6-30-2019

EN-fuels from solid waste biomass by thermo-catalytic reforming

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EN-Fuels from solid waste biomass by thermo-catalytic reforming

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Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes

June 16 – 20, 2019 in Cork
Recycling and Waste Management

*TCR® und iCycle® – Technologies for Recycling & Energy Production*

<table>
<thead>
<tr>
<th>Biogenic Residues (TCR®)</th>
<th>Composites und Minerals (iCycle®)</th>
</tr>
</thead>
</table>

Energy carrier from biomass & recycling of composites
General thoughts- How to store carbon by using fuel and producing plastics!

530 billion tonnes, 82 percent of all C in biomass (650 billion tonnes) on earth is stored in wood, the rain forest is storing as much as people burn in 10 years from various sources. 

1/3 of world anthropogenic CO₂ emissions are taken up every year by world wide forests. 

But, CO₂ is also again released by natural processes 
Carbon dioxide, naturally captured in wood can be captured as carbon in char. 

Feedstocks should show a wider range than wood only, residues from agriculture or sewage sludge and digestates as well as residues from modern processes producing ethanol from straw as well as macro algae 

Capturing the carbon as a stable bio-coal or charcoal as single product is just too expensive. 

Side products are required to close the bill. 
Those products can be liquids, in best case fuels and green hydrogen.
Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries

Characteristics of TCR®-bio-crude-oil

- Comparable to crude oil
- High carbon content
- Low water content
- Low total acid number
- Miscible with fossil fuels and biofuels
- High heating value

Source: [1] [2]
Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries

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Pyroformer – Intermediate Pyrolysis and combined Reforming – Moderate heat transfer by char

Drying - Torrefaction - Pyrolysis Reforming - Char Conditioning
Intermediate Pyrolysis

The Thermo-Catalytic Reforming (TCR®) technology

Feedstock

Char

Syngas

Bio-oil

Catalytic Reforming
From Biomass to Bio-chemicals or Bio-fuels

Overview

Biomass

- Pyrolysis
- Reforming

TCR process

- Condensation
- Phase separation

Bio-fuel
EN 228 & EN 590
The Thermo-Catalytic Reforming technology

Process parameters

- Wide range of potential feedstocks
- Feedstock dry matter ~ 80% (optional pre-drying)
- Particle size > 2 mm
- Residence time 4-10 min
- Heating rate ~10 K/s
- Intermediate pyrolysis temperature ~450 °C
- Reformer temperature up to 750 °C
Thermo-Catalytic Reforming TCR®

Level of development: 2017

TCR300
Demonstration
Operational capacity: 300 kg/h
Heat Source: flue gas
Purpose: scale-up, sludge treatment

Scale Up x10
Thermo-Catalytic Reforming TCR®
Level of development – today

TCR500
Long-term demonstrator
Operational capacity: 500 kg/h
Heat Source: flue gas
Purpose: pre-commercial demonstrator
Up-Scaling of the TCR® Technology
Energy and mass balance for sewage sludge

**MASS BALANCE**
- Carbonisate: 46.2%
- Process water: 28.8%
- Oil: 9.2%
- Syngas: 15.8%

**ENERGY BALANCE**
- Carbonisate: 39.5%
- Oil: 26.7%
- Syngas: 24.6%
- Losses: 9%
Up-Scaling of the TCR® Technology
Energy and mass balance for sewage sludge

Results from TCR300-trials – highlights

**TCR-Gas:**
- Hydrogen content ~30 Vol.-%, up to 50 %
- H:CO → 3:1
- LHV ~ 14 MJ/kg

**TCR-Oil:**
- LHV ~34 MJ/kg
- TAN < 10 mgKOH/g

**TCR-Carbonisate:**
- H < 1 Ma.-%
- C < 1 Ma.-%
TCR®-Fuel
GC-MS analysis for TCR crude oil from digestate

Aromatic Hydrocarbons: 28.7%
• Monoaromates (BTX): 9.2 %
• Polyaromates: 19.5 %

Phenole: 26.2%
N-components: 3.2%
TCR®-Fuel
GC-MS analysis for TCR crude oil from sewage sludge

Aromatic Hydrocarbons: 30.0%
  • Monoaromates (BTX): 11.5 %
  • Polyaromates: 18.5 %

Phenole: 12.1%
N-components: 1.8%
### Comparison of the diesel fraction with EN 590

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>HDO TCR® diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel standard EN 590</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>max</td>
<td></td>
</tr>
<tr>
<td>Cetane Number</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>Cetane Index</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>Density at 15 °C</td>
<td>kg/m³</td>
<td>✓</td>
</tr>
<tr>
<td>PAH % (m/m)</td>
<td>8</td>
<td>✓</td>
</tr>
<tr>
<td>Sulfur mg/kg</td>
<td>10</td>
<td>✓</td>
</tr>
<tr>
<td>Flash point °C</td>
<td>55</td>
<td>✓</td>
</tr>
<tr>
<td>Ash content % (m/m)</td>
<td>0.01</td>
<td>✓</td>
</tr>
<tr>
<td>Water content mg/kg</td>
<td>200</td>
<td>✓</td>
</tr>
<tr>
<td>Copper strip corrosion (3 hours at 50 °C)</td>
<td>Class 1</td>
<td>✓</td>
</tr>
<tr>
<td>Lubricity at 60 °C µm</td>
<td>460</td>
<td>✓</td>
</tr>
<tr>
<td>Viscosity at 40 °C mm²/s</td>
<td>2</td>
<td>✓</td>
</tr>
<tr>
<td>CFPP °C</td>
<td>-20 (Winter) 0 (Summer)</td>
<td>✓</td>
</tr>
<tr>
<td>Volume at 250 °C %V/V</td>
<td>&lt; 65</td>
<td>✓</td>
</tr>
<tr>
<td>Volume at 350 °C %V/V</td>
<td>85</td>
<td>✓</td>
</tr>
<tr>
<td>95 % (V/V) recovered at °C</td>
<td>360</td>
<td>✓</td>
</tr>
</tbody>
</table>

* Achievable by an adjustment of the hydrotreating
Comparison of the gasoline fraction with EN 228

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>HDO TCR® naphtha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>✓</td>
</tr>
<tr>
<td>Evaporation residue</td>
<td>mg/100ml</td>
<td>✓</td>
</tr>
<tr>
<td>Aromates</td>
<td>% (V/V)</td>
<td>✓</td>
</tr>
<tr>
<td>Benzene</td>
<td>% (V/V)</td>
<td>✓ 1.5*</td>
</tr>
<tr>
<td>Benzol</td>
<td>% (V/V)</td>
<td>✓</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/kg</td>
<td>✓</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/l</td>
<td>✓</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/l</td>
<td>✓ **</td>
</tr>
<tr>
<td>Oxygen</td>
<td>% (m/m)</td>
<td>✓ **</td>
</tr>
<tr>
<td>E70</td>
<td>% (V/V)</td>
<td>✓</td>
</tr>
<tr>
<td>E100</td>
<td>% (V/V)</td>
<td>✓</td>
</tr>
<tr>
<td>E150</td>
<td>% (V/V)</td>
<td>✓</td>
</tr>
<tr>
<td>End of Boiling Point</td>
<td>°C</td>
<td>✓</td>
</tr>
<tr>
<td>Distillation residue</td>
<td>% (V/V)</td>
<td>✓ **</td>
</tr>
<tr>
<td>Vapour pressure DVPE</td>
<td>kPa</td>
<td>✓</td>
</tr>
</tbody>
</table>

* Achievable by an adjustment of the hydrotreating

** Lack of light boilers due to laboratory distillation without cryocooler
TCR®-Fuel

Spectra of Diesel: Shell V-Power vs. TCR®-Diesel

Retention Time 1

Retention Time 2

Retention Time 2

Retention Time 1

Shell V-Power

Hydrogenated TCR®-Diesel
Direct application of up to 30% TCR-oil made from sewage sludge in other fuels without modification of the engine of the car or a CHP system.
Direct application of TCR-diesel made from biomass without modification of the engine
Product application
Pre-commercial demonstrator within ToSynFuel-project

Former rally world champion Walter Röhrl at ground breaking ceremony
Hydrogenation of TCR® Bio-oils from Sewage Sludge

**TCR® BIO-OIL**

- C: 76.6 wt%
- H: 9.0 wt%
- N: 7.3 wt%
- S: 1.6 wt%
- O (diff.): 3.5 wt%
- H₂O: 2.0 wt%
- Ash: < 0.005 wt%

- LHV: 34.8 MJ/kg
- TAN: 4.2 mg KOH/g
- Viscosity: 9.1 mm²/s
- Density: 960 kg/m³

**HYDROGENATED TCR® BIO-OIL (HBO)**

- C: 86.2 wt%
- H: 13.8 wt%
- N: < 0.1 wt%
- S: 0.0015 wt%
- O (diff.): < 0.1 wt%
- H₂O: 0.0016 wt%
- Ash: < 0.005 wt%

- LHV: 42.8 MJ/kg
- TAN: < 0.1 mg KOH/g
- Copper corr.: Grade 1
- Flash point: < -20 °C
- Yield: ~ 80%

- Lab tests for Hydrotreatment at UMSICHT facilities
- Strategical partner VTS (Schwedt) for Hydrogenation
Sustainable transportation of fuels by co-processing of TCR®-bio-oil in conventional petroleum refineries

Distillation summary for crude oil and TCR®-bio-crude-oil

- More atmospheric distillable compounds in bio-oil than in the used crude oil
- Distillation results are comparable to calculated distributions (blend 50:50)
- Hydrotreatment removes 99.99% of sulfur content
- No polymerization or coking during the upgrade
Green fuels from biomass residues and waste

Thermo-Catalytic Reforming technology – TCR®

Product utilization – Bio-Oil – Drop-in for Refineries

- TCR®-Oil is:
  - Thermal stable
  - Direct miscible with fossil crude oil
- Direct drop-in possible
Conclusion

- Crude TCR®-oil highlights
  - Thermally stable (atmospheric distillation)
  - Directly suitable for hydrotreating
  - Required hydrogen from TCR®-gas

- Hydrotreating highlights
  - Renewable chemicals extractable
  - Renewable gasoline (EN 228) and diesel (EN 590)
  - TCR® / Hydrotreatment demonstration at large scale within two EU-projects
To-Syn-Fuel and FlexJet
Demonstration of Waste Biomass to Synthetic Fuels

Budget: 14,5 Mio. €
Partner:

FlexJet:
Sustainable Jet Fuel from Flexible Waste Biomass

Start: May 2018 (Horizon 2020)
13 partners
13,4 Mio. € (10 Mio. € funding)
Content: TCR®500 for the production of 1.200 tons green jet fuel
Recycling and Waste Management

TCR® und iCycle® – Technologies for Recycling & Energy Production

Biogenic Residues (TCR®)  Composites und Minerals (iCycle®)

Energy carrier from biomass & recycling of composites
Stepwise pyrolysis for raw material recovery from plastic waste

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Received 18 July 1997; accepted 17 February 1998

Energy Production

Biogenic Residues (TCR®)
Composites und Minerals (iCycle®)

Energy carrier from biomass & recycling of composites
Feedstock recycling of polymers
Fraunhofer UMSICHT developments

Selective monomer recovery from complex waste plastic mixtures through stepwise degradation

- Important: reaction control and reactor design
- Fraunhofer UMSICHT designed and developed a special reactor (cyccoli-spheres reactor) and phase change materials
- Both enable a selective initiation of c-c bond cracking in melting reactions

Energy carrier from biogenic residues (TCR®) and minerals (iCycle®) – Technologies for Recycling & Energy Production
Biogenic Residues (TCR®) and Minerals (iCycle®) – Technologies for Recycling & Energy Production

Energy carrier from biomass & recycling of composites
SeaCycle by Fraunhofer Umsicht, to save the world climate and to protect the environment for future generations

Combined TCR and iCycle technologies

360 remote controlled boats

15 interfacing ships to transfer the crudes to off-shore oil stations
FEEDSTOCK – „The sleeping beauty“

Punjab region burns more than 20 Mt of biomass a year

The Hinterland in Brasil offers more than 300 Mt of biomass rotting every year.

Canadian forest are dying from beetles attack – Mt of dry matter per year

Sewage is available all over the world usually close to mankind. Almost 10 Mt/a dry matter are reached in China

Up to 14 billion dry tonnes of macro algae can be made available worldwide
Conclusion – via intermediate pyrolysis/reforming it is possible to

produce green crude for refineries, getting to fuels and jet fuel

naphtha via refineries for chemical industry

produce three times the amount of crude as used today for plastic production in cultivation of macro algae (up to 14 billion dry matter)

close the phosphate cycle via gasification of anthracitic biochar

create a new sustainable end of life route - Converting green plastics into green fuels
Team in Sulzbach-Rosenberg
EN-Fuels from solid waste biomass by thermo-catalytic reforming

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