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Prediction of pyrolysis kinetics with models of different complexity for isolated biomass components

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1. Motivation

- Pyrolysis describes the endothermic decomposition of solid fuels in an inert environment.
- Pyrolysis products are categorised by light gas, tar and char.
- Influence on ignition, flame stability and pollutant formation
- Mathematical models of different complexity are available depending on the application type (laboratory reactor vs. full scale CFD).
- Biogenic fuels are typically treated as an independent composition of cellulose, hemicellulose and lignin.

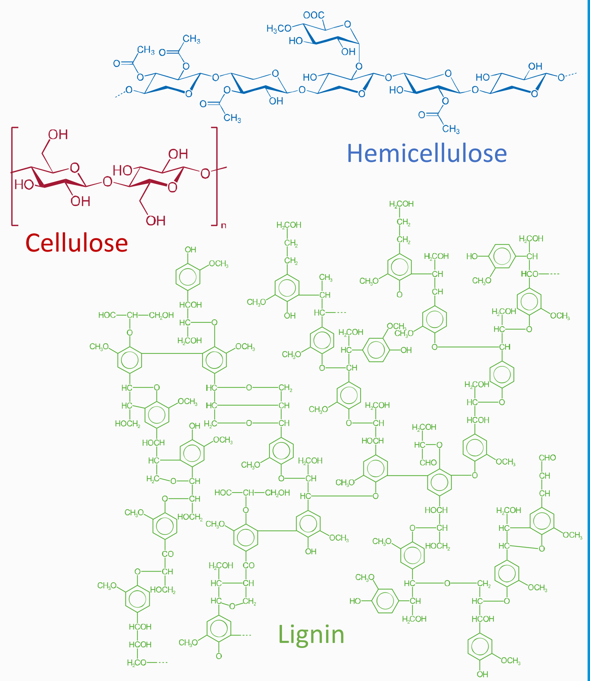

Fig. 1: Chemical structures of biomass components

2. Modelling

Single first-order model (SFOR)

- One reaction step with characteristic reaction rate r
- No distinction between products (only volatiles)

Fig. 2: Reaction scheme SFOR model

CRECK model[1]

- Multiple first-order reactions (parallel and sequential)
- Variety of reaction products (single gas species)
- Reactions: Cellulose (4), hemicellulose (6), lignin (8)

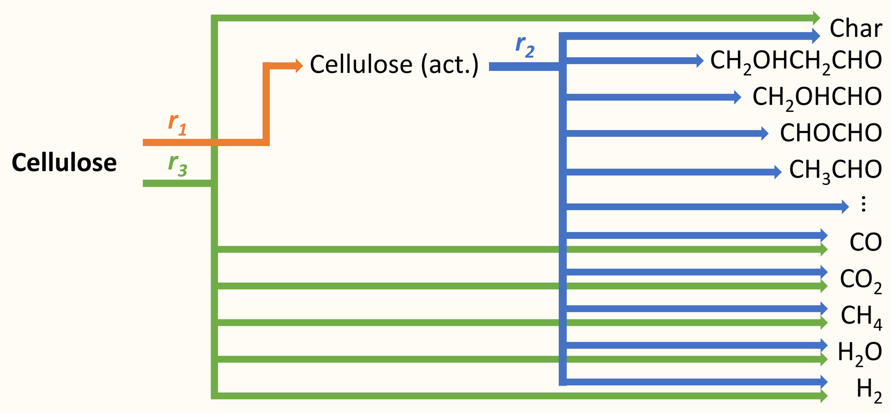

Fig. 3: Reaction scheme of CRECK model for cellulose

Bio chemical percolation devolatilization (Bio-CPD)[2,3]

- Phenomenology-based model considering molecular network structure of the solid fuel
- Bridge conversion mechanism (stabilisation, breaking, split-off)
- Determination of unbound fragments (metaplast) via percolation theory depending on bridge population
- Split of fragments into liquid and vapour phase (VLE)
  - Release of the vaporous fragments as tar
  - Crosslinking of liquid fragments with char matrix
- Additional release of light gases due to stabilisation reaction and side chain split-off
- Preliminary parameter study for evaluation of best-fitting kinetic and structural parameters[3]

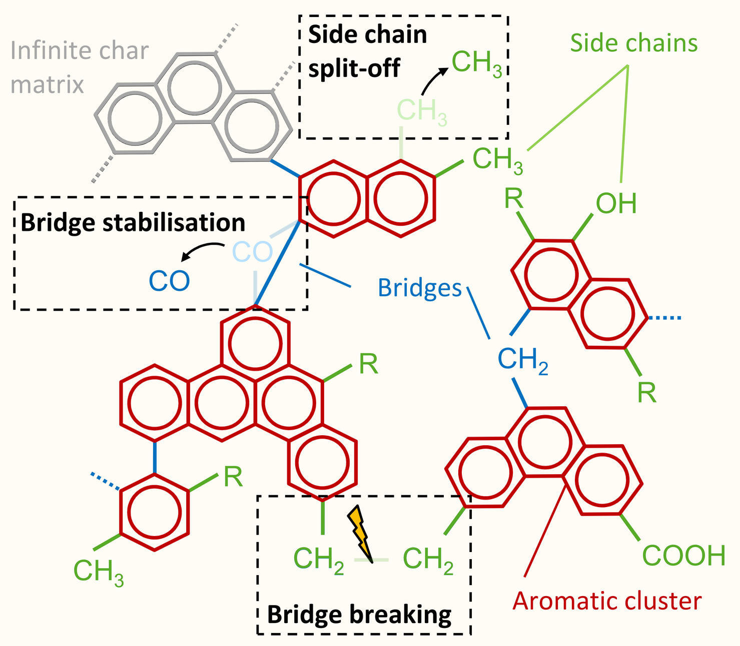

Fig. 4: Reaction scheme of Bio-CPD model

3. Setups for experimental reference data

TGA[4] (Netzsch 409CD)

- Temperature: up to 1150 K
- Heating rate: 5 K/min
- Gas flow: 200 l/min N_2
- Sample mass: 20 mg

FBR[5]

- Temperature: 673–973 K
- Heating rate: ≈ 10^4 K/s
- Fluidising gas: 300 slph N_2
- Sample mass: 15–50 mg

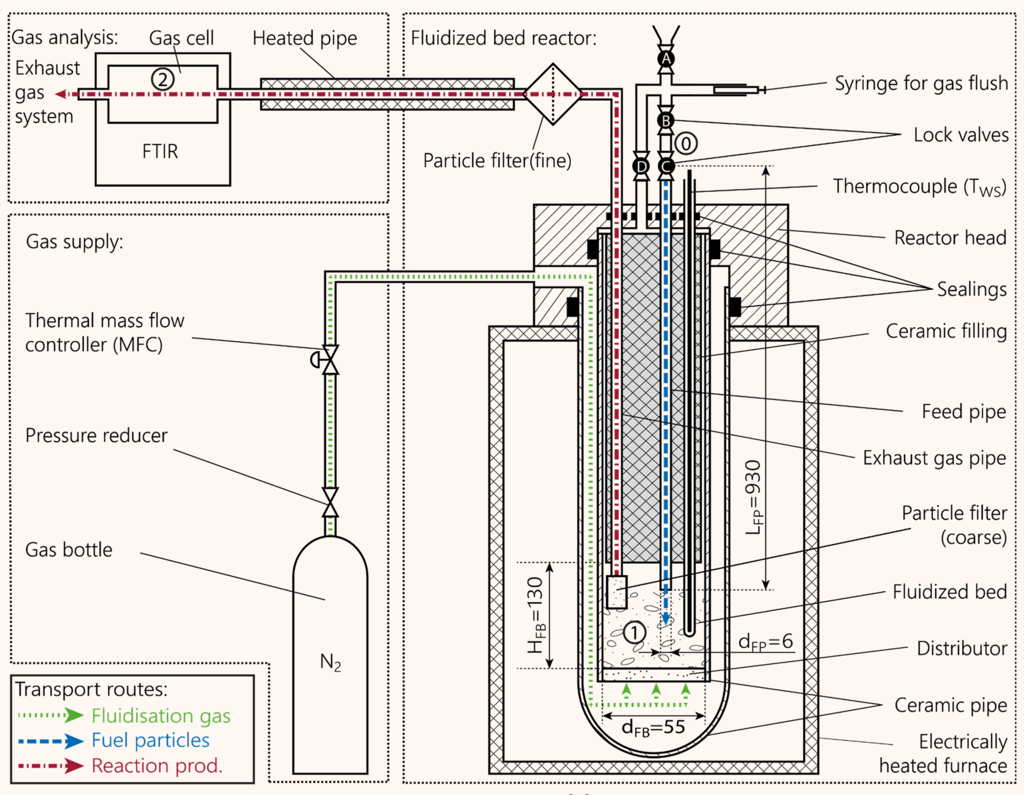

Fig. 5: Sketch of fluidised bed reactor setup[5]

4. Results

Thermogravimetric analysis

- Trends are represented by all models.
- Cellulose: All models follow trend of reference [5].
- Hemicellulose: Very well captured by SFOR and CRECK
- Lignin: Satisfactorily mapped by SFOR and Bio-CPD (but not the details → bond diversity)

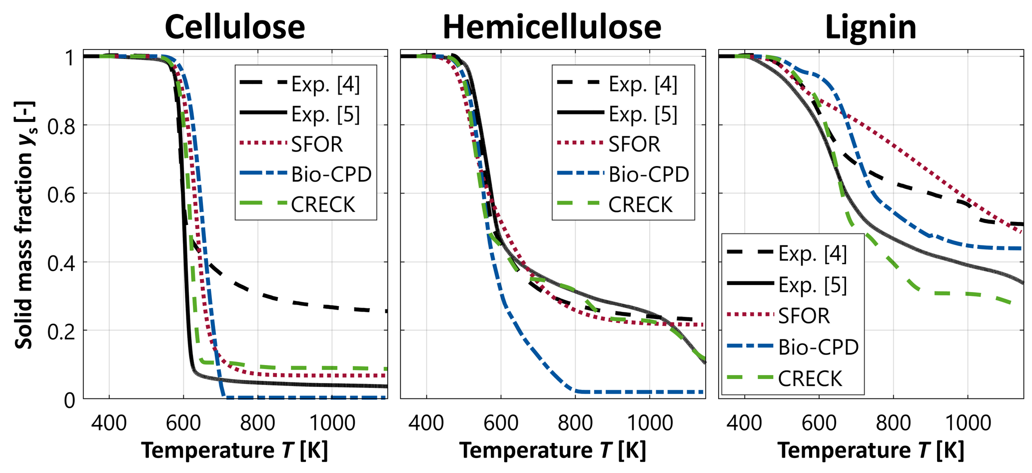

Fig. 6: Experimentally obtained mass loss in the TGA[4,5] in comparison with model predictions

Fluidised bed reactor

- The descriptive quality of the SFOR model (fitted to experimental data) increases with the temperature.
- The CRECK model tends to overpredict the total volatile release rate (especially low temperatures and lignin).
- Bio-CPD shows good prediction (especially high temperatures), but reveals inaccuracies for lignin.

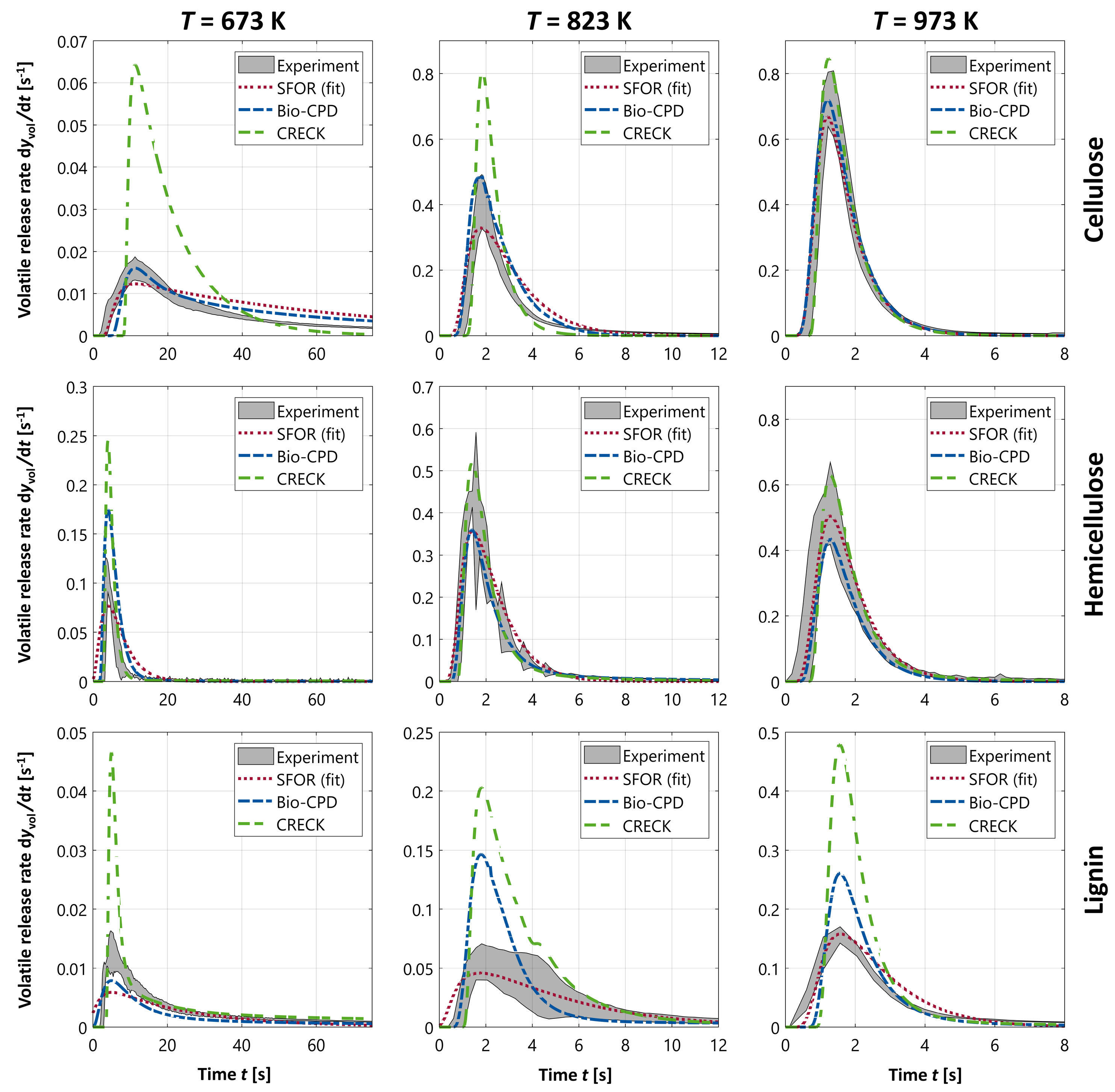

Fig. 7: Experimental volatile release rates obtained in the FBR[5] in comparison with model predictions

5. Conclusion

- SFOR can describe the trends, but depends on initial calibration and lacks on precision at low temperatures.
- CRECK works well on most TGA data but overpredicts the release rates in the FBR under all conditions.
- Bio-CPD is best predictive for the fluidised bed reactor, but overestimates the conversion in the TGA.

References

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