



UNIVERSITY of OULU  
OULUN YLIOPISTO

# POKE Symposium 2014

## Catalytic Oxidation of Dimethyl Disulphide by Monometallic Catalysts

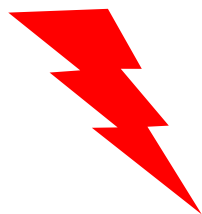
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# CONTENTS



→ Introduction

*Dissertation topic:*

*“Novel Catalyst Materials in Volatile Organic Compound Abatement: Development of Industrial VOC Abatement for Harmful Compounds”*

\*\*\*

## Developing the Application of Catalytic Oxidation

\*catalyst preparation \*characterization

\*reaction \*reactor set-up \*activity testing \*stability

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## Further objectives

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## Hydrothermal Carbonization



# Introduction

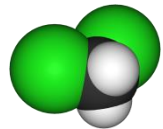
VOCs cause direct and indirect air pollution

- Direct (e.g. **toxicity, odour**) - indirect (e.g. **smog formation**)

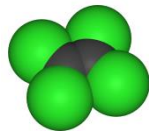
e.g. **sulphur** is present virtually in **all hydrocarbon feedstock**.



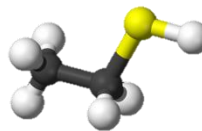
VOCs originate from natural sources as well as from pharmaceutical, solvent, coating, and wood industry (pulp), chemical production, landfill sites, and wastewater treatment plants



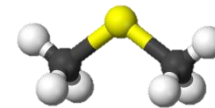
dichloromethane  
DCM



perchloroethylene  
PCE

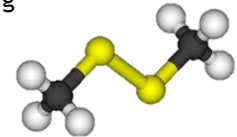


methyl mercaptan  
MM



dimethylsulfide  
DMS

wikipedia.org



dimethyldisulfide  
DMDS

- CVOCs can be **extremely toxic** for the environment and human health
  - SVOCs not extremely toxic but repulsively **malodorous** at very low concentrations
- Both require highly efficient treatment methods
- Regulations under **EU legislation**



Catalytic oxidation is a tempting possibility for the abatement due to its **high energy and purification efficiencies**

→ **Poisoning** and further **deactivation** is problematic

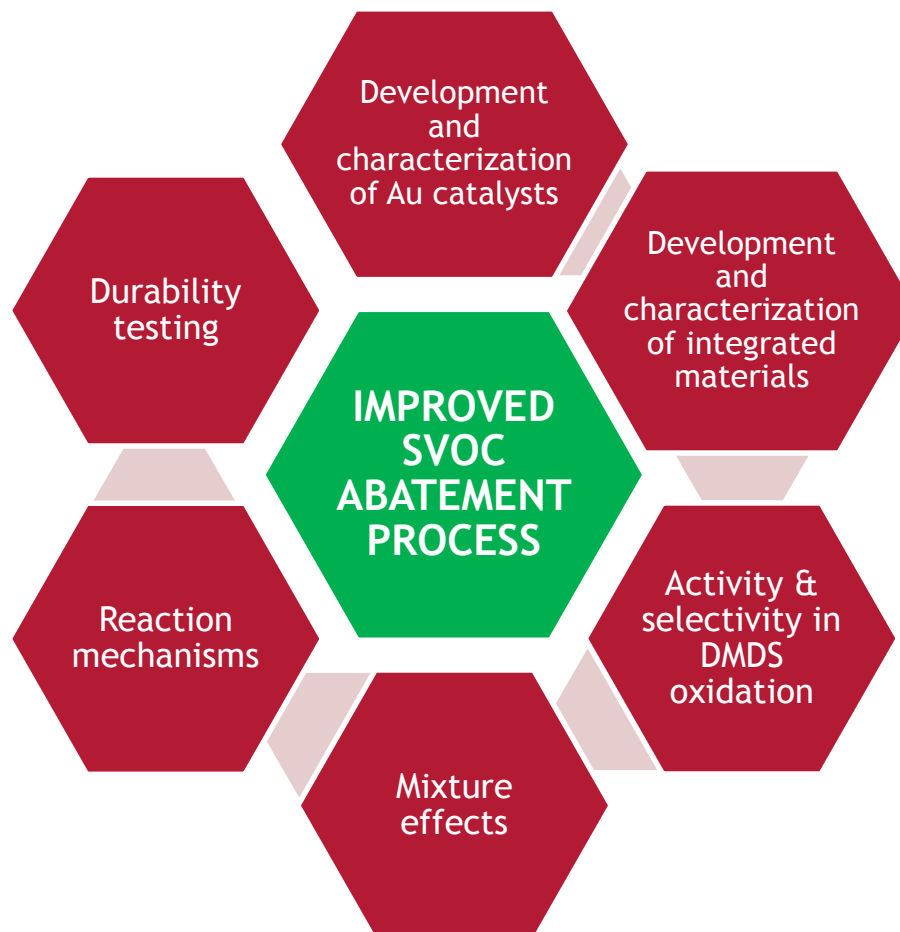
→ **Durability, activity, and stability** need to be improved



# TASKS

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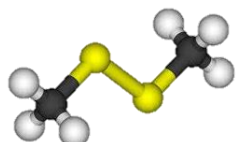
*“Novel Catalyst Materials in Volatile Organic Compound Abatement”*



# DEVELOPMENT OF CATALYTIC TREATMENT METHOD <sup>5</sup>

*“Novel Catalyst Materials in Volatile Organic Compound Abatement”*

- Oxidation of DMDS over mono and bimetallic materials  
**activity, deactivation, optimization**
- Preparation, characterization, and testing of catalysts  
BET, H<sub>2</sub>-TPR, H<sub>2</sub>-chemisorption, TPIE, IIE, ICP-OES, XRD, TEM, TG-DTA, acidity, activity and stability
- Target properties - **active, durable, selective**

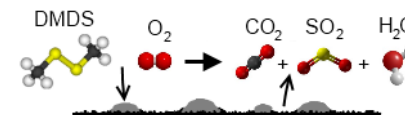


wikipedia.org

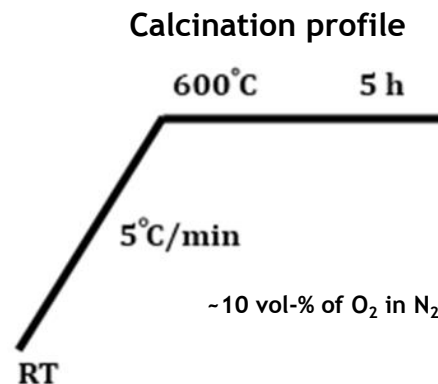
ENERGY EFFICIENCY

MAINTENANCE COSTS

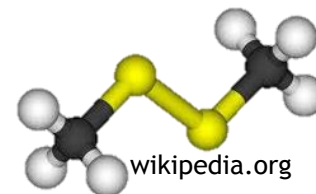
DESIRED PRODUCTS



Catalyst	Preparation method
1/A	Deposition-precipitation
2/A	Wet impregnation
3/A	Wet impregnation
1/B	Deposition-precipitation
2/B	Wet impregnation
3/B	Wet impregnation
1/C	Deposition-precipitation
2/C	Wet impregnation
3/C	Wet impregnation
1-2/A	Redox reaction
1-3/A	Redox reaction
1-2/B	Redox reaction
1-3/B	Redox reaction
1-2/C	Redox reaction
1-3/C	Redox reaction

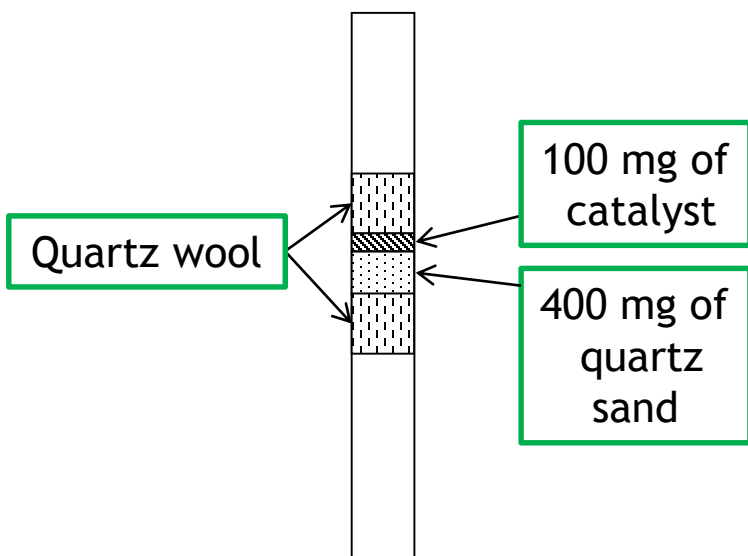
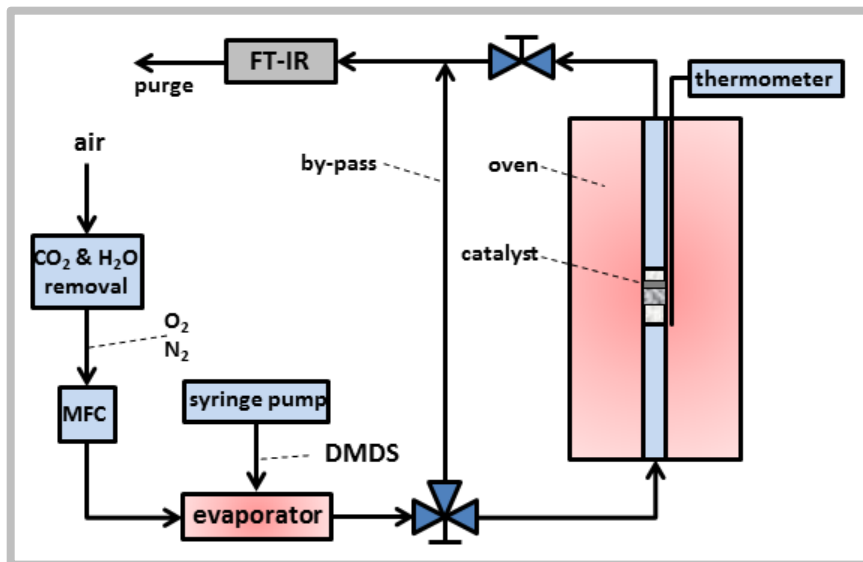


# LIGHT-OFF TEST

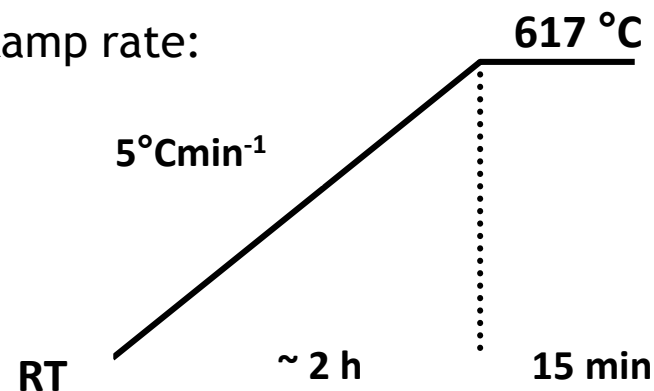


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Schematic of the experimental setup



- ~ 500 ppm of DMS
- Air flow rate: 1000 mlmin<sup>-1</sup>
- CO<sub>2</sub> and water removed from incoming gas by an adsorber unit
- Ramp rate:

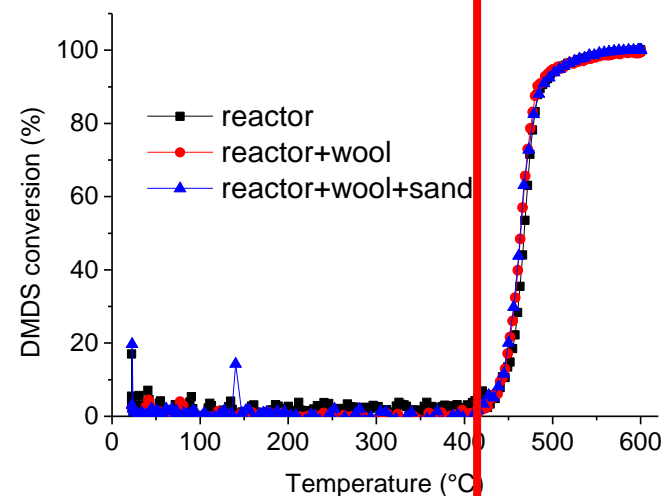
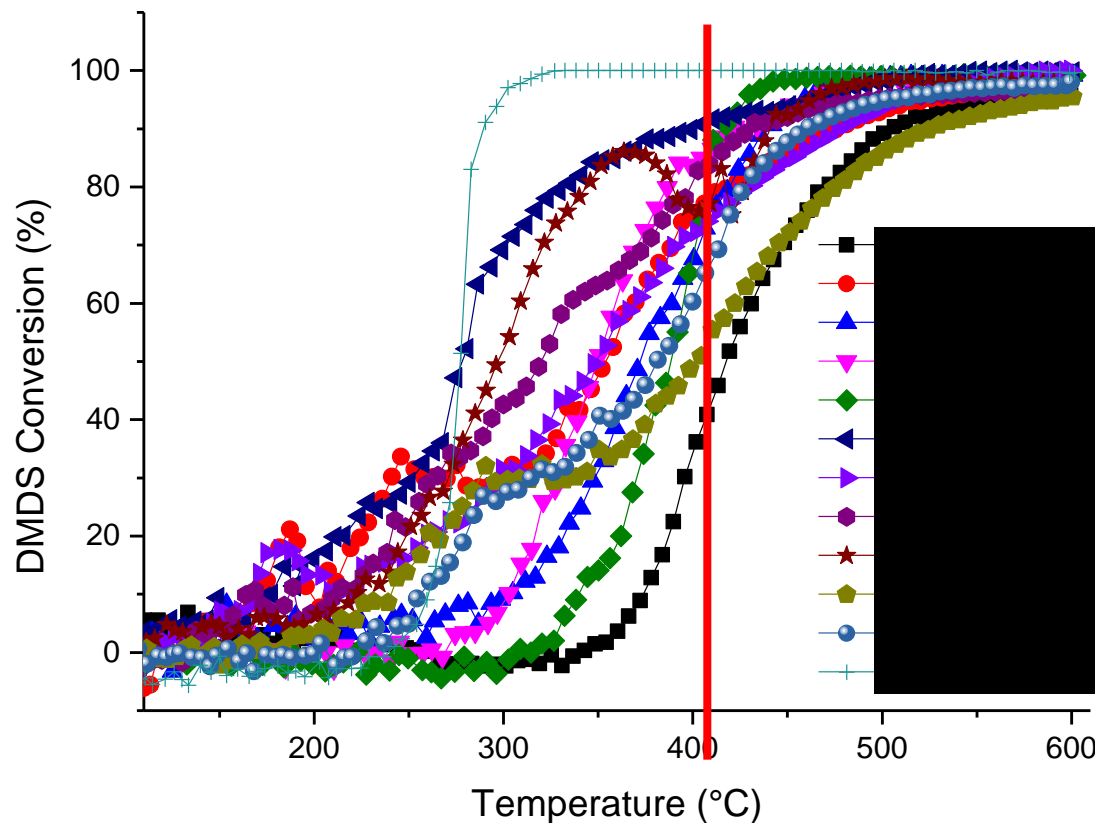
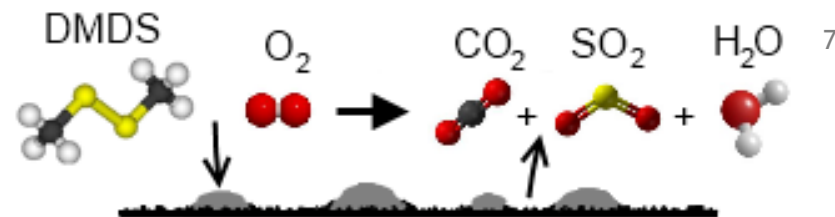


- Continuous measurement of product concentrations by FTIR gas analyzer



# ACTIVITY

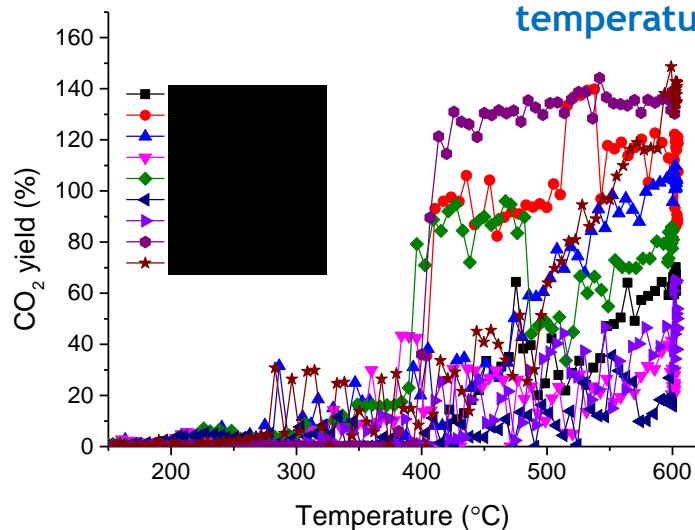
## *light-off tests*



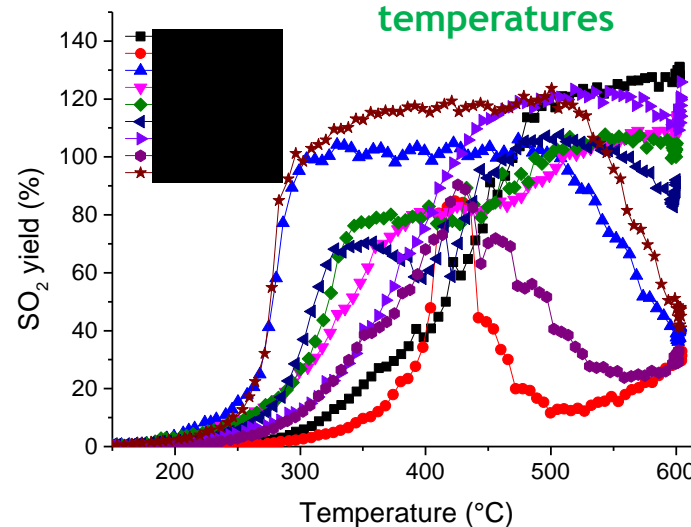
# YIELDS

## $CO_2$ , $SO_2$ & $CH_2O$ yields

Pt catalysts  $CO_2$ -selective at higher temperatures



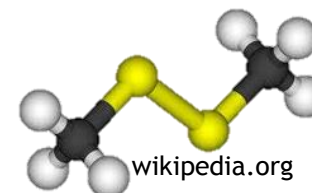
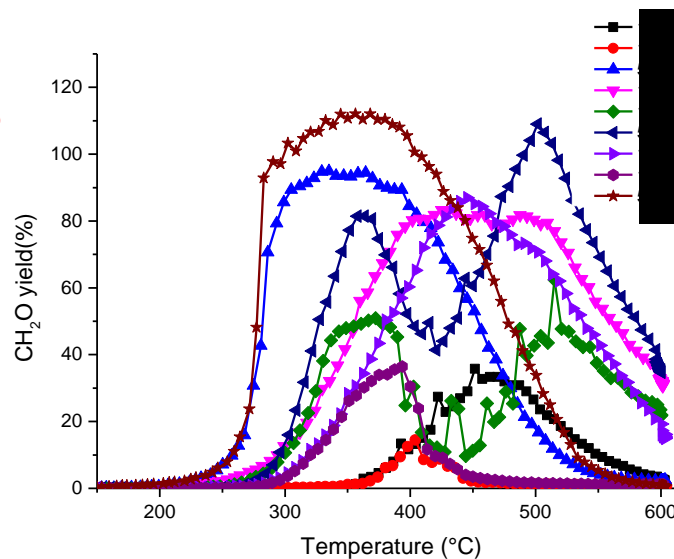
Au catalysts  $SO_2$  selective at higher temperatures



Cu catalysts very  $CH_2O$  selective at temperatures of ~300-400 °C

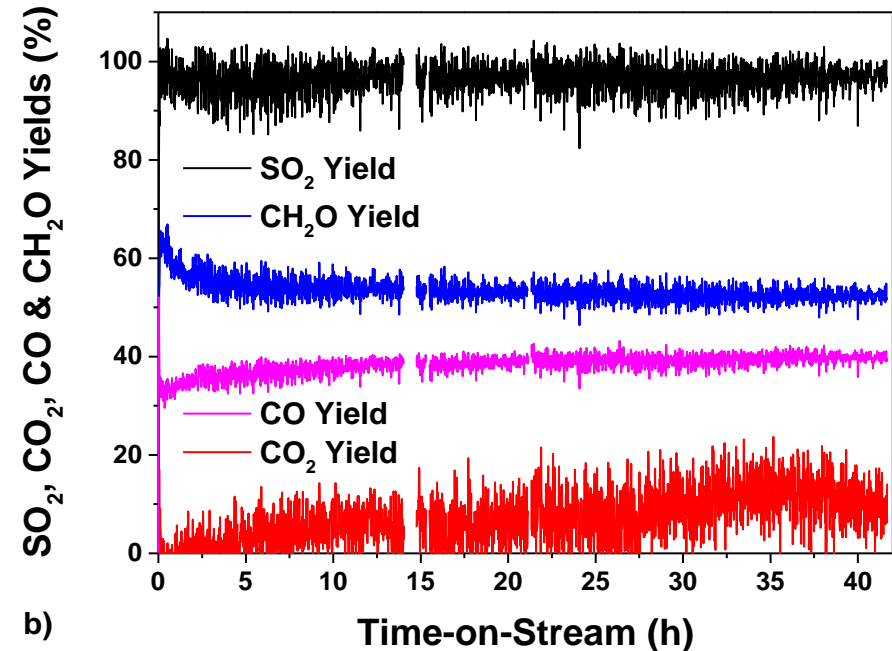
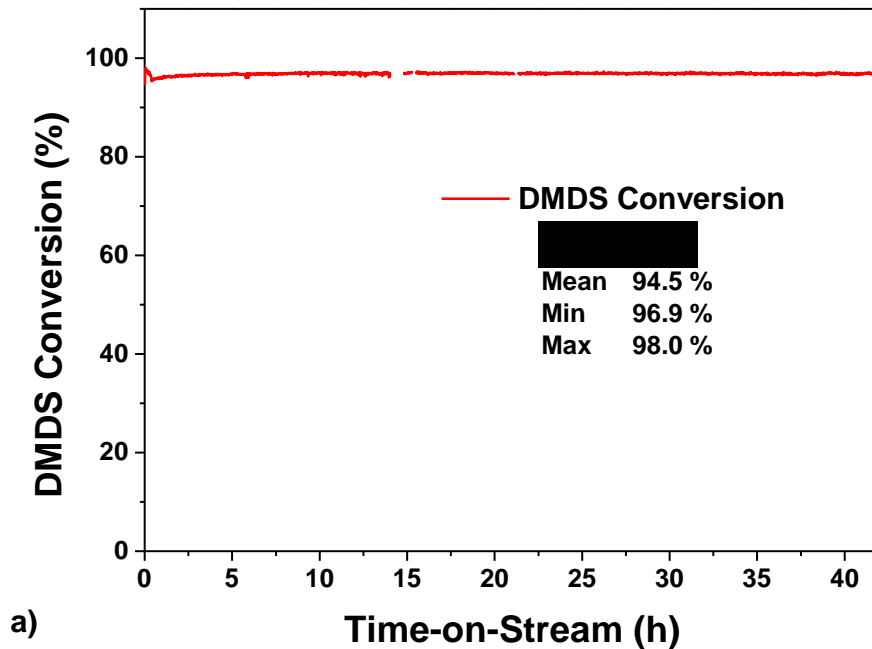
Au less  $CH_2O$  selective

Pt  $CH_2O$  selective barely at all





# STABILITY OF Au CONTAINING CATALYST

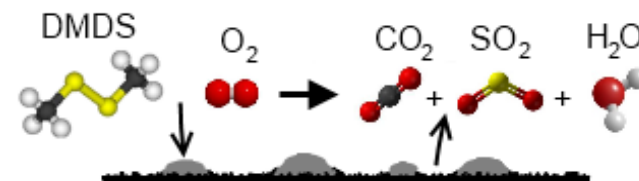


- **stable** catalyst
- selectivity must be improved
- to combine properties of two tested catalyst (**activity, selectivity**) and (**durability**) as a bimetallic catalyst



# OBJECTIVES

- 2 publications
  - Mono/bimetals
- TPDx (reaction mechanisms)
- Activity tests for bimetallic catalysts
- Characterizations:
  - TEM, acidity



# Research visit to Federal Institute of Goiás, Brazil<sup>11</sup>

## Work plan

- Preparation of **carbon-like material** via hydrothermal carbonization
- Utilisation as an **adsorbent, support, or catalyst material** in the treatment of industrial air emissions
- Physical and chemical properties are investigated:
  - optical microscopy, dry mass, absorbent capacity, ion exchange properties, SEM, BET, BJH, XRD, ICP-OES
- Testing in the **treatment of industrial air emissions** in lab scale



# Hydrothermal carbonization

*“Hydrothermal carbonization (HTC) exhibit attractive advantages allowing the production of a variety of inexpensive and sustainable carbonaceous products with beneficial porosity at nanoscale and functionalization structures for a diverse range of applications.”*

- Considering the concepts of sustainability in terms of environmental, economic, and social impacts, HTC potentially a model case

Follows “chimie douce”:

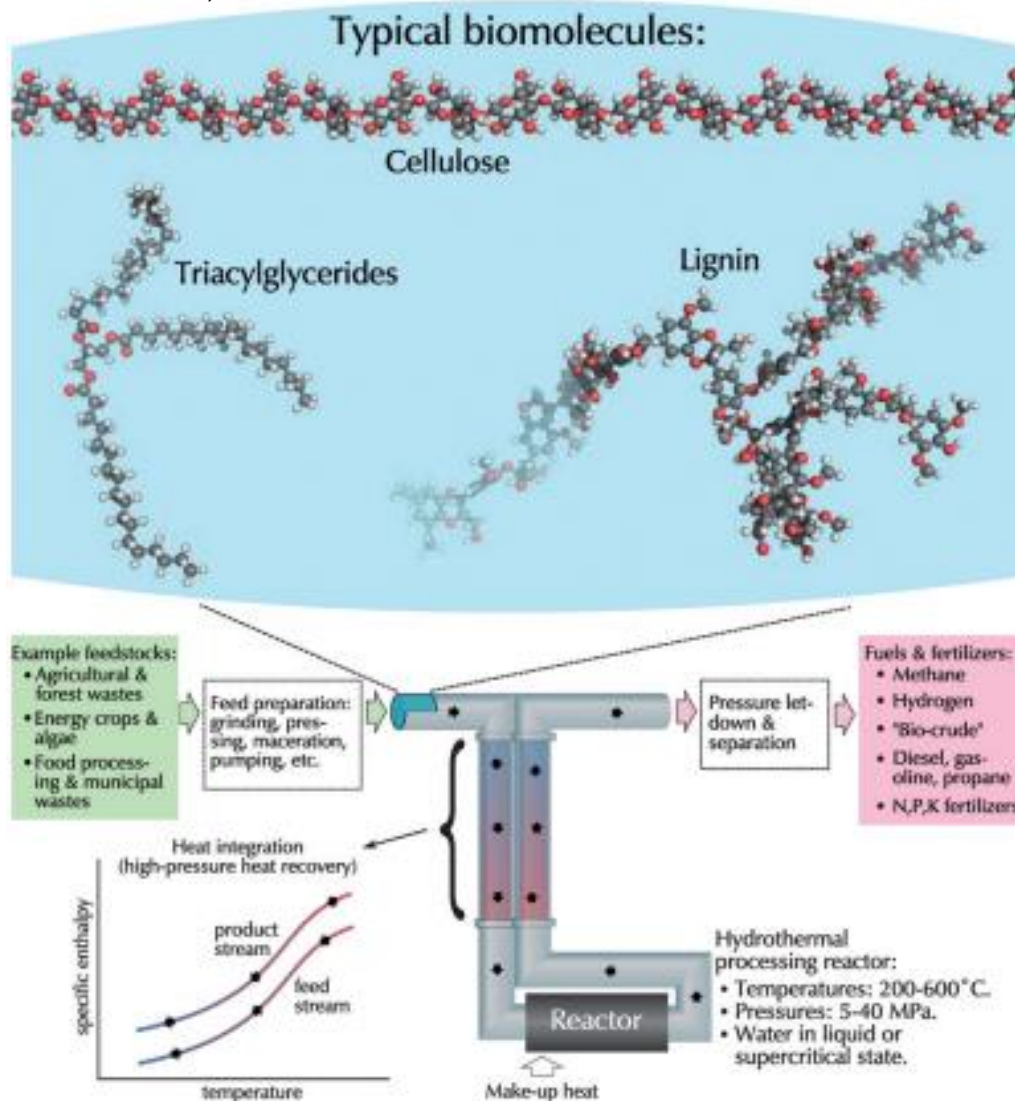
- 1.reaction preferably occur in a solvent medium, favorably water or water-alcohol mixture
- 2.less extreme conditions compared to other applications in terms of temperature, or used additives
- 3.chemical condensation and single step generation of various shapes



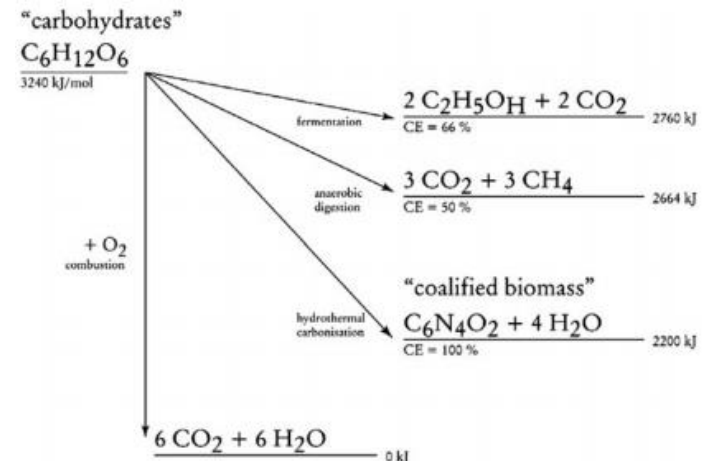
# Hydrothermal carbonization

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Peterson et al. (2008) Energy Environ. Sci. 1, 32-65.

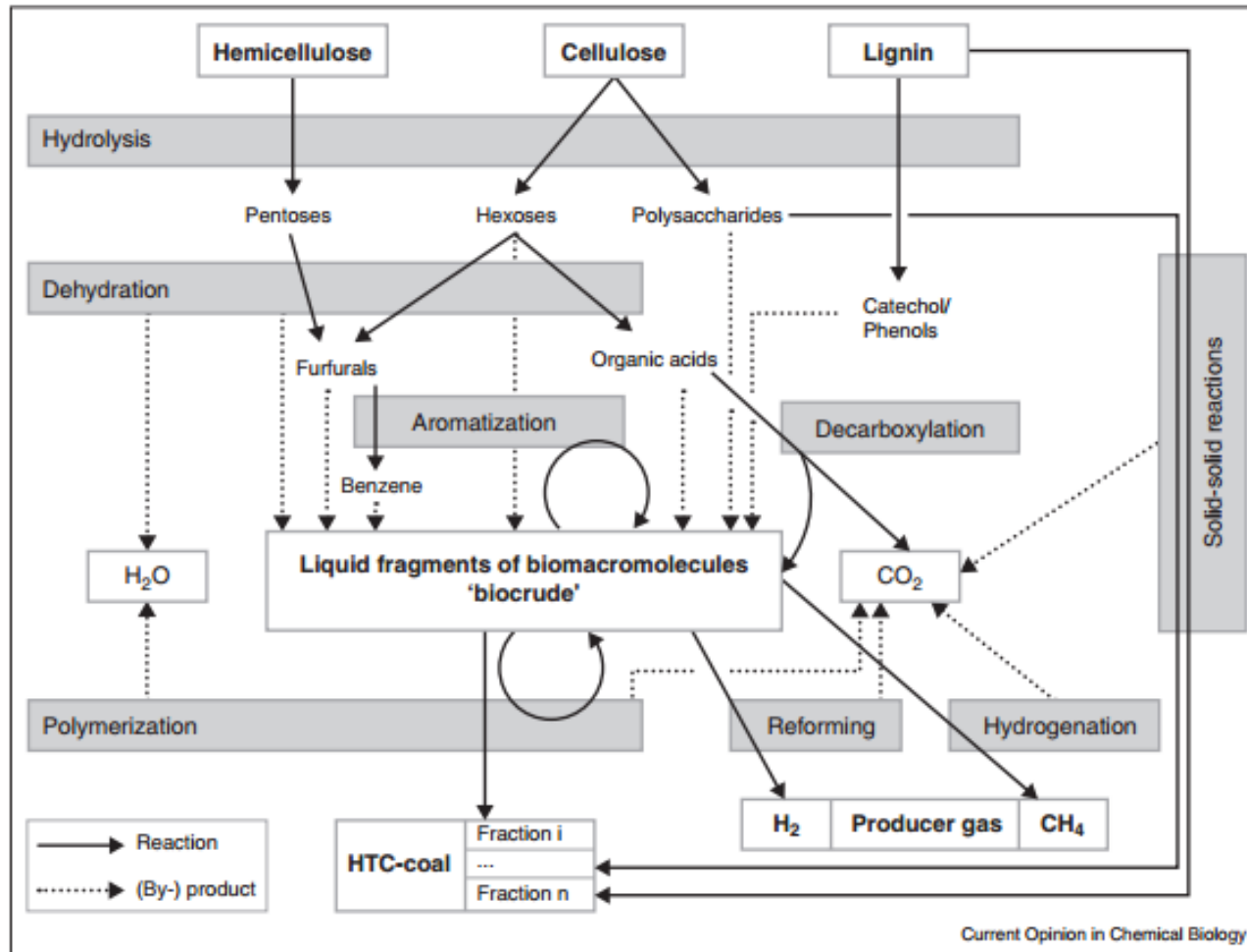


Titirici, Thomas & Antonietti (2007) New J. Chem. 31, 787-789.



# Htc reaction pathways

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Principle reaction pathways of hydrothermal carbonization.  
Adapted from A Funke, PhD thesis, Technische Universität Berlin, 2012.



# Example products

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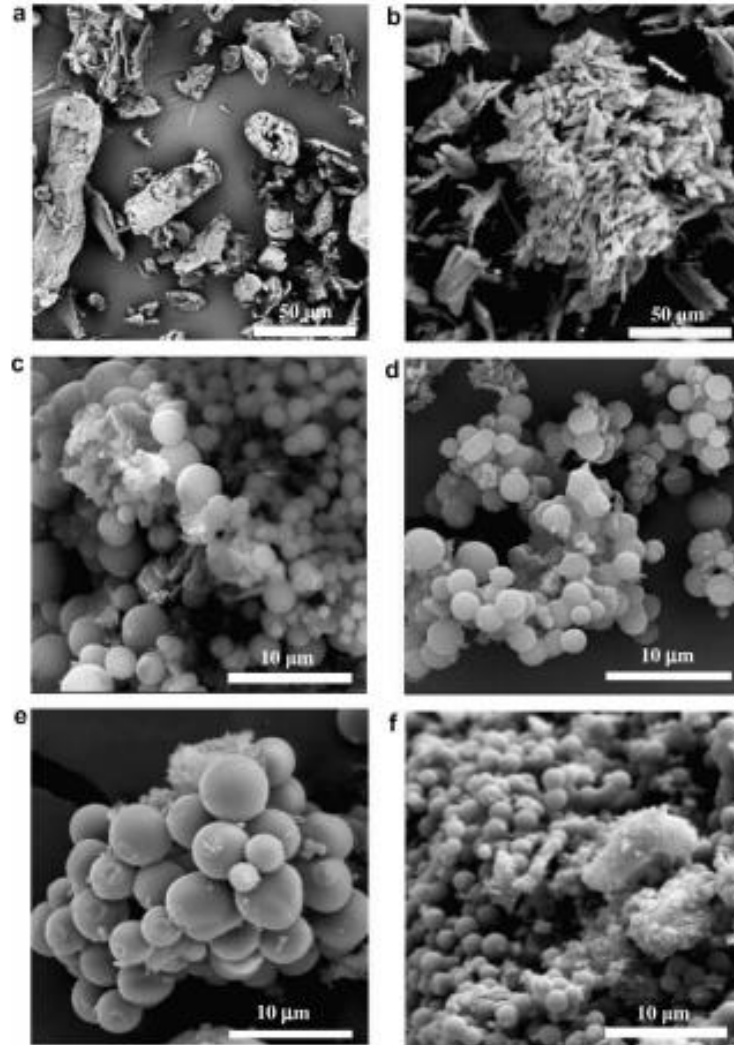


Fig. 1 – SEM images: (a) raw cellulose and (b–f) hydrothermally treated cellulose at: (b) 210 °C/40 g L<sup>-1</sup>, (c) 220 °C/40 g L<sup>-1</sup>, (d) 230 °C/40 g L<sup>-1</sup> (CE-1), (e) 250 °C/40 g L<sup>-1</sup> (CE-3) and (f) 250 °C/160 g L<sup>-1</sup> (CE-4).

Sevilla & Fuertes (2009) Carbon  
47, 2281-2289.

Properties of the material can be modified using different reaction conditions e.g.

- temperature
- reaction time
- additives
- pH
- concentrations





HTC reactor



Sugarcane bagasse pith



Bagasse in reactor core



Product biochar



Hydrothermal  
carbonization

2h  
>180°C  
max. 33 bar





Thank You for Your Attention.

