CENTRO NACIONAL DE ENERGÍAS RENOVABLES
NATIONAL RENEWABLE ENERGY CENTER OF SPAIN

CLARA: Chemical Looping gAsification foR sustainAble production of biofuels
WP2 Development of a Concept for Pre-treatment of Straw

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INDEX

01

WP2 OBJETIVES

02

WORK PERFORMED & RESULTS

03

CONCLUSIONS

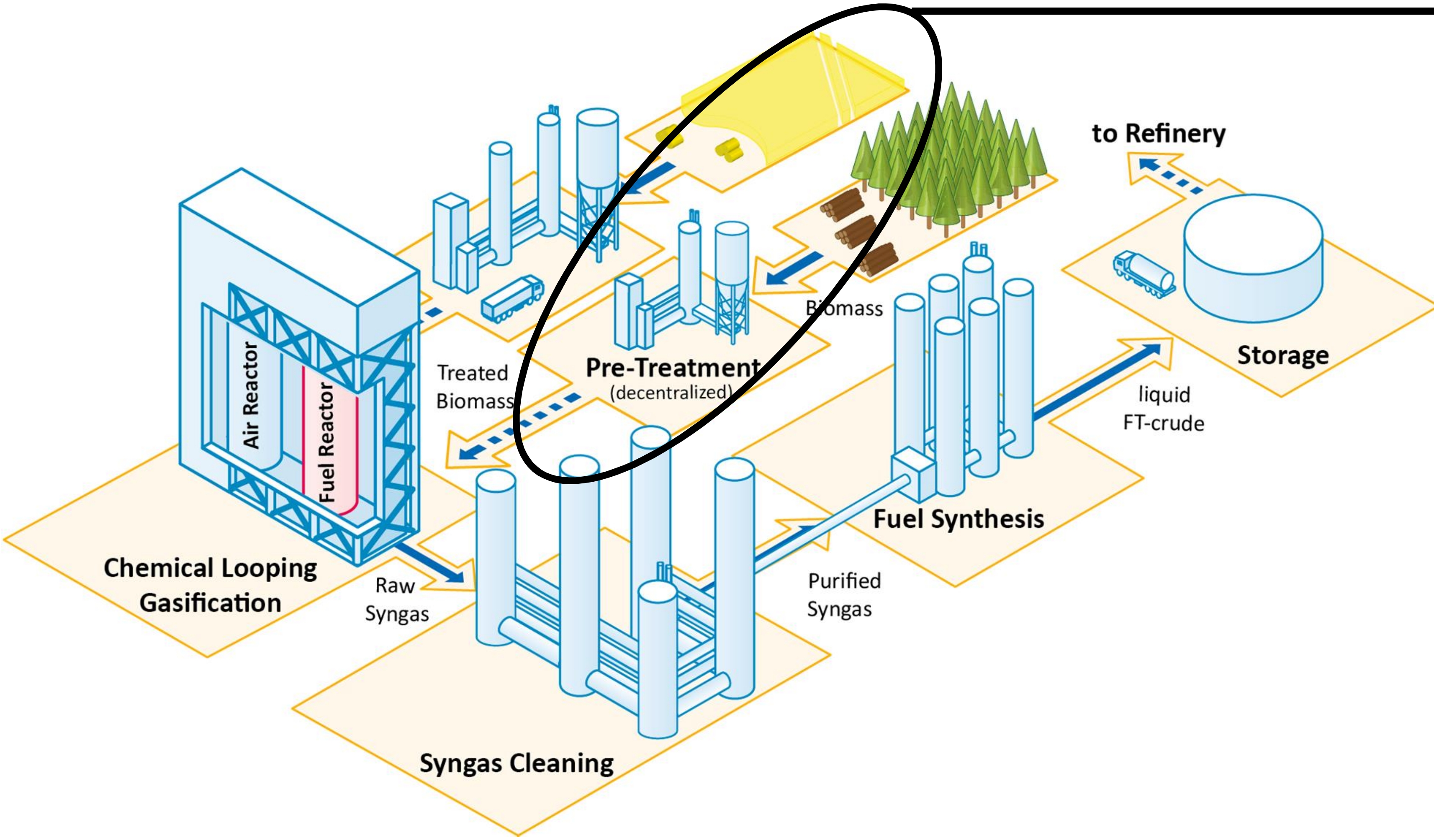
04

NEXT STEPS

01

WP2 OBJECTIVES

CLARA - WP2



to Refinery
Biomass
Treated Biomass
Pre-Treatment
(decentralized)
Storage
liquid FT-crude
Air Reactor
Fuel Reactor
Fuel Synthesis
Chemical Looping Gasification
Raw Syngas
Purified Syngas
Syngas Cleaning

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WP2: OBJECTIVES

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Optimize fuel properties for CLG: energy density (NCV), Cl, contaminants (N, S, K…), ash melting temperature

Up-Scaling

→ Pre-treatments
Chemical Characterization
Modelling

JÜLICH Forschungszentrum

Behavior and Control of Inorganics: release & melting behavior

→ Modelling
Hot stage microscope: melting
MBMS: release

SAMPLES

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Gasification properties and interaction with gasifier bed inventory

→ Steady-state gasification tests
Gas yield and composition
Dynamic pressure fluctuations
SEM-EDS

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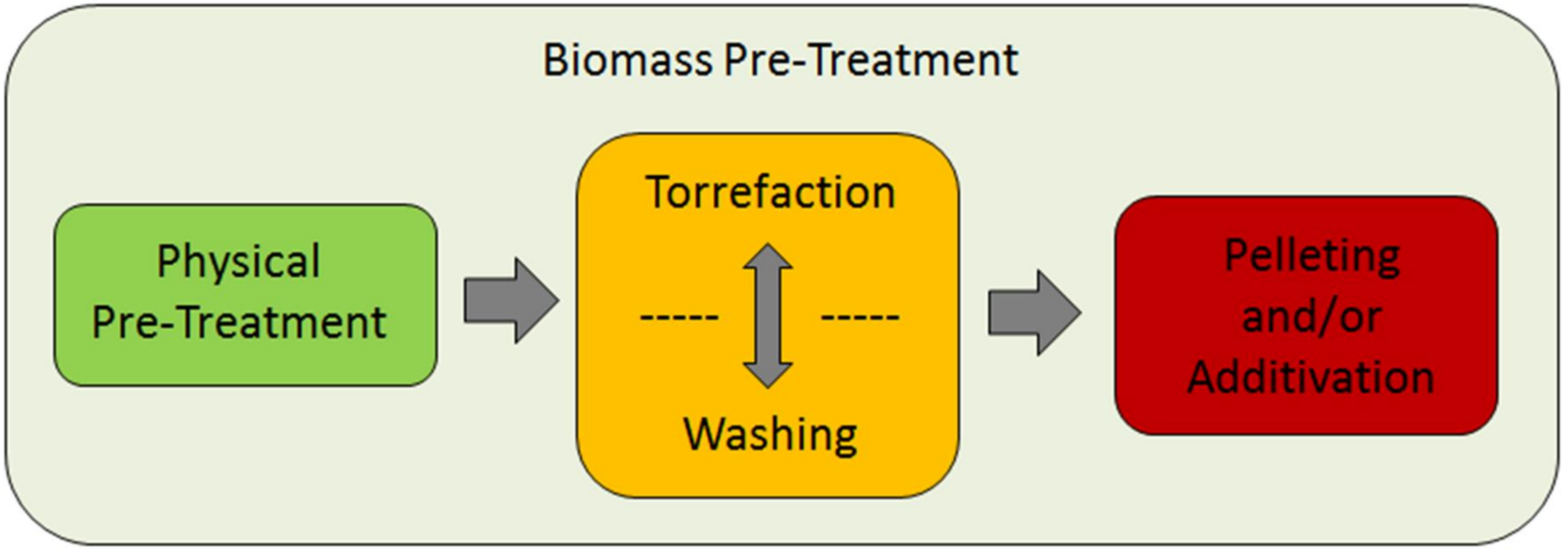
WP2: Development of a Concept for Pre-treatment of Straw



Chopping
¿Washing?→Drying
Pelleting

¿Washing?→Drying
Pelleting
¿Additives?

¿? = EVALUATED

Step	Torrefaction	Washing	Additives
Effect on	NCV, CHN, Cl	Inorganics + S & Cl	Molar Ratios

02

WORK PERFORMED & RESULTS

Biomass pre-treatment method development

Torrefaction

NCV ↑ 20-28 %

Volatile matter ↓ 8-15 %

Nitrogen slightly increased

De-chlorinating: Cl ↓ 45-55%

Washing

Kinetic Model → up-scaling

S ↓ 50-60 %

K ↓ 40-70 %

Cl ↓ 90-100 %

- ✓ **TORREFACTION: increase $H_2S_{(g)}$, reduce $KCl_{(g)}$, slight changes in melting**
- ✓ **WASHING: reduce $H_2S_{(g)}$, $KCl_{(g)}$, $KOH_{(g)}$ but no changes in melting**

Additive

Bentonite: no effect on release and melting

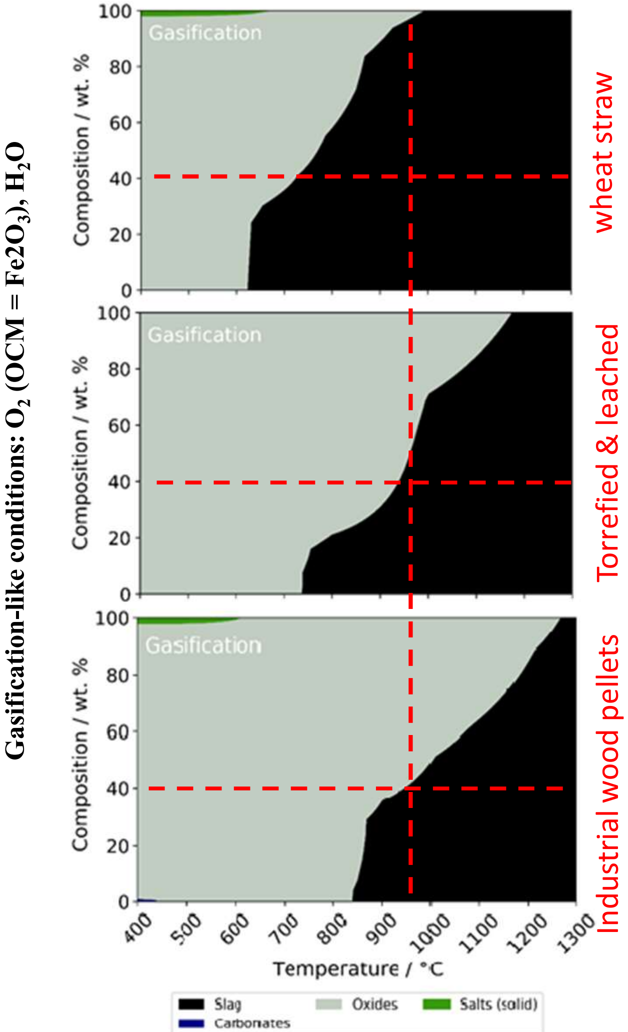
Ca-based: no effect on release

- ✓ **IMPROVES for non-washed and washed samples**

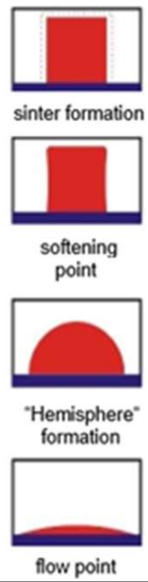
P-based: melting → **K-P silicates formation !!! Ca/P & P/K molar ratios CRITICAL**

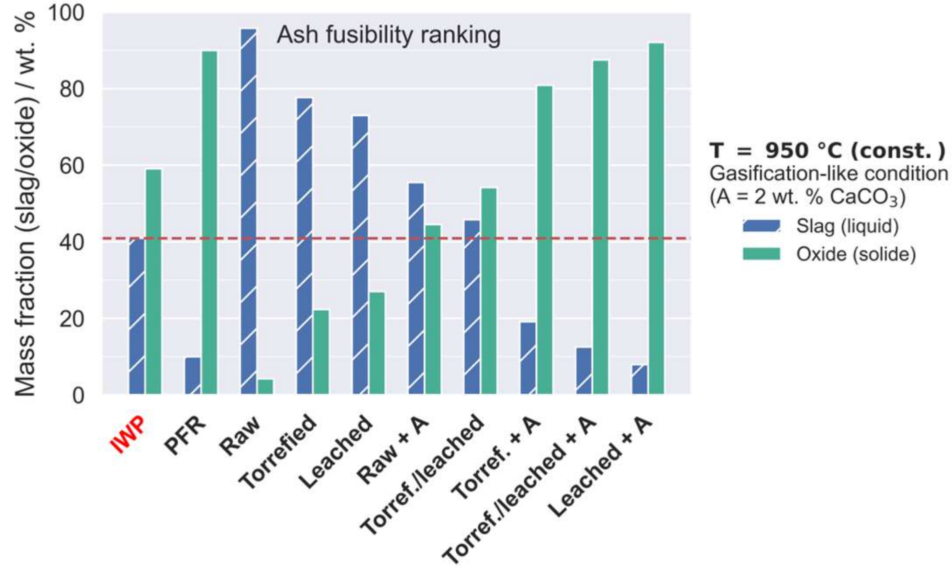
Behavior and control of inorganics

Bed agglomeration: Thermodynamic calculations

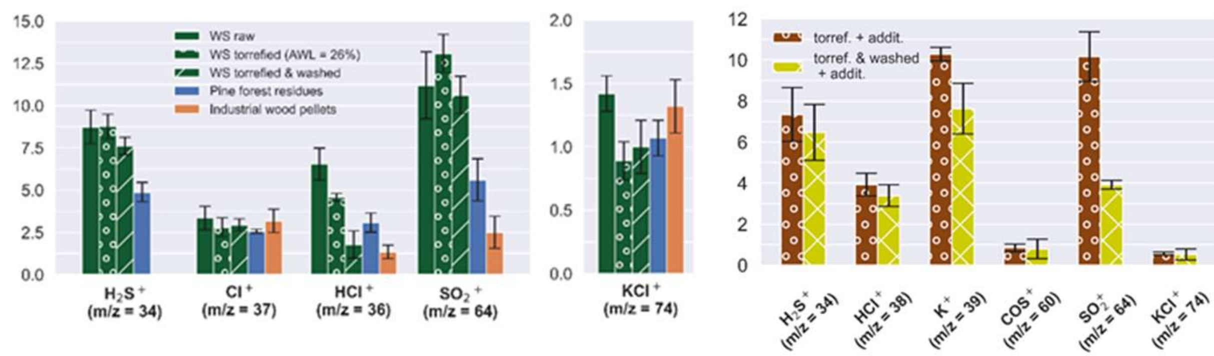


Hot Stage Microscope (HSM)





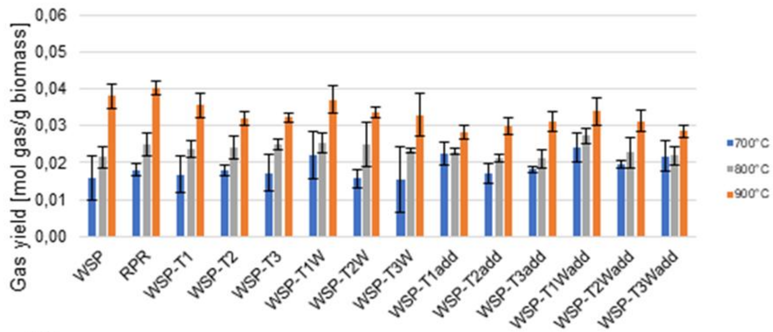
Release of inorganics (MBMS)

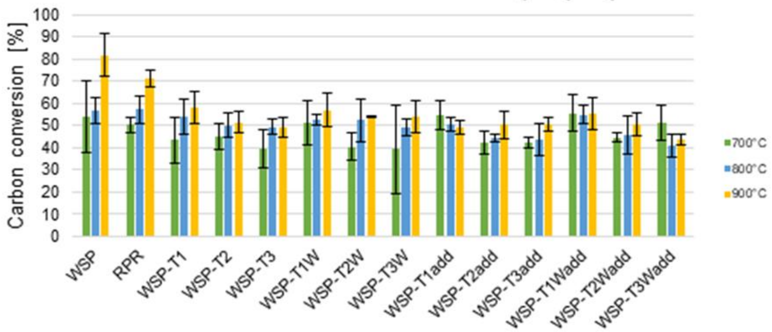


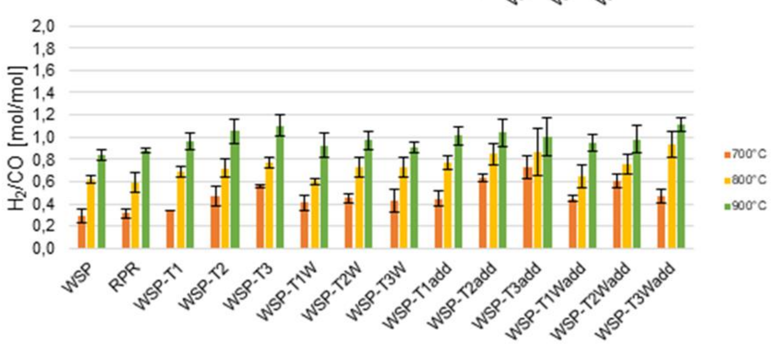
Assessment of fluidized bed gasification

<u>Gasification tests</u> in a bench-scale reactor

Gas yield, composition, tar content, carbon conversion & mass balance







Torrefaction + Washing:

- ↑ H_2/CO (mainly torrefaction)
- ↑ H_2+CO yield
- Gas yield (mainly H_2 and CO at 900 °C)

<u>Dynamic pressure fluctuations</u> measurements

(O.C.: ILM) sintering phenomena

$ILM\text{-}N_2\text{-}2u_{mf}$	700°C	750°C	800°C	850°C	900°C	950°C	1000°C
WSP-T1	green	green	green	green	green	green	red
WSP-T2	green	green	green	green	green	green	red
WSP-T3	green	green	green	green	green	green	red
WSP-T1W	green	green	green	green	green	green	red
WSP-T2Wadd	green	green	green	green	green	red	red
WSP-T3W	green	green	green	green	green	green	red
WSP	green	green	green	green	red	red	red
RPR	green	green	green	green	green	red	red
WSP-T1add	green	green	green	green	green	yellow	red
WSP-T2add	green	green	green	green	green	yellow	red
WSP-T3add	green	green	yellow	red	red	red	red
WSP-T1Wadd	green	green	green	green	green	yellow	red
WSP-T2Wadd	green	green	green	green	yellow	red	red
WSP-T3Wadd	green	green	green	green	green	red	red
WSPadd	green	green	yellow	red	red	red	red
WSPWadd	green	green	yellow	yellow	red	red	red

$ILM\text{-}N_2\text{-}3u_{mf}$	700°C	750°C	800°C	850°C	900°C	950°C	1000°C
WSP-T1							red
WSP-T2							green
WSP-T3							green
WSP-T1W	green	green	green	green	green	green	green
WSP-T2W	green	green	green	green	green	green	green
WSP-T3W	green	green	green	green	green	green	green
WSP							red
RPR							
WSP-T1add	green	green	green	green	green	green	green
WSP-T2add	green	green	green	green	green	green	green
WSP-T3add	green	green	green	green	green	green	green
WSP-T1Wadd	green	green	green	green	green	green	red
WSP-T2Wadd	green	green	green	green	green	green	green
WSP-T3Wadd	green	green	green	green	green	green	green
WSPadd	green	green	green	green	green	green	yellow
WSPWadd	green	green	green	green	green	green	yellow

green = bubbling bed
yellow = bubbling fluidization fading out
red = no bubbling

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03

CONCLUSIONS

CONCLUSIONS

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Torrefaction

Washing

Additive

Reduction (in mg/kWh) of 70% K, 80% Cl & 35% S

Increase NCV by 20%, up to 20 MJ/kg.

Energy density (MWh/m^3) increased by 700% up to approx. 3.9 MWh/m^3 → positive impact on logistics costs.

JÜLICH

Washing

Additive

Reaching IWP quality in terms of fouling, slagging and high temperature corrosion

Additive significantly reduce the risk of agglomeration

Torrefaction not effective removing alkalis and even chlorine

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Torrefaction

¿Washing?

ILM appeared as the most chemically and mechanically stable

Best fluid dynamic performances (ILM & SIB) → Torrefaction

Benefits from washing nullified by low melting elements from ILM, SIB and LD

CONCLUSIONS

- Not possible to derive clear conclusions from laboratory setups used in WP2:
  - Regarding interactions between inorganic matter in pre-treated straws and O.C.
  - Experimental conditions differences between CLG lab and larger scale reactors

- Further testing is required
- Each pre-treatment step on biomass performance for CLG should have a clear effect

- Optimized pre-treatment process conditions must be defined based in the following criteria:
  - Suitability for CLG gasification: fluidization behavior and interactions with O.C.
  - Feasibility/cost of transport
  - Feeding requirements for CLG plant
  - Production cost

04

NEXT STEPS

NEXT STEPS

- Based on technical criteria derived from testing in WP2:
  - Sustaining fluidization
  - Activity of oxygen carrier
- And economic criteria:
  - Production cost
  - Transport cost

- Pre-treatment steps should be reduced to the minimum amount necessary
- Fist step:
  - Tests with non-torrefied wheat straw with additives in the 50 kW unit (WP3)
  - Elucidate if agglomeration occurs

- Depending on results → torrefied wheat straw for further experiments in WP3 and WP5

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