas of the project are saving and producing energy at the • network nodes to reduce power dissipation as much as possible.







# **Energy-efficient products and processes**



#### **Control of fouling of heat exchangers**

# Energy efficiency of heat exchangers may be diminished by fouling

- **Fouling:** unwanted material deposits on the heat transfer surface
  - Reduces heat transfer
  - Increases the pressure drop of the system
- It is estimated that fouling costs are about 0.2% of the countries Gross National Product
  - Cost of fouling to industry is about 30 milliard €/yr in EC
- Mechanical methods are expensive and not very efficient
- Chemical detergents may damage the product and negative environmental effects
- Research need:
  - Understanding fouling phenomena
  - Develop new design methods and coatings to decrease fouling
- Tested: non-fouling surfaces, verified in industrial scale testing in the connection with an industrial process







Contact: Prof. Riitta Keiski, riitta.keiski@oulu.fi Department of Process and Environmental Engineering



# Mitigating the environmental impacts of energy generation Chemical utilisation of CO<sub>2</sub>

- Recovered CO<sub>2</sub> can be used for the production of chemicals, fuels and other useful products.
- Motivations to producing chemicals from CO<sub>2</sub>:
  - CO<sub>2</sub> is cheap, non-toxic feedstock that can replace toxic chemicals
  - Production of chemicals from CO<sub>2</sub> can lead to totally new materials
    - Examples: syngas, methanol, dimethyl carbonate (DMC), carbonic esters, DME
  - New routes to existing chemical intermediates and products could be safer, more efficient and economical than current methods
  - The production of chemicals from CO<sub>2</sub> could have a minor (Mt scale) but positive impact on the global carbon balance







Contact: Prof. Riitta Keiski or Eva Pongracz Department of Process and Environmental Engineering



# **Chemical utilisation of CO<sub>2</sub>** On-going and earlier research

- CO2-USE
  - CO<sub>2</sub> as a raw material for fuels and petrochemical components
- CO2H2 and ReGenGas
  - Reforming of CO<sub>2</sub> to syngas, CO<sub>2</sub> recycling
- CO2UTIL, SuSe
  - Sustainable production of methanol, dimethyl carbonate (DMC) and carbonic esters from carbon dioxide by green chemistry principles

#### Our target: Secondary CO<sub>2</sub> as a raw material for valuable chemicals/products inside the company that produces CO<sub>2</sub>, e.g. oil, chemical, power, pulp and paper, and metallurgical industry

Contact: Prof. Riitta Keiski or Eva Pongracz Department of Process and Environmental Engineering







# **CO2UTIL**, Towards utilization of CO<sub>2</sub> as a green and versatile commodity chemical - Clean synthesis of Methanol and Dimethyl Carbonate



#### DMC selectivity 100 %, Better activity

Under one phase reaction conditions
Recycling of Catalytic Species
Water trapping

#### **Future activities**

Catalyst Design for Continuous Flow Reactors
Heterogenization of the catalyst
New catalytic materials

- Developing green chemicals via a sustainable process in accordance with Green Chemistry principles
- Value enhancement of a secondary resource, CO<sub>2</sub>
- The conventional method for methanol production is based on fossil feedstock and the production of DMC involves the use of toxic phosgene or CO
  - Reduction of the hazard from solvents and chemicals
  - Explore safe and environmentally sound reaction routes and energyefficient processes
  - Identify new, effective catalysts for methanol and DMC syntheses
- Develop a **dynamic simulation system** that can be used in studying the realization of different process routes from process control viewpoint







Contact: Prof. Riitta Keiski or Eva Pongracz Department of Process and Environmental Engineering

.

•

UNIVERSITY of OULU

# Reforming

- Process for producing synthesis gas  $(H_2 + CO)$
- Synthesis gas is an important raw material e.g. in methanol synthesis, hydrocarbons production)
- Synthesis gas can be produced from almost any carbon source ranging from natural gas to biomass
- CO<sub>2</sub> as a feedstock in dry reforming: CO<sub>2</sub> + CH<sub>4</sub>  $\rightarrow$  2H<sub>2</sub> + 2CO
- **Bioethanol reforming** (COST Action 543, REFORMH2)
- Other biomass based materials (COST Action 543, REFORMH2)
- Challenges:
  - Sufficient conversion  $\rightarrow$  high temperature is needed
  - Carbon formation problem  $\rightarrow$  catalyst resistive of carbon or regeneration is needed
- Research focus:
  - Catalyst development and optimization, Reaction conditions optimization
  - Miniaturization, microreactor concept
  - Catalytic membranes, phenomena integration
  - Industry specific solutions
- Dynamic simulations will be done for the whole reaction chain, from secondary CO<sub>2</sub> to different products such as synthesis gas, methanol and DMC.

Contact: Prof. Riitta Keiski or Eva Pongracz Department of Process and Environmental Engineering









# **Methanol synthesis**

- Methanol is an important product and feedstock in chemical industry
- Commercially methanol is produced from synthesis gas  $CO + 2H_2 \leftrightarrow CH_3OH$
- It is possible to use CO<sub>2</sub> as a feedstock in methanol synthesis
  - $CO_2 + \bar{3}H_2 \leftrightarrow CH_3OH + H_2O$

### Challenges



- Reaction is thermodynamically unfavorable
- More active and selective catalysts are needed
  - » Catalyst development and optimization
    - » Zr-based catalysts selective (Cu/ZnO/ZrO<sub>2</sub>)
    - » Proper preparation, phase structure important

**Example of our results:** co-precipitated Cu/ZnO/ZrO<sub>2</sub>; activity tests: T = 250°C, p = 30 bar and H<sub>2</sub>/CO<sub>2</sub> = 3.

Contact: Prof. Riitta Keiski, riitta.keiski@oulu.fi Department of Process and Environmental Engineering







#### The objectives of the project are

 To design hybrid catalysts for carbonic esters synthesis via employing the best features of homogeneous and heterogeneous catalysis,

#### • To use CO<sub>2</sub> + bio-alcohols in carbonic esters synthesis,

• To design catalyst recovery and recycling for the best process performance, e.g. catalyst immobilization, use of ionic liquids, continuous operation,

 To design metrics for assessing the benign by design approach, to perform environmental assessment analysis.

Contact: Prof. Riitta Keiski, riitta.keiski@oulu.fi Department of Process and Environmental Engineering

# Sustaining carbonic esters synthesis with carbon dioxide feedstock, SUSE



UNIVERS

01

OULUN YLIOPISTC

KESTÄVÄ TUOTANTO

JA TUOTTEET



www.cleantechoulu.fi/air/skypro-oulu/

## Science into products and production technologies







European Union European Regional Development Fund



Continued development of clean air know-how in Oulu Region

#### Contact: Prof. Riitta Keiski Department of Process and Environmental Engineering

# **SkyPro Oulu** Science into products and production technologies

- The main goal is to establish a research centre on air-related technology in the Oulu Region.
- SkyPro Oulu is launched by the project Science into Products and Production Technologies 2008-2011 with two main activities: •
  - 1) building up the SkyPro Oulu (Clean Air Cluster) collaboration net
  - 2) executing a research project to demonstrate the collaboration
- The budget of the launching project: 650 000 € (ERDF and Finnish Government 572 000 €, City of Oulu 58 000 €, Micropolis technology centre 20 000 €)
- The lead partner of the launching project: University of Oulu •
- Co-partner: Micropolis Technology Centre

#### Incorporating science to products and production technologies

- Transmitting information
- Improving the visibility of Oulu region in the air pollution control branch
- **Boosting innovations**











COST Action 543 Training School June 2-6, 2008, University of Oulu, Finland



Training School: Sustainable Production and Energy: Catalysis by Nanomaterials, Catalytic Microstructures



:ost

Prof. Riitta Keiski



University of Oulu, Department of Process and Environmental Engineering

P.O.Box 4300, FIN-90014 University of Oulu

riitta.keiski@oulu.fi, http://cc.oulu.fi/~polamwww

Financed by COST Action 543, Graduate School for Energy Science and Technology, Graduate School in Chemical Engineering, University of Oulu



Prof. Riitta Keiski 06.10.2009

COST Action 543, 540, P19 Training School May 4-8, 2009, University of Oulu, Finland

ost

**COST Action P19:** 

Multiscale modelling of

materials

Collaboration between COST Actions 543, 540, P19



# **Photocatalysis**

Prof. Riitta Keiski



University of Oulu, Department of Process and Environmental Engineering

Laboratory of Mass and Heat Transfer Process Engineering

P.O.Box 4300, FIN-90014 University of Oulu

riitta.keiski@oulu.fi, http://cc.oulu.fi/~polamwww



Financed by ESF/COST Action, University of Oulu (CEWIC and SkyPro Oulu), Graduate School for Energy Science and Technology (EST) and Graduate School in Chemical Engineering (GSCE)







**Contact Information: Prof. Riitta Keiski, D.Sc.(Tech.), Docent** Head of the Laboratory Vice-head of the Department Vice-rector of the University

Laboratory of Mass and Heat Transfer Process Engineering Department of Process and Environmental Engineering **Center of Expertise in University Education in 2004-2006, 2007-2009, 2010-2012** FI-90014 University of Oulu, POB 4300 Phone: +358-8-553 2348, +358-40-726 3018; Fax: +358-8-553 2304 E-mail: riitta.keiski@oulu.fi, firstname.lastname@oulu.fi;

http://www.oulu.fi/pyolam/



