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Two-stage thermochemical valorisation of sugar-derived humins

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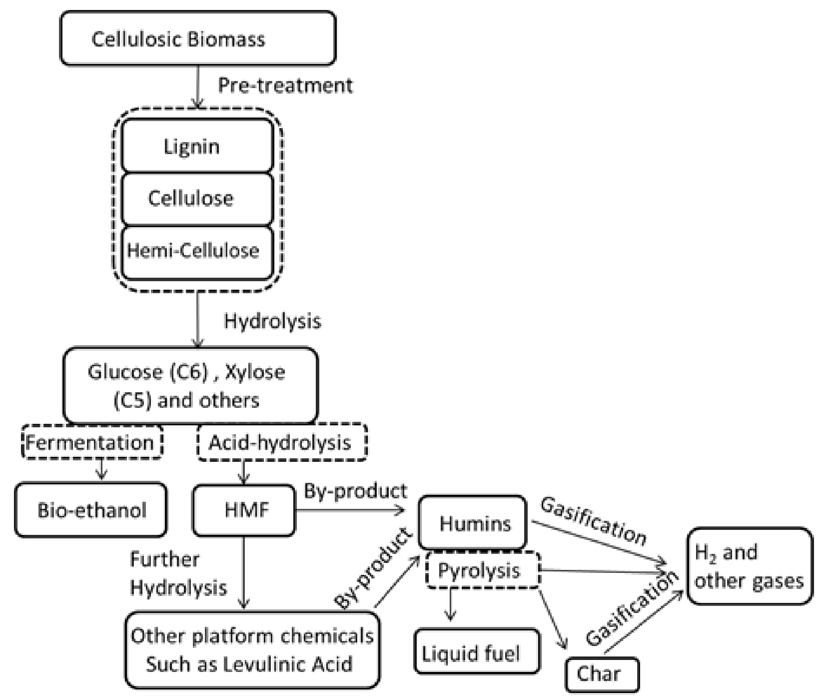
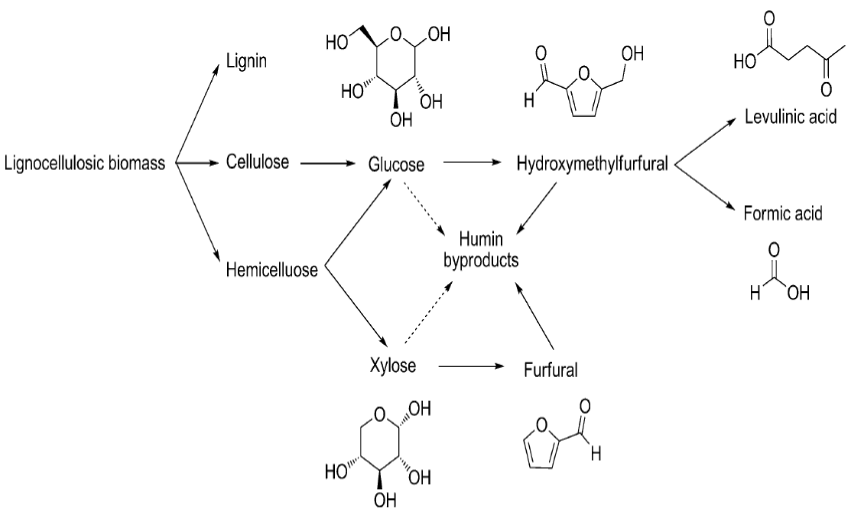
Biomass processing for chemicals, fuels and energy

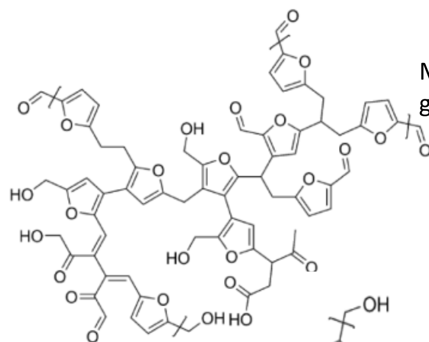
- The majority of commercial bulk chemicals is still derived from fossil resources
- The development of green bio-based chemicals is high on the global R & D agenda
- Lignocellulosic biomass and particularly the cellulose and hemicellulose fraction are considered interesting feeds
- Sugar processing yields humins as by-product



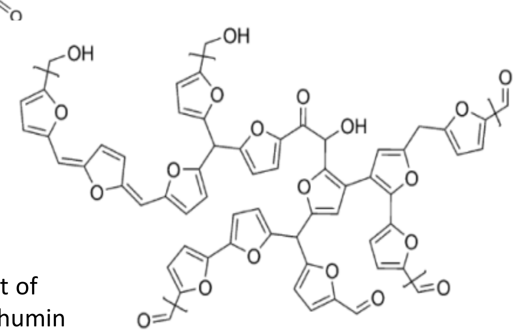
Humins

- Efficient chemo-catalytic conversion technologies for C5 and C6 sugars are under development. Humin byproducts are formed during acid-catalyzed dehydration of sugars under conditions typical for biorefinery operations
- To improve the economic viability of the proposed value chains, it is mandatory to valorize byproducts such as humins
- The structure of humin or humin-like components is based on characterization of functional carbon materials prepared by hydrothermal treatment of carbohydrates





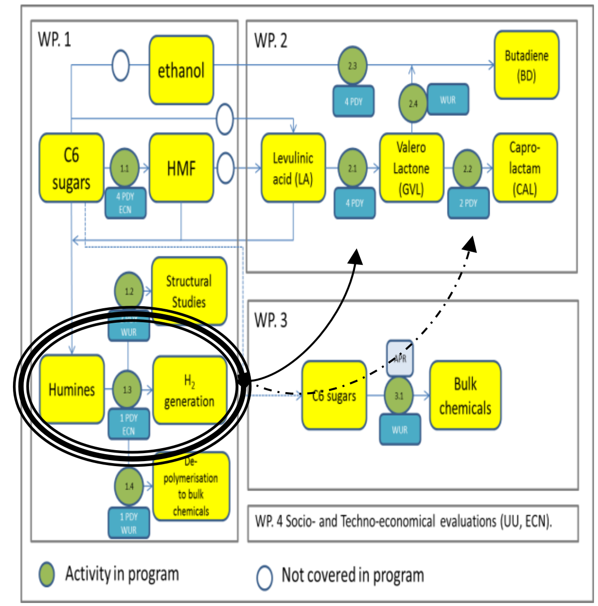
Model fragment of glucose-derived humin



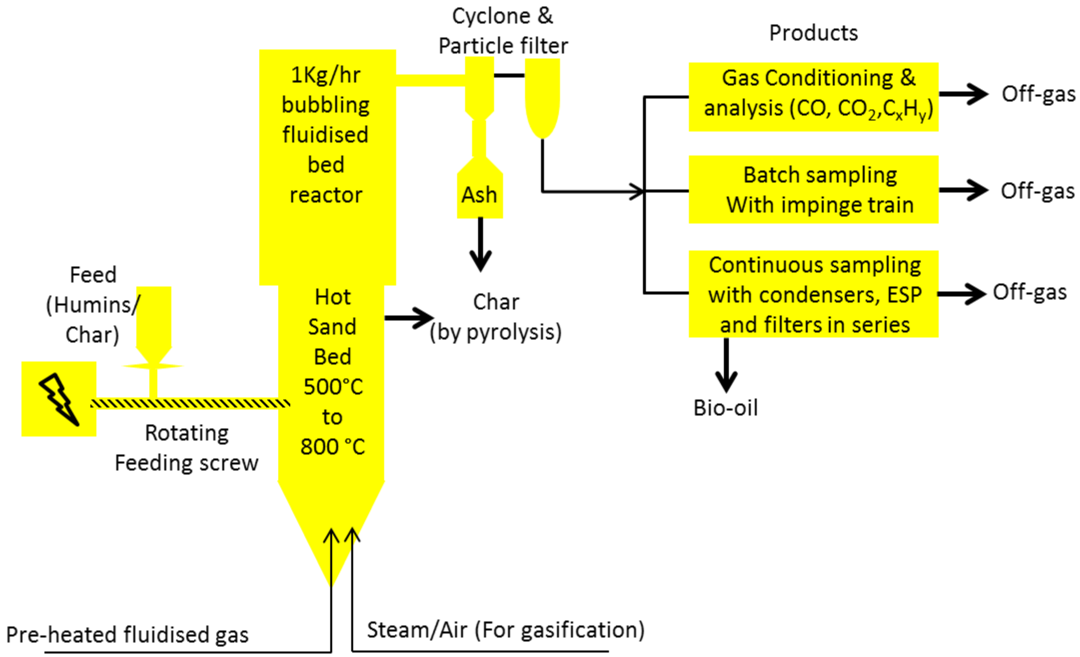
Model fragment of xylose-derived humin

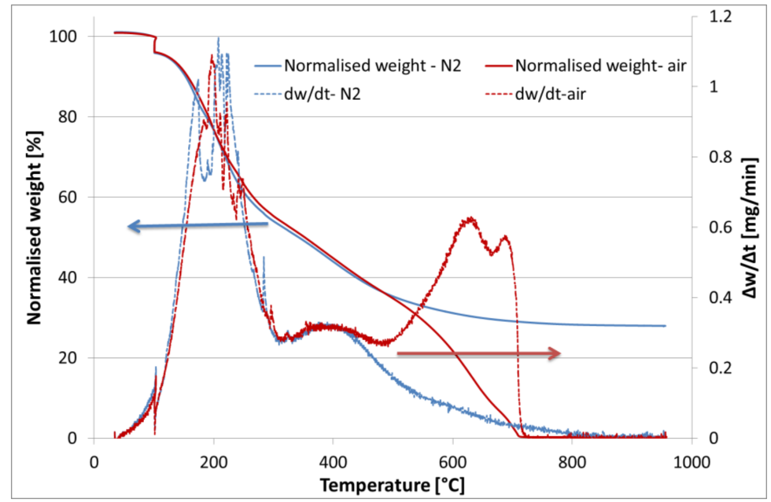
Examples humin valorisation via pyrolysis and/or gasification

- The national SMARTMIX – CatchBio-Carbohydrates programme is aiming at chemo-catalytic conversion of sugars to valuable chemicals.
- To improve the economic viability humins need to be valorised to bulk chemicals and/or H_2 gas
- Target value-added chemicals are:
  - Gamma-valero-lactone (GVL) via hydrogenation of levulinic acid
  - Caprolactam (CAL) via reaction of GVL with humin-derived syngas (CO / H_2)
- Techno- and socio economic evaluations are currently underway to establish the viability of the chosen routes.



Experimental set-up





Thermal degradation under pyrolysis and combustion conditions of a representative humins

- Humins are gasified / pyrolysed in a dedicated bubbling fluidized bed reactor around 500°C – 800 °C and atmospheric pressure into synthesis gas, bio-oil and char.
- The equipment is used for pyrolysis and gasification, feed is either humins (gasification and pyrolysis) or humin-derived char (steam gasification)

Overview of experiments

- Characteristics of used humin as supplied by Avantium
  - Brittle, porous material, low density, partially devolatilised
  - High ash (~5-10 wt%) and low volatile content
- Gasification
  - Gasification in a bubbling fluidised bed (WOB)
  - 800°C, sand bed, ER 0.3, air as fluidisation gas (Test-1)
  - 700°C, sand bed, ER 0.3, air fluidisation gas (Test-2)
  - 700°C, olivine bed, ER 0.3, air fluidisation gas, tar measurements (Test-3)
- Pyrolysis followed by char gasification
  - Pyrolysis at 550°C, olivine bed, N_2 fluidisation gas
  - Gasification at 800°C, olivine bed, steam for gasification

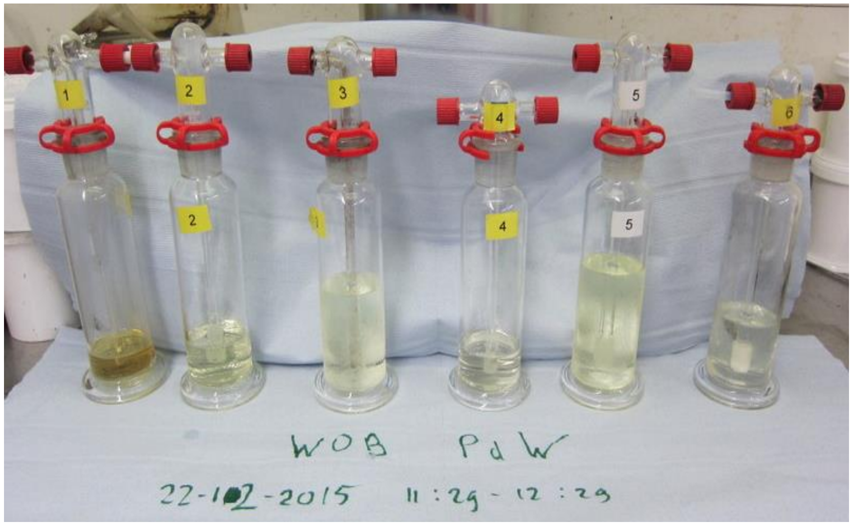
Humins gasification
Test 1 and Test-2

Test-1
800°C, N_2 as fluidisation gas, sand bed, agglomeration due to slagging / fouling from low-melting Na-silicates

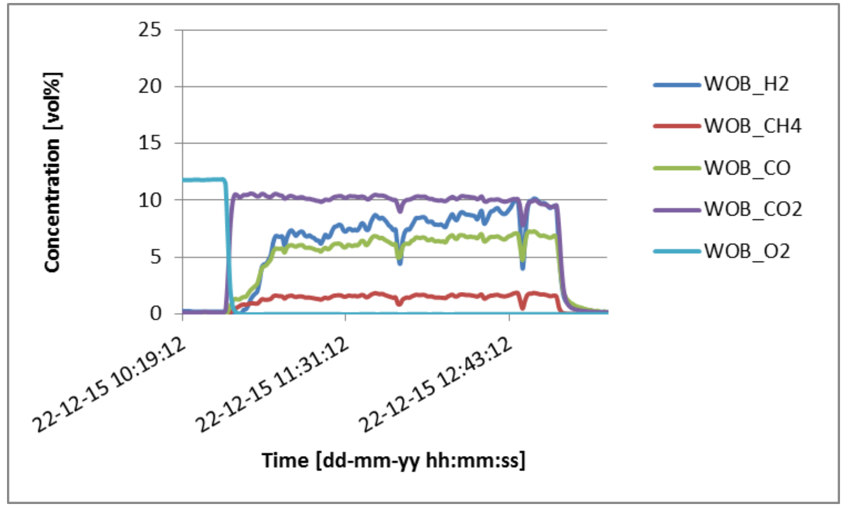
Test-2
700°C, N_2 as fluidisation gas, sand bed
Less than at 800°C, but still agglomeration

Humins gasification
Test-3: successful!

700 °C, olivine bed
No agglomeration!



Tar capture in different IPA-filled washing bottles according to ECN's tar measurement protocol



Concentration profiles

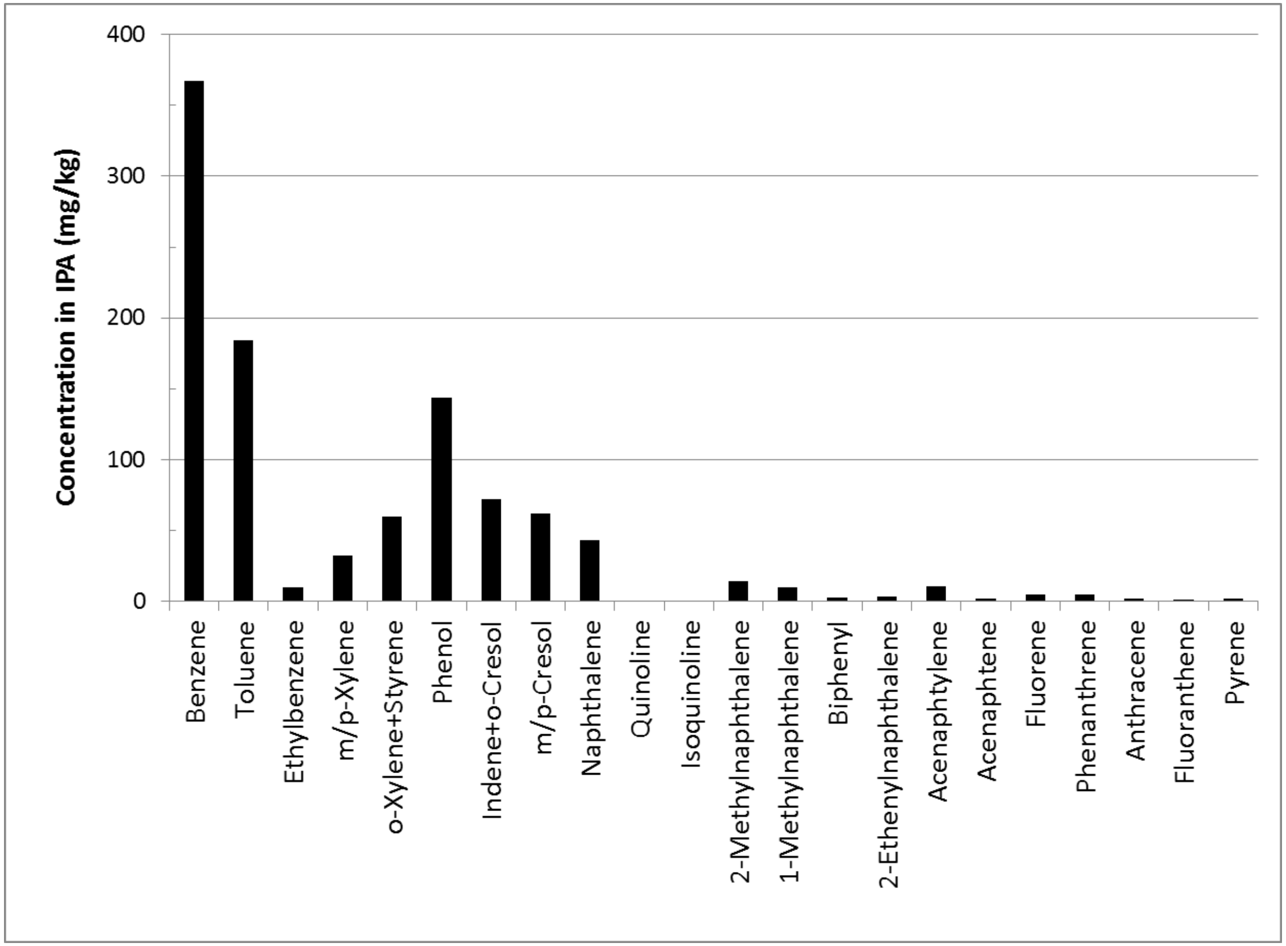
Mass Balance (dry basis by weight)

Solids: 25.1 %

Gases: 74.9 %

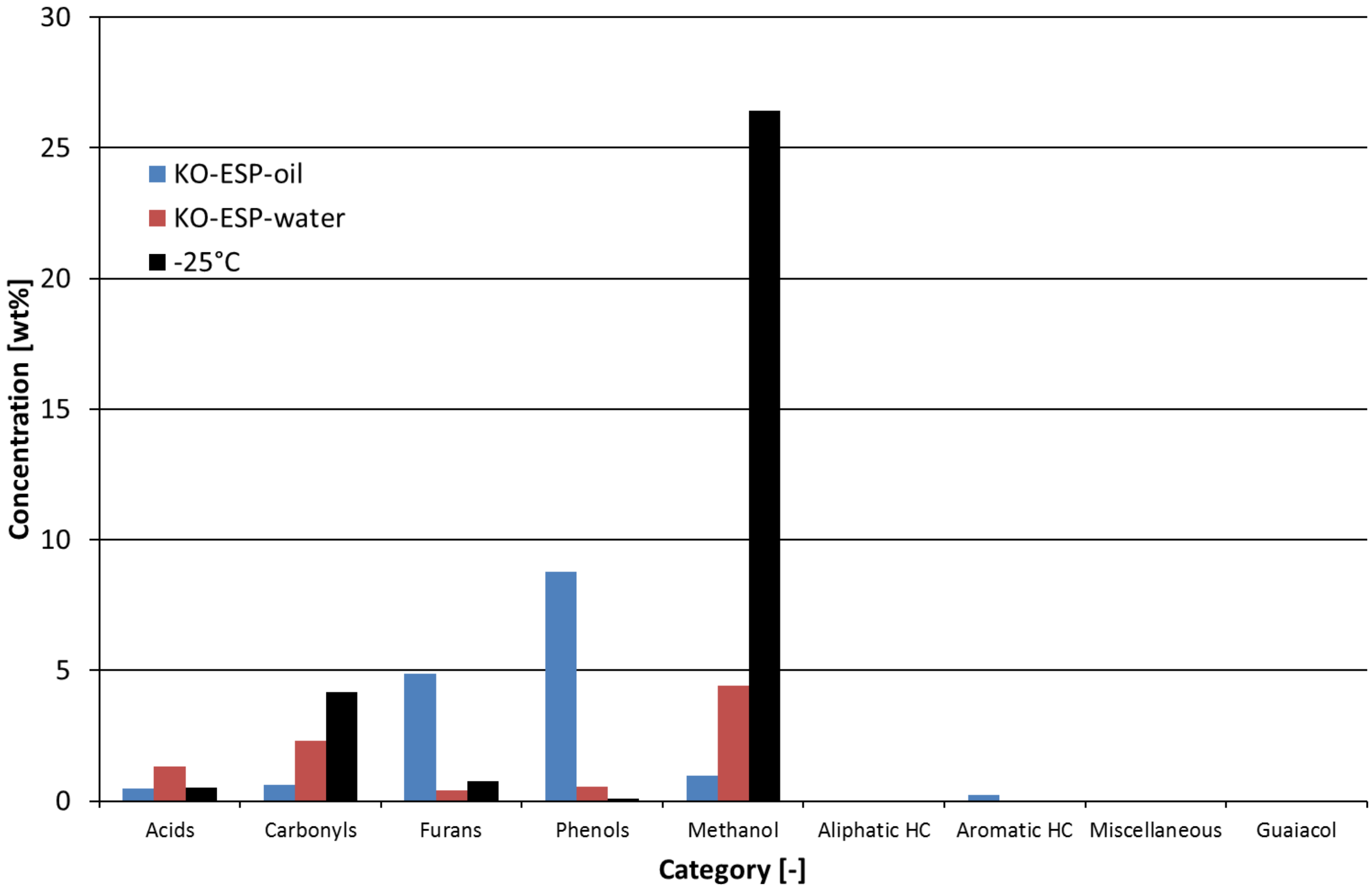
H_2 yield: 1.8 %

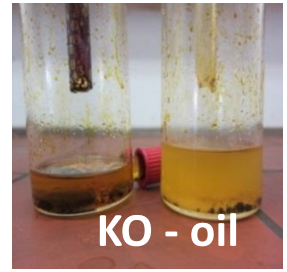
Typical gasification tars

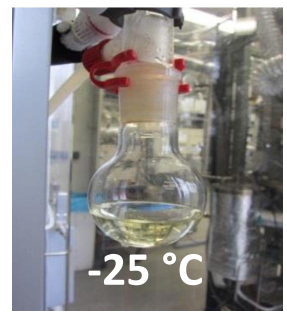


- Major compounds with single benzene ring structures
- Minor amounts of PAH's

Humin liquid pyrolysis products







Mass balances Humins gasification and pyrolysis

- Humin pyrolysis

Mass Balance	
% Liquids	20%
% Solids	35%
% Gases	30%
Mass balance	85%
H_2 Production	0.5%

- Char gasification with steam (dry basis by weight)

Mass Balance (Char + Steam)	
% Gases	30.4%
% CO_2	21.6%
% CO	6.1%
%CH_4	0.2%
%H_2	2.6%

Conclusions

- Bubbling fluidised bed pyrolysis and gasification seem to be viable thermochemical valorisation routes for sugar-derived humins.

- Humin pyrolysis yields a predominantly aqueous pyrolysis liquid, containing some value-added chemicals, whereas a subsequent steam gasification of the pyrolysis char can be deployed to generate hydrogen that can be used as reactant for other processes.

- Using appropriate reaction conditions, direct gasification of humins can be conducted to generate synthesis gas.

Thank you for your attention!; questions?

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