

Energy Systems and Technology Prof. Dr.-Ing. B. Epple Otto-Berndt-Str. 2 64206 Darmstadt / Germany Phone: +49 6151 16 23002 www.est.tu-darmstadt.de



Lara

<u>Chemical Looping gAsification foR</u> sustain<u>Able production of biofuels</u>

2. German Doctoral Colloquium Bioenergy, Nürnberg, 30.9 - 1.10.2019













Concept (I)



- Biomass-to-biofuel process chain
- Novel biomass pre-treatment, gasification and syngas treatment concepts
- Deployment of established fuel synthesis and upgrading technologies for the production of drop-in biofuels



TECHNISCHE

UNIVERSITÄT DARMSTADT

Concept (II)







Cost competitive and environmentally compatible fuels for road transport



Biomass Pre-Treatment





- Pre-Treatment of "difficult" feedstocks (e.g. straw)
 - Large amount of contaminants (CI, Alkali)
 - Low volume specific heating value
 - Low ash melting temperature
- Concept: Combination of torrefaction, leaching & pelletization
 - Better handling (transport, storage, feeding)
 - Better fluidized bed characteristics
 - Larger heating value







- Feedstock gasification with H₂O/CO₂ assisted by solid phase oxygen
- Circulation of Me_xO_y for oxygen & heat transport between reactors
 - No air separation required → cost-efficient
 - CO_2 concentrated in syngas \rightarrow facilitation of net negative CO_2 emissions
- Low λ (~0.3 0.5) to achieve partial fuel oxidation \rightarrow formation of synthesis gas
- Oxygen carriers: Fe₂O₃/Fe₃O₄, Fe₂TiO₅/FeTiO₃

Chemical Looping Gasification (CLG) -Reactions

- Air Reactor (T~1000 1050 °C)
 - re-oxidation of oxygen carrier $Me_xO_{y-1} + 0.5 O_2 \rightarrow Me_xO_y$
 - Combustion of unconverted char $C+O_2 \rightarrow CO_2$







- Fuel Reactor (T~900 950 °C)
 - Gasification of biomass $C + CO_2 \rightarrow 2 CO$
 - $C + H_2 \bar{O} \rightarrow CO + H_2$
 - Heterogeneous $Me_xO_y gas reactions$ $4 Me_xO_y + CH_4 \rightarrow 4 Me_xO_{y-1} + 2 H_2O + CO_2$ $Me_xO_y + CH_4 \rightarrow Me_xO_{y-1} + 2 H_2 + CO$ $Me_xO_y + CO \rightarrow Me_xO_{y-1} + CO_2$ $Me_xO_y + H_2 \rightarrow Me_xO_{y-1} + H_2O$
 - Tar cracking e.g. $C_8H_{18} \rightarrow C_3H_6 + C_5H_{12}$
 - Steam methane reforming $CH_4 + H_2O \leftrightarrow 3H_2 + CO$
 - Water gas shift reaction $CO + H_2O \leftrightarrow H_2 + CO_2$

> Continuous conversion of feedstock to syngas without N_2 -dilution



Chemical Looping Gasification (CLG) – Mode of Operation (I)





Control of heat & oxygen transport through circulation rate of Me_xO_y a) Gas composition CO_2 exothermic 1 H₂ CO CH_4 H_2 0.8 CO Fuel Reactor $\begin{bmatrix} - & 0.6 \\ - & 2 \\ x^i & 0.4 \end{bmatrix}$ Air Reactor Less $O_2 \rightarrow$ formation of syngas 0.2 endothermic 0 6000 5000 3000 2000 1000 4000 $\dot{m}_{Me_xO_y}$ [kg/h] Fuel Reactor Air Reactor b) Heat duty AR: Heat release -200 $\dot{Q}_i \,\, [\mathrm{kW}]$ adequate λ 0 200 Reactor Fuel \dot{Q}_{FR} FR: Heat demand Q_{AR} 400 5000 2000 1000 Not in heat balance! 6000 4000 3000 \geq $\dot{m}_{Me_xO_y}$ [kg/h]

> Challenge: achieving adequate λ and sufficient heat transport



Chemical Looping Gasification (CLG) – Mode of Operation (II)

(Lara



- Challenge: achieving adequate λ , while guaranteeing sufficient heat transport
- a. Adjustment of reactor temperature gradient (lower T_{FR})
- b. Decoupling of heat and oxygen transfer
 - Approach I: Dilution of metal oxide with solid inert (e.g. Sand)
 - Oxygen transport capability decoupled from heat capacity







- Approach II: Metal oxide exhibiting low O-transport capacity & high c_p
- Oxygen & heat transport in the required "ratio"

FR:

FR:



- Approach III: Operation of air reactor in O₂ deficient atmosphere
- Oxygen availability in fuel reactor controlled through air supply
 - AR:
- Different approaches are currently being investigated



Chemical Looping Gasification (CLG) – Plant Configuration



TECHNISCHE UNIVERSITÄT DARMSTADT

- Two coupled circulating/bubbling fluidized bed reactors (FR, AR)
 - Good heat & mass transfer characteristics
- Gas-solid separation via cyclones
- Loop seal (LS) as pressure seal
- Cone valve/L-valve for control of global solid circulation



Syngas Treatment

(Lara

Treated

Syngas



- Hot gas filter for solids removal
- Scrubbing column (HCI removal)
- CO-Shift to adjust H₂/CO-ratio
- Efficient tar removal via biodiesel washing column
- Acid gas removal: Amine/NaOH/H₂O₂ scrubbers
 - Ensures required syngas purity for Fischer Tropsch catalyst
 - Lower investment & fuel production costs than RectisolTM





Full Process Chain







infrastructure \rightarrow lower CAPEX



Summary & Outlook





- Novel biomass-to-biofuel process chain for second generation biofuels
- Innovative pre-treatment, gasification and syngas treatment concepts
- Investigation of full process in 1 MW_{th} pilot scale







This project has received funding from the European Union's Horizon 2020 research and innovation programme

under grant agreement No 817841: Chemical Looping gAsification foR sustainAble production of biofuels (CLARA).



Thank you for your attention!



TECHNISCHE UNIVERSITÄT DARMSTADT



