ERA-NET Bioenergy project “EnCat”

Enhanced catalytic fast pyrolysis of biomass for maximum production of high quality biofuels

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EnCat Enhanced catalytic fast pyrolysis of biomass for maximum production of high quality biofuels

Duration: 42 months (project start: 02/2017)

The project is carried out in the core of the ERA-NET Bioenergy programme “10th Joint Call for Research and Development Proposals of ERA-NET Bioenergy”

Partner from Austria

BIOS BIOENERGIESYSTEME GmbH
Partners from the Netherlands

University of Twente (project coordinator)
Alucha Management B.V.
OPRA Turbines International BV

Partners from Sweden

KTH Kungliga Tekniska högskolan
RISE Research Institute of Sweden

Partners from Poland

ICHPW Institute for Chemical Processing of Coal
HIG Polska Sp. z. o.o.
Fast pyrolysis of biomass is one of the most promising ways to directly generate liquid fuels from biomass.

However, the produced pyrolysis oil may have several drawbacks which suppress its application for power and heat generation or transportation fuels:

- high oxygen content
- high water content
- high contents of water-soluble acids which affect negatively the
  - acidity (corrosion effects)
  - miscibility with petroleum-based fuels (separation of fractions)
  - chemical stability (aging)
  - viscosity
  - energy density
The Enhanced Catalytic Pyrolysis (EnCat) project investigates a new concept for the production of high-quality bio-oil.

The EnCat concept consists of the following components:

- A novel biomass pre-treatment step to make the concept suitable for both woody biomass and biomass residues from agriculture.
- Biomass pyrolysis in a reactor making use of deoxygenation catalysts.
- Simultaneous CO₂ capture with sorbents and via the water-gas-shift reaction in-situ production of hydrogen.
- After cleaning, the oil vapours will be mildly hydrogenated to produce a high-quality bio-oil.
- Utilisation of the bio-oil in gas engines and a gas turbines.
- Further upgrading by a new method of downstream hydrogenation.
EnCat concept
Overall objectives

- Development of a new concept for the production of biofuels based on an enhanced catalytic flash pyrolysis process including deoxygenation and hydrogenation for the high-yield production of high-quality bio-oil from both woody and residual biomass streams.

- To test the high-quality oil in gas turbines and diesel engines for the production of heat and power.

- To further increase the applicability of the bio-oil as transportation fuel by downstream hydrogenation.

- To evaluate the new concept from biomass to biofuels with respect to sustainability and techno-economic feasibility.
Scientific objectives (I)

- Get insight in the catalytic pyrolysis mechanisms of different biomass streams (woody biomass, agricultural residues)
  ➤ University Twente, KTH

- To develop a leaching process for the biomass feedstock in order to remove alkaline and alkaline earth metals (AAEMs) and to optimize this process
  ➤ BIOS

- Understand and develop the application of CO$_2$ sorbents in catalytic pyrolysis reactors for in-situ production of hydrogen
  ➤ University Twente

- Development of a downstream hydrogenation process for the production of bio-oil with low oxygen contents that can be used as transportation fuel
  ➤ ICHPW
Scientific objectives (II)

- Improve atomization and combustion of bio-oil in gas turbines and to optimize existing gas turbines for (catalytic) pyrolysis oil applications with low emissions and high efficiencies via experimental research and numerical (CFD) simulations
  ➔ OPRA, BIOS, University Twente

- To investigate bio-oil combustion in gas engines
  ➔ ICHPW

- To design a full-scale plant based on enhanced catalytic pyrolysis and to develop a roadmap for further commercialization
  ➔ Alucha

- Evaluation of the new concept from biomass to biofuels with respect to sustainability and techno-economic feasibility
  ➔ RISE, BIOS
Objectives

- High contents of alkaline and alkaline earth metals (AAEM – Ca, Mg, K and Na) in agricultural biomass feedstocks cause problems during pyrolysis (reduced oil and sugar yield)

- Development and lab-scale test of leaching methods with the aim to reduce the AAEM contents of agricultural biomass feedstocks to make them applicable for the pyrolysis process

Methodology

- Leaching tests of woody and agricultural biomass with acids and water

- Comprehensive parametric study regarding the influence of
  - acidity
  - temperature and
  - residence time
  - fuel to leaching liquid ratio on the leaching efficiency
Preliminary results

- Leaching of woody biomass (beech wood)
  - with acids: 75% AAEM reduction
  - with water: 33% AAEM reduction

- Leaching of agricultural biomass (miscanthus)
  - with acids: 85% AAEM reduction
  - with water: 60% AAEM reduction

Leaching at mild conditions: 30°C, 30 minutes residence time, acid leaching: 1% acetic acid in water

- Even when leaching with water the AAEM contents of miscanthus can be reduced below the AAEM level of beech wood
## Enhanced catalytic pyrolysis – KTH (I)

### Objectives
- Experimental study of catalytic fast pyrolysis with MCM-41 and HZSM-5 zeolite catalysts
- Improve the bio-oil quality
- Determine the effects of catalysts on the bio-oil quality

### Methodology

1. Reactor heated up to the target temperature for the catalysts (500°C)
2. The evolved volatiles from the sample are passed directly to the ex-situ beds containing catalysts
3. The ratio of MCM-41 and HZSM-5 zeolite catalyst was altered to give the required ratio
4. The ratio of sample to catalysts was 1:1
## Enhanced catalytic pyrolysis – KTH (II)

Results for different catalyst ratios of H-ZSM-5 and Al-MCM-41

<table>
<thead>
<tr>
<th>Experiment</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>Deoxygenation degree (%)</th>
<th>HHV Dulong (MJ/kg)</th>
<th>Heavy Oil (g)</th>
<th>HHV Dulong (MJ)</th>
<th>Relative Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-catalytic</td>
<td>47,25</td>
<td>7,91</td>
<td>43,10</td>
<td>0,50</td>
<td>1,60</td>
<td>19,55</td>
<td>57,95</td>
<td>1,13</td>
<td>100%</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>73,50</td>
<td>7,79</td>
<td>21,00</td>
<td>0,61</td>
<td>52,05</td>
<td>32,28</td>
<td>7,08</td>
<td>0,23</td>
<td>20%</td>
</tr>
<tr>
<td>HA 7:1</td>
<td>74,90</td>
<td>8,00</td>
<td>15,00</td>
<td>0,59</td>
<td>65,75</td>
<td>34,15</td>
<td>5,66</td>
<td>0,19</td>
<td>17%</td>
</tr>
<tr>
<td>HA 3:1</td>
<td>82,05</td>
<td>8,37</td>
<td>8,60</td>
<td>0,50</td>
<td>80,37</td>
<td>38,26</td>
<td>4,25</td>
<td>0,16</td>
<td>14%</td>
</tr>
<tr>
<td>HA 2:1</td>
<td>80,00</td>
<td>8,11</td>
<td>10,30</td>
<td>0,61</td>
<td>76,48</td>
<td>36,89</td>
<td>3,54</td>
<td>0,13</td>
<td>12%</td>
</tr>
<tr>
<td>HA 1:1</td>
<td>84,20</td>
<td>8,24</td>
<td>6,70</td>
<td>0,62</td>
<td>84,70</td>
<td>39,15</td>
<td>2,83</td>
<td>0,11</td>
<td>10%</td>
</tr>
<tr>
<td>Al-MCM-41</td>
<td>85,60</td>
<td>8,20</td>
<td>4,80</td>
<td>0,63</td>
<td>89,04</td>
<td>39,91</td>
<td>1,42</td>
<td>0,06</td>
<td>5%</td>
</tr>
</tbody>
</table>

Deoxygenation degree (%) = (1-(O-biooil/O-biomass))x100
HHV Dulong = 338.2C+1442.8(H-(O/8))/1000
Aim of the work:

- **Improve Quality of pyrolysis oil (reduce acidity i.e., carboxylic acids)**

**Enhanced catalytic pyrolysis – UT (I)**

- **Catalyst:** Deoxygenation Reactions (e.g., remove acids)
- **Sorbent:** Capture CO$_2$ and shift equilibrium of WGS CO + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$ (Exothermic Reaction) for in-situ hydrogen (H$_2$) production

Hydrotalcite and Dolomite are selected due to their ability for both deoxygenation and CO$_2$ sorption reactions.
Enhanced catalytic pyrolysis – UT (II)

Test results with Dolomite in a fluidized bed reactor

- Clear indication of equilibrium shift of WGS Reaction (CO+H₂O ⇌ CO₂+H₂)
- 40.4% bio-oil yield
- 5.74 % of H in the feed converted to Hydrogen via water gas shift reaction

Pyrolysis Temperature: 500°C
Experimental Time: 60 Min.
Test results with Hydrotalcite

- Minor increase in H₂ Production
- Increase in Hydrocarbon
- Elimination of Acids
Bio-oil combustion tests – OPRA (I)

Full-scale gas turbine combustor tests at atmospheric conditions

Measurement of:
- Temperatures (inlet, outlet)
- Pressures
- Air and fuel mass flow
- Liner metal temperatures by thermochromic paint
- Emissions (CO, CO₂, NO, NO₂, O₂)

Atmospheric combustor test rig at OPRA
Design of the OPRA 3C low calorific fuel combustor

3C combustor* designed for burning low-calorific gaseous and liquid fuels

- Diffusion type combustor
- Significantly larger volume than conventional combustor
- Impingement cooling

*Patent US 8,844,260
Low calorific fuel combustor for Gas Turbine
Wood pyrolysis oil successfully tested during the EnCat project by applying a new nozzle design

- Good atomization is a key parameter for operating liquid fuels
- High viscosity and polymerization at high temperatures make pyrolysis oil atomization challenging
- New nozzle has been developed by OPRA which allows stable operation with 100% wood pyrolysis oil over wide load range
- Nozzle has been successfully tested in the atmospheric combustor test rig with multiple fuels
- CFD simulations of BIOS and UT for further combustor optimisation are ongoing
Bio-oil combustion tests – OPRA (IV)

Efficient combustion of pyrolysis oil in a gas turbine combustor

- Efficient combustion of wood pyrolysis oil has been achieved in a full-scale gas turbine combustor
- Low CO levels have been reached over whole load range
- Elevated NOₓ emissions due to the nitrogen content of pyrolysis oil (0.2 wt%)

Explanation: emissions normalised
The experimental work performed within the project is in its final phase.

Presently process design and process simulations regarding the overall full-scale EnCat process are on-going.

Process design is accompanied by techno-economic analyses and life-cycle assessments of the whole process chain.

The project shall be finalized in August 2020.
Thank you for your attention

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