Emission abatement using integrated catalysts in log wood stoves

Ingo Hartmann
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Challenges – General remarks

• Increasing importance of **energetic use of biomass**
• Energetic use mostly coupled **combustion process → Flue gases**
• **Primary measures** not sufficient to meet **future emission limits**
• Use of different biomasses → requires different **secondary measures**
### Challenges – Biomass Combustion

**Wood log for heat production**

- Instationary process
- Strong influence of the catalyst on the overall system
- $T > 770\,\text{K}$
- High dust emission

➢ This leads to…

<table>
<thead>
<tr>
<th>Requirements for emission control catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated catalyst</td>
</tr>
<tr>
<td>Very low back pressure</td>
</tr>
<tr>
<td>High temperature resistance (ca. &gt; 1150 K)</td>
</tr>
<tr>
<td>(ca. &gt; 1150 K) ➔ metal oxide</td>
</tr>
<tr>
<td>High activity towards total oxidation of CO and $C_XH_Y$ at high T</td>
</tr>
</tbody>
</table>
**Background: Micro-scale biomass combustion**

**Small-scale combustion systems in Europe**

- Heating appliances in the capacity range 0-15 kW on the European market are basically fireplaces and stoves (26 Mio wood log stoves in EU 27)
  - batch operation, upper flame combustion, user influence
  - high emissions of CO, OGC and PM
- Pellet boilers and stoves: \( \geq 10 \text{ kW} \)
- Wood log gasification boiler (downd draught): \( \geq 15 \text{ kW} \)

**Better energy performance of buildings**

- Decrease of heat demand (<< 10 kW, for low-energy houses < 5 kW)
- Currently available systems achieve small annual utilization ratios, frequently operation at partial load with low efficiency and high emissions

**Development of continuous biomass combustion systems < 5 kW**

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1 Mudgal S. et al., LOT 15 Solid fuel small combustion installations – Economic and market analysis, Bio Intelligent Service S.A.S, France, 2009
For the development of micro-combustion systems 3 research topics were identified:

- fuel preparation and feeding (automatic and continuous fuel supply)
- Furnace construction (down draft, grate design)
- control systems (air supply, combustion control)
Development of a micro-scale installation

Temperature profile in the oxidation reactor

High temperature stable catalyst (Alumina foam)
Emission reduction by catalysis

• Some catalysts are commercially available for biomass combustion systems
  ◦ Noble metals as active material on metal or ceramic support with $\gamma$-Al$_2$O$_3$ washcoat

• Challenges for Application of Catalysts in small scale biomass combustion
  ◦ Fluctuating temperatures and flue gas composition
  ◦ Wide range of pollutants: CO, VOC, soot...

• Deactivation of catalyst
  ◦ Catalyst poisons
  ◦ Thermal
  ◦ Blockage with particles

Main effects observed during use of commercial available catalysts
Emission reduction by catalysis

Application of ceramic foam in micro-scale installation

• Mixed metal oxides on alumina foam
  ◦ Cell density: 10 ppi
  ◦ Reduction of CO and VOC up to 70 % possible (tested in downdraught stove)

• Integration into the combustion chamber

• No blockage after 25 h of operation

• Heat accumulation
  ◦ Temperature increase of 100-150 K in flame zone
    (Flue gas temperature zone: 700-800 °C)

• Aim of Investigations: Characterization and analysis of materials and occurring processes during catalytic gas treatment in biomass combustion systems
Emission data with Alumina foam

Mean Values (13 Vol.-% O₂)

<table>
<thead>
<tr>
<th>Air Supply PA/SA</th>
<th>TSP (mg/m³)</th>
<th>O₂ (Vol.-%)</th>
<th>CO (mg/m³)</th>
<th>Org.-C (FID)</th>
<th>NO₂Äqui (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7/1.0</td>
<td>4</td>
<td>8.3</td>
<td>0</td>
<td>0</td>
<td>193</td>
</tr>
<tr>
<td>0.7/0.6</td>
<td>2</td>
<td>2.7</td>
<td>125</td>
<td>1</td>
<td>165</td>
</tr>
<tr>
<td>0.7/1.4</td>
<td>5</td>
<td>12.2</td>
<td>28</td>
<td>1</td>
<td>223</td>
</tr>
<tr>
<td>0.7/1.0</td>
<td>3</td>
<td>9.6</td>
<td>2</td>
<td>0</td>
<td>185</td>
</tr>
</tbody>
</table>

- System Low emission combustion
  - PM < 5 mg/m³
  - CO < 5 mg/m³
  - Lambda: 1.1 – 2.2

- Reproducible operation with automatic feeding of comminuted wood

- Development towards practical system is going on

- System is used for catalyst screening
  - Activity
  - Ageing
  - Abatement Soot
Emission reduction by catalysis

Possible emission reduction by integration of catalytic active foams

- University Leipzig, DBFZ and Specht GmbH: Development of catalyst for biomass combustion systems
  - Mixed metal oxides on Alumina foam
  - Patent application has been approved (2012)

- Effect and long-term stability for application in downdraught stove

- Comprehensive characterization for transfer to other installations
  - Occurring catalytic reactions and catalyst properties (range of application)
Starting point for the development

**xeoos „TwinFire“ wood log stove from German company Specht:**

Patent: Stove for solid fuels (EP 1340943 A2)
Starting point for the development

xeoos „TwinFire“ wood log stove from German company Specht:

Patent: Stove for solid fuels (EP 1340943 A2)
Recent Developments - Catalyst

DBFZ, Specht Modulare Ofensysteme GmbH & Co. KG, Universität Leipzig

- **spinel-type mixed metal oxides**
  promising to meet the requirements
  \(\rightarrow\) Catalyst screening

- Synthesis of mixed metal oxides on surface of monolithic structures
  via RSSA-Synthesis [1]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Reference no cat.</th>
<th>New cat.</th>
<th>Aged 1</th>
<th>Aged 2</th>
<th>Aged 3</th>
<th>Aged 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time on stream</td>
<td>mg/m³ with 13 % O₂</td>
<td>0 h</td>
<td>185 h</td>
<td>338 h</td>
<td>458 h</td>
<td>654 h</td>
</tr>
<tr>
<td>CO / ppm</td>
<td>1718</td>
<td>725</td>
<td>833</td>
<td>222</td>
<td>837</td>
<td>677</td>
</tr>
<tr>
<td>org.-C.</td>
<td>156.4</td>
<td>65.1</td>
<td>33.0</td>
<td>8.6</td>
<td>64.1</td>
<td>71.0</td>
</tr>
<tr>
<td>dust</td>
<td>19.6</td>
<td>17.0</td>
<td>15.0</td>
<td>9.0</td>
<td>16.6</td>
<td>13.9</td>
</tr>
</tbody>
</table>

\(\rightarrow\) CO and CₓHᵧ conversion of > 50 %

References
[1] DE 102013020398 A1, 12.06.2014, Assignee: DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Germany; Specht Modulare Ofensysteme GmbH & Co. KG, Germany; Universität Leipzig, Germany; By: Specht, Bodo et al..
Down draft wood log stove NEKO
DBU: AZ: 28412/02

Project partner: Specht Modulare Ofensysteme GmbH and Co. KG, Universität Leipzig, DBFZ

- **Integration of catalyst:** $\alpha$-$\text{Al}_2\text{O}_3$ support with spinel-type catalyst
  - Chamber integration of catalyst, stable under high temperature conditions
  - Without use of noble metals: RSSA synthesis of metal oxide catalysts
  - Without use of washcoat, catalyst coating by solid-state reaction route

- **Redesign of the furnace on the basis of xeoos X8**
  - Lengthening of lower chamber: Higher residence time and avoidance of flame contact
  - New development of double plate
  - Spliting of stove door and use of IR reflecting ceramic glass

- **Development of cost-effective control system**
  - Operation with natural draft!
  - Only one flapper valve (possible because use of down draft combustion)
  - Thermocouple for flame temperature („$\text{O}_2$-Sensor“)
  - Electronic control unit with display for refueling
  - Optional: Mass flow sensor for combustion air and lambda sensor
Emissions at 13 % O₂, standard conditions

- Particulate matter: < 10 mg/m³
- CO < 200 mg/m³
- VOC (Org.-C) < 20 mg/m³
- 2 Prototypes (of identical construction!)
  - Prototype 1 was presented in USA at „Wood Stove Design Challenge“ 2014: 2. Place!
    (4.-7. Nov. at BNL:http://www.forgreenheat.org/, „Team Wittus“)
  - Prototype 2 operated and demonstrated in field test at Coswig/Dresden by private user (Nov. 2014 - Mrz. 2015)

- Spin-off: Engineering office:
  ETE EmTechEngineering GmbH
  Homepage: www.ete-ing.de
Flyer for Download:
http://www.ete-ing.de/sites/default/files/ETE_Flyer_English.pdf
NEKO catalyst: First References
AZ: 28412/02

ETE EmTechEngineering GmbH
Homepage: www.ete-ing.de

References:

1. New Zealand: xeoos with NEKO catalyst
http://www.xeoos.co.nz/
“German Design”
“Brought to New Zealand to meet the need for Canterbury residents to install log burners, this German engineered range combines innovation with quality materials such as stainless steel, glass, wood and aluminum”
See also: Environment Canterbury’s Air Quality Programme: Ultra-Low Emission Wood Burners
http://ecan.govt.nz/advice/your-air/Pages/uleb.aspx

2. Sauna stove (Anonymous Manufacturer) with NEKO catalyst to comply with regulations according to the 2nd stage of the 1st BImSchV

3. Two privat users in Regensburg: xeoos X5 with NEKO catalyst (Demonstration campaign)

4. Other furnaces / manufacturers in progress
Future catalysts under development
Example: ALL-CERAMIC CATALYST

Transition metal + Al Oxide „Solid phase synthesis“

Transition metal + Si Oxide „Liquid phase synthesis“
Working Group Small scale furnace systems,
Department Thermo-chemical Conversion
„Small scale furnaces and catalytic emission reduction“

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E-Mail: info@dbfz.de
www.dbfz.de
Development of a micro-scale installation

Continuing Developments

- Improvement of insulation and tight connections
- Ash removal

Modification of flue gas sampling