



BECOOOL

Brazil-EU Cooperation for Development
of Advanced Lignocellulosic Biofuels

Towards advanced biofuels production from energy crops; Gasification and gas cleaning

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TNO innovation
for life

2020



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The BECOOL project

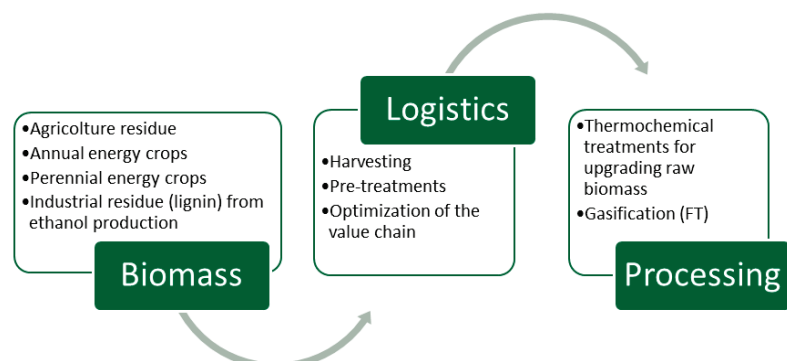
BECOOOL is a research and innovation project to promote the cooperation between EU and Brazil in the development of advanced biofuels (especially kerosene), from sustainable agricultural value chains, based on lignocellulosic biomass.



Horizon 2020

Objectives

- Developing and validating integrated technology packages
- Strengthen EU-Brazil cooperation



Thermochemical conversion of biomass

Different biomass and bio residues are considered for gasification and upgrading (100 MW)

The two main conversion strategies towards kerosene (FT liquids):

A: Pyrolysis followed by EF gasification, gas cleaning/upgrading, FT-S

B: Solid biomass gasification in Fluidized Bed Gasification, gas cleaning/upgrading, FT-S

B1: Gasification -> high temperature (cat.) cracking -> gas cleaning

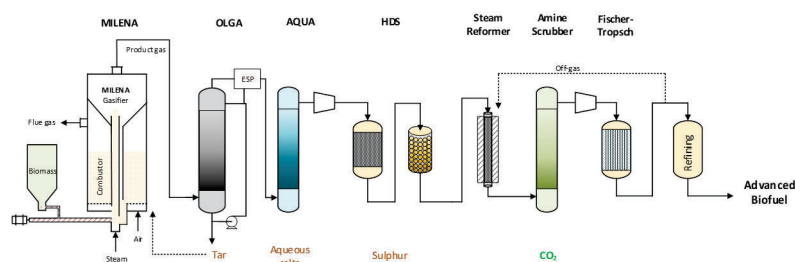
B2: Gasification -> tar scrubbing -> gas cleaning

- Process feasibility study;
 - Experimental validation
 - Setup and benchmarking of Aspen plus models
 - TE analysis of most promising routes

3

Biofuels via gasification

Route B2; Applying CFB gasifier (MILENA)



Mass/energy balance

- Overall energy efficiency ~45%, carbon conv.~ 34%
- Wood; 18 MJ/kg, Liquid Product; 43 MJ/kg

Economics

- Production costs; IEA (2019)*: 21-40 €/GJ
- Shown approach on high end of that range (part of project scope)

What are (technological) challenges with biomass other than wood?

This presentation: Gasification results and S removal

* IEA report (2019) Advanced Biofuels – Potential for Cost Reduction

4

BECOOL biomass

Eucalyptus, Sorghum and Giant Reed were grown and harvested as part of the BECOOL project by the University of Bologna



Eucalyptus (EUC)



Biomass Sorghum (SO)



Giant Reed (GR)

5

Giant Reed pretreatment for gasification



1. Shredding
(cannot be fed; low density and possible bridging)



2. Pelletisation

3. Grinding
(high density particles)

As received moisture content 23 wt%, final ground pellets 9 wt% (fed to gasifier)

6

Feedstock analysis

Feedstock proximate/ultimate analysis pretreated feedstock

		EUC	SO	GR
LHV	[MJ/kg], ar	16.0	15.8	15.8
LHV	[MJ/kg], daf	17.8	17.4	18.6
Volatile content	[%], dry	77.8	74.3	74.1
Ash content	[%], dry	1.5	5.0	5.6
Moisture	[%], ar	7.9	3.8	8.5
C	[%], dry	47.4	44.8	46.3
H	[%], dry	6.1	5.9	5.8
O	[%], dry	44.0	41.8	42.1
N	[%], dry	0.40	0.90	0.60
S	[%], dry	0.034	0.10	0.19
Cl	[%], dry	0.13	0.15	0.36

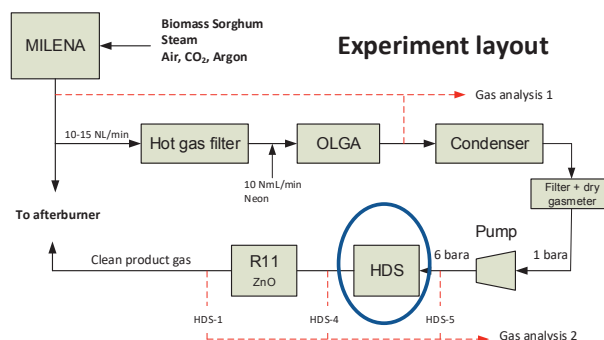
- Very similar heating value and CHO composition
- Much ash in SO and GR, resp. 5.0 and 5.6%
- Up to 6x more Sulfur in SO and GR than EUC

7

Experiment setup

How does the sulphur removal (HDS-ZnO) perform with high-S product gas?

- SO gasification by lab-MILENA (30 kW), 1-day experiment
- SO product gas is cleaned, dried and compressed prior to HDS-ZnO



8

The HDS reactor

Organic-S (thiophenes, mercaptans) are converted by HDS to $\text{H}_2\text{S}/\text{COS}$, which is adsorbed by ZnO

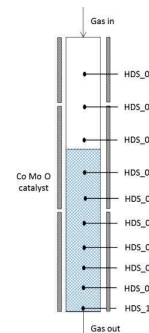
Mostly thiophenes and mercaptans, heavier S/N-HCs captured upstream

Unsat. HCs are hydrogenated (main reaction, high exotherm $>100^\circ\text{C}$), ethylene good activity indicator

Lessons from the past (SNG production);

- HDS temperature: $300\text{--}500^\circ\text{C}$
 - High(est) T required for complete thiophene conversion
- Higher overall pressure increases conversion (1-6 bar tested)
 - No "extra" H_2 required
- Steam addition decreases conversion (dilution)
- More catalyst improves conversion

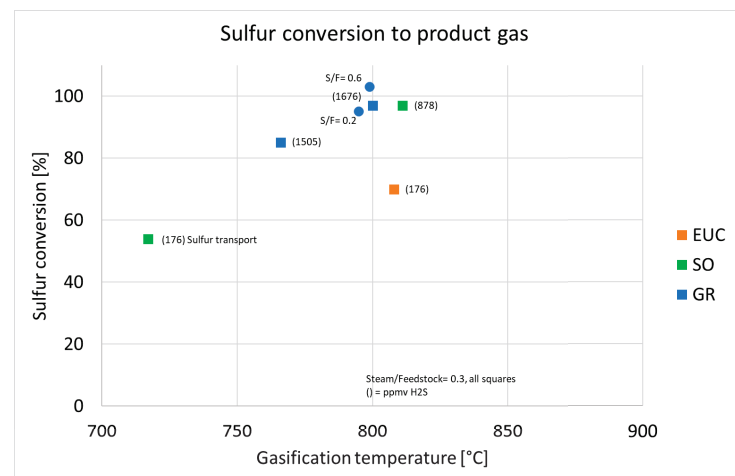
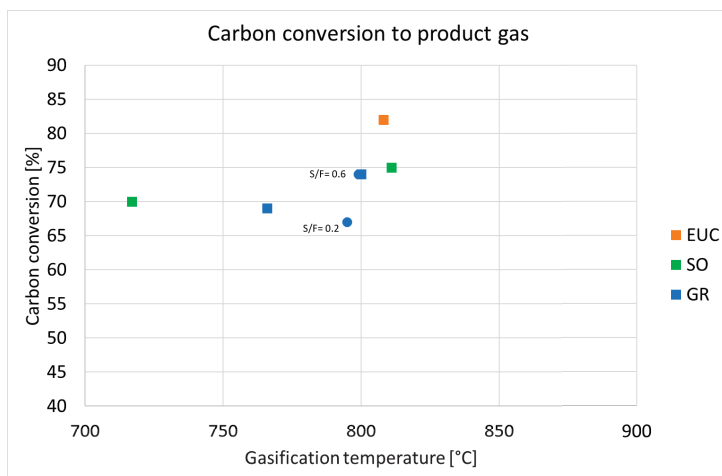
HDS reactor



Conditions:
6 bara, $350\text{--}500^\circ\text{C}$, 10-15 NL/min,
T: 450°C , GHSV: 300 h^{-1} .

9

(Steam) gasification results



- Carbon conversion 70-80%, higher CC at higher T, rest to combustor.
 - Quasi equilibrium due to heat loss at small scale, real CC will be somewhat higher
- $>90\%$ of S ends up in product gas for SO and GR.

10

S-removal over HDS-ZnO

Sorghum gasification, 1-day experiment

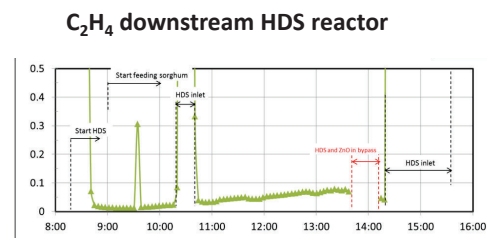
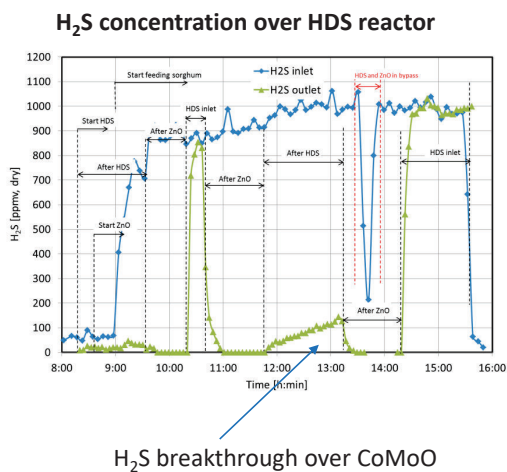
- S-analysis via gas bags and S-GC

Sorghum				Reference; beech wood	
		Upstream HDS	Downstream HDS-ZnO	Upstream HDS	Downstream HDS-ZnO
H ₂	[vol%]	12	6	29	25
C ₂ H ₄	[vol%]	4.8	<< -- 0.048	2.9	0
H ₂ S	[ppmv]	956	0.71	121	<0.05
COS	[ppmv]	34	0.08	6	<0.05
Thiophene	[ppmv]	9.2	0.1 -- 1.34	10	<0.05
Methyl mercaptan	[ppmv]	106	<0.05 -- 0.06	2	<0.05

- Much mercaptan in SO gas, facile conversion in HDS
 - Thiophene is not removed completely and removal decreases over time (99% to 85%)
 - Reason; Low H₂ concentration and very high S concentration (H₂S and trace organic-S)
- Compared to beech wood (H₂: 29% vs 12%, H₂S: 212 ppm vs 956 ppm)

11

HDS performance



C₂H₄ conversion decreases in parallel with thiophene conversion

- Lower cat activity due to S saturation

- Activity decrease is caused by S saturation of catalyst bed

12

Conclusions

- Successful pretreatment and gasification of EUC, SO, GR
 - Nature of SO, GR makes it require pretreatment (for lab-scale)
 - Carbon conversion in the range of 70-80% at 800°C
 - Temperature can be increased to improve CC (decrease char to combustor)
 - SO and GR more challenging for downstream gas cleaning due to (S/N-) impurities
- HDS can be applied for organic-S conversion in SO/EUC gas
 - However, some additional research is required
 - Higher overall/H₂ pressure
 - Upstream bulk H₂S/COS removal or even ethylene (through ethylene aromatization), increase H₂?
 - Is HDS required at all i.c.w. high T reforming?

13

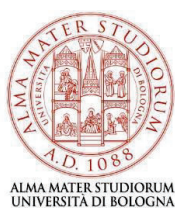
The TNO biomass group, Petten, NL

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14

Partners



Thank you for your attention!

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