Numerical simulation of thermal decomposition of polyethylene with a single-particle model

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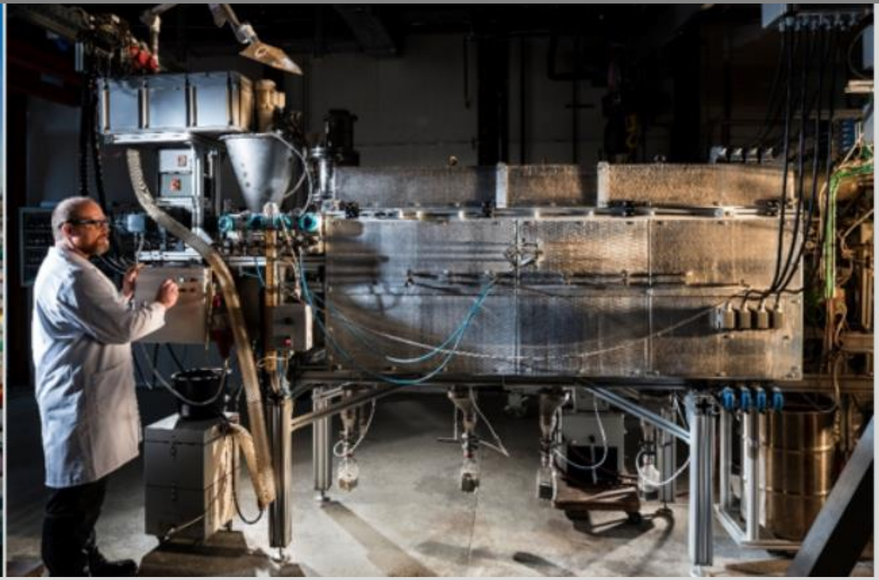


Outline

- Motivation
- Simulation method
- Validation via TG experiments
- Simulation at isothermal conditions
- Summary

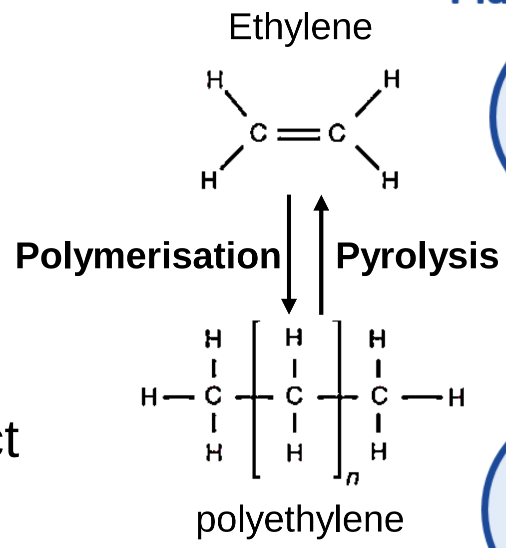
Chemical recycling of plastic wastes

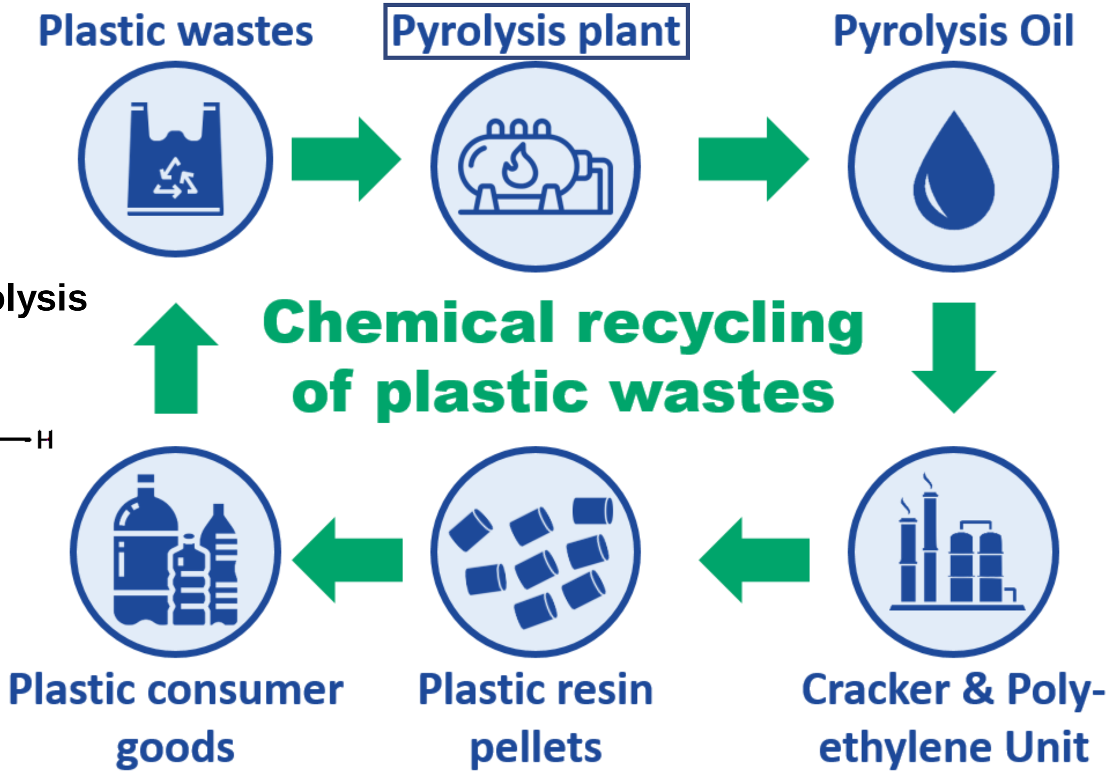
- ~350 Mt plastics waste per year
  - 22% mismanaged, 9% recycled
- Chemical recycling of plastic wastes
  - Contaminated/mixed plastics
  - Potential as ultimate solution
- Challenges
  - Process design, efficiency, product
  - Scale-up, economic viability

Simulation of plastic pyrolysis

Heat transfer vs. pyrolysis reaction

Pyrolysis: Degradation of polymers at high temperature and oxygen-free environment into short-chain hydrocarbons





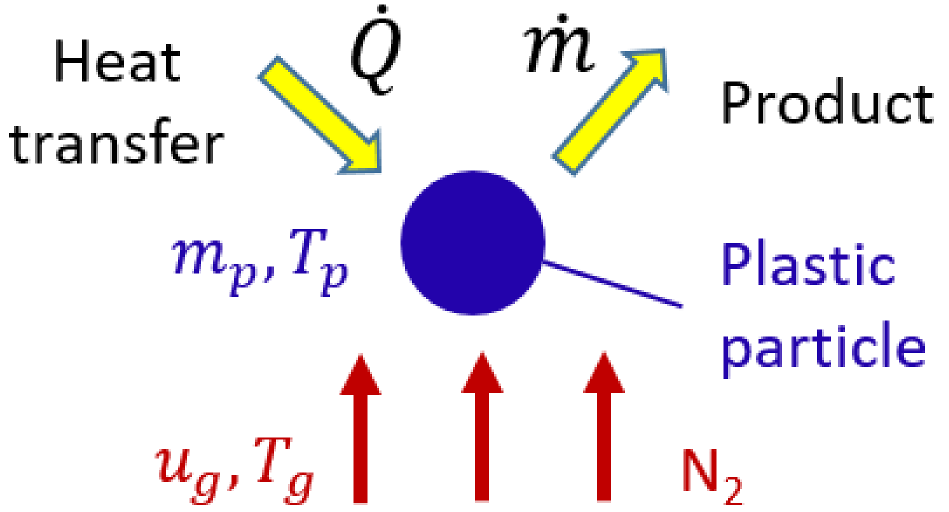
https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.htm

Mismanaged 22% | Landfilled 49% | incinerated 19% | recycled

Simulation method

Assumptions

- Single spherical particle
- Thermally-thin
- No phase change
- One-step chemistry



Mass and energy equations

$$-\frac{dm_p}{dt} = \dot{r}, \qquad \dot{r} = k_0\, e^{\frac{-E_a}{RT_p}} \cdot m_p{}^n \cdot m_{p,0}{}^{1-n}$$

$$m_p c_{p,p} \frac{dT_p}{dt} = \alpha A_p (T_g - T_p) - \Delta h_r \dot{r}$$

Heat transfer coefficient:

$$\alpha/\alpha_0 = 1,5$$

$$\alpha_0 = Nu \frac{\lambda_{g,0}}{d_{p,0}}, \qquad Nu = 2$$

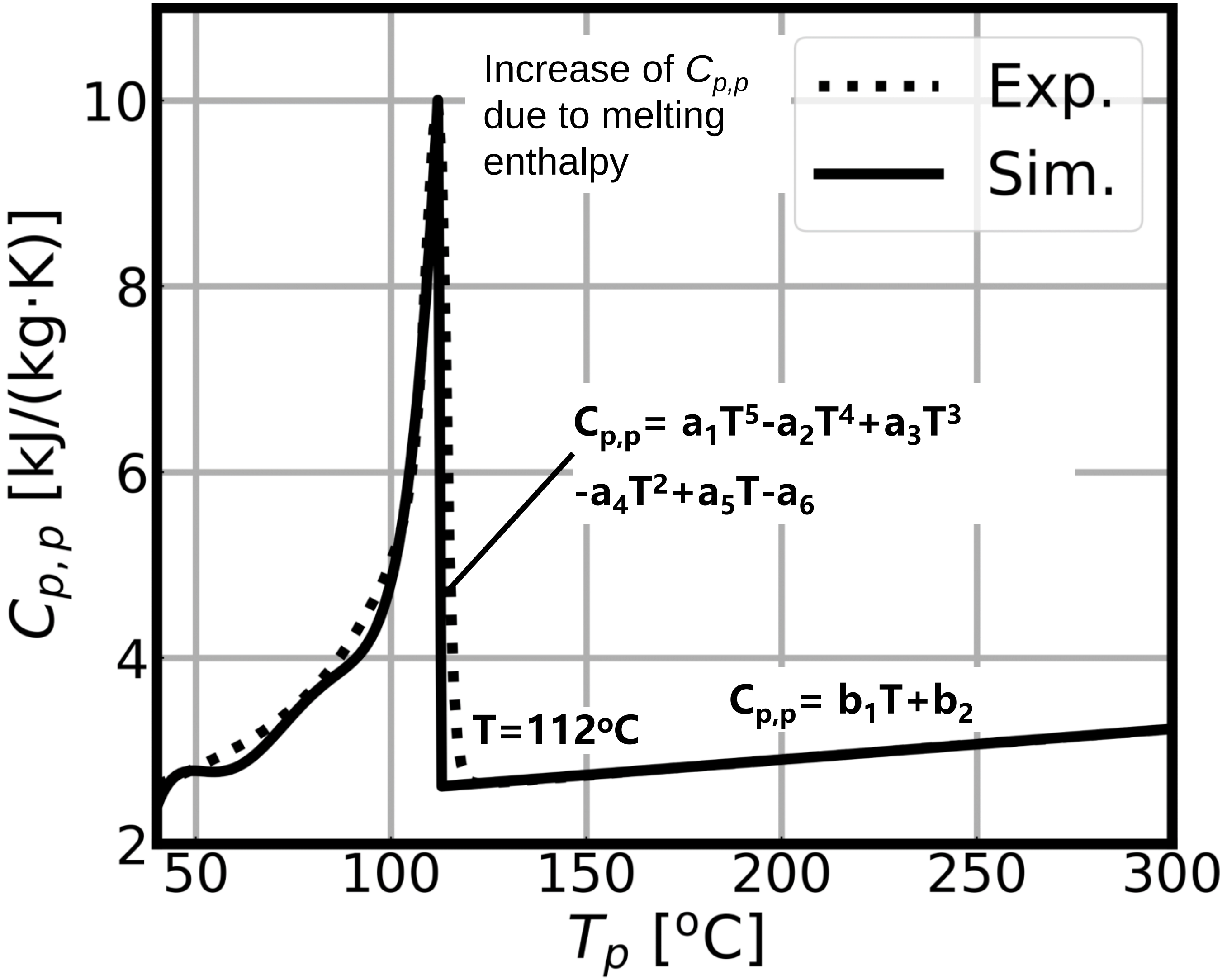
Model validation

Thermogravimetry (TG) experiments

- **Low-density polyethylene (LDPE): 10 mg**
  - ρ_p = 924 kg/m^3
  - Δh_r = 500 kJ/kg
  - k_0 = 2.279×10^{19} min^{-1}
  - E_a = 280.820 kJ/mol
  - n = 0.941

- **High-density polyethylene (HDPE): 10 mg**
  - ρ_p = 950 kg/m^3
  - Δh_r = 500 kJ/kg
  - k_0 = 4.989×10^{18} min^{-1}
  - E_a = 275.141 kJ/mol
  - n = 0.939

- **Gas: N_2 at u_{gas} = 0 m/s**
  - Heating rate: β = 5, 10, 20, 40 °C/min
  - T_0 = 40 °C, T_{max} = 850 °C

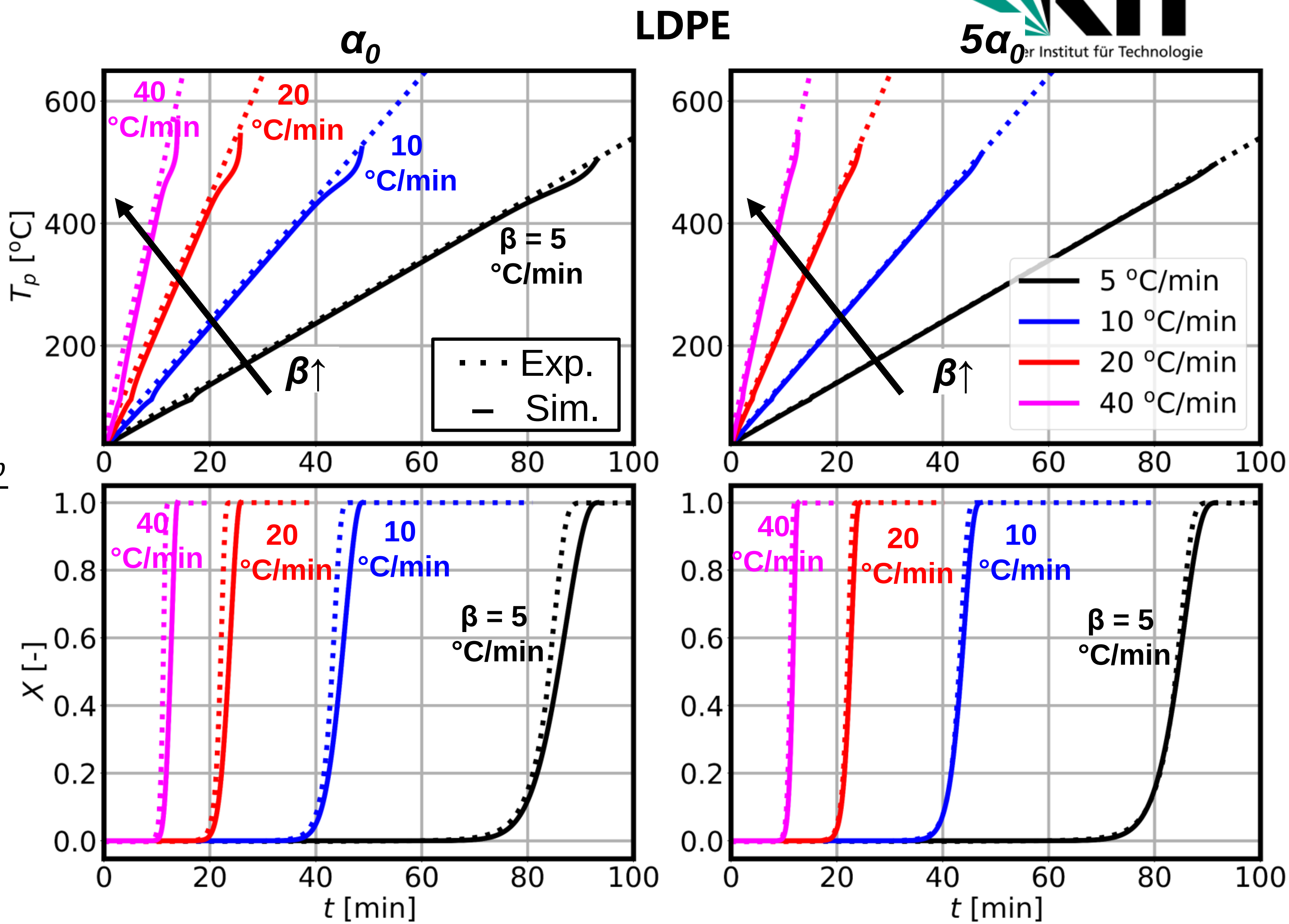


Particle temperature and conversion progress

- Time delay between measured and calculated T_p and X
- Faster heating and conversion at larger β

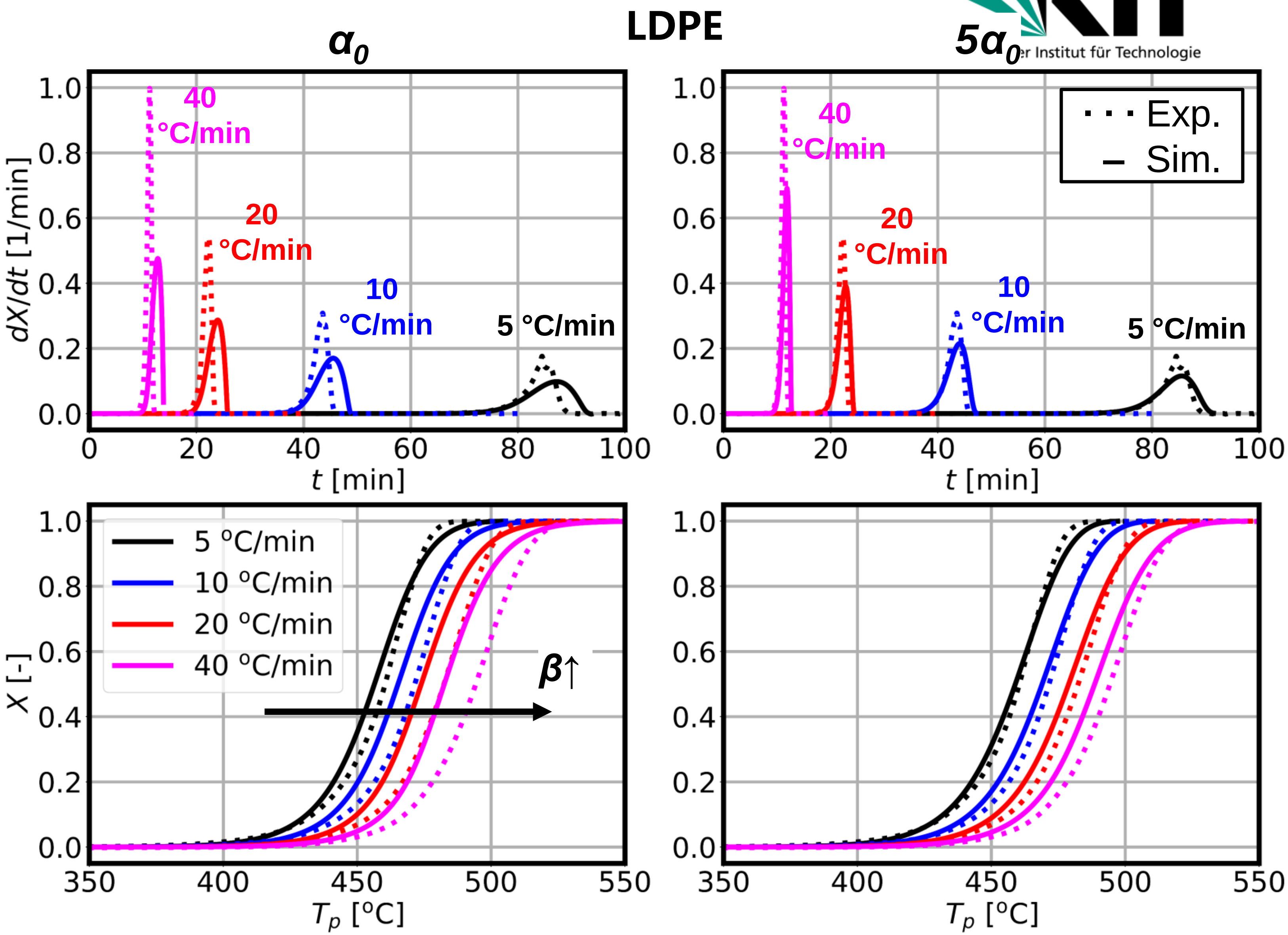
$$X = \frac{m_{p,0} - m_p}{m_{p,0}}$$

- Increase of α leads to faster heating and pyrolysis process
- Good agreement between experiments and simulations



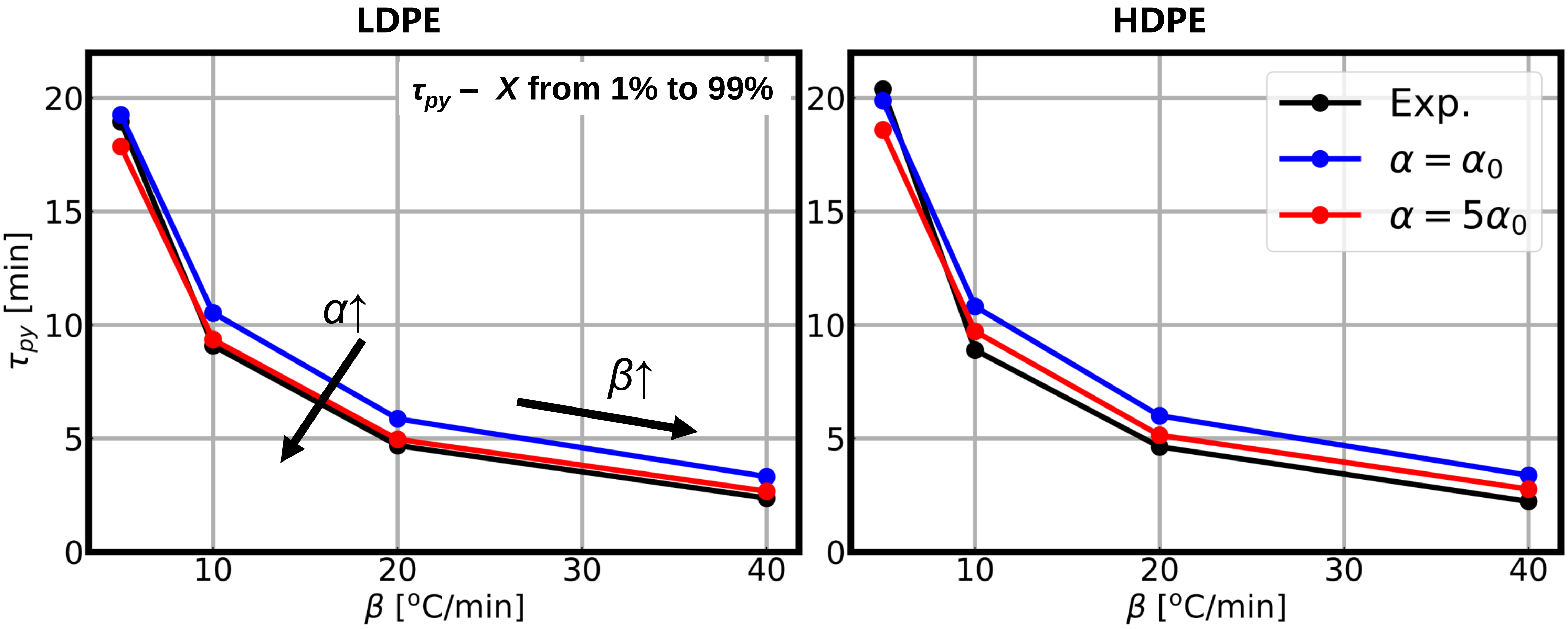
Conversion rate and pyrolysis temperature

- Increase of conversion rate dX/dt and pyrolysis temperature T_{py} with β and α
- Calculated dX/dt and T_{py} are smaller compared with measured data due to heat transfer from gas to particle
- 420 °C < T_{py} < 520 °C



Pyrolysis time

- ❑ Decrease of τ_{py} with β and α
- ❑ Good agreement between experiments and simulations



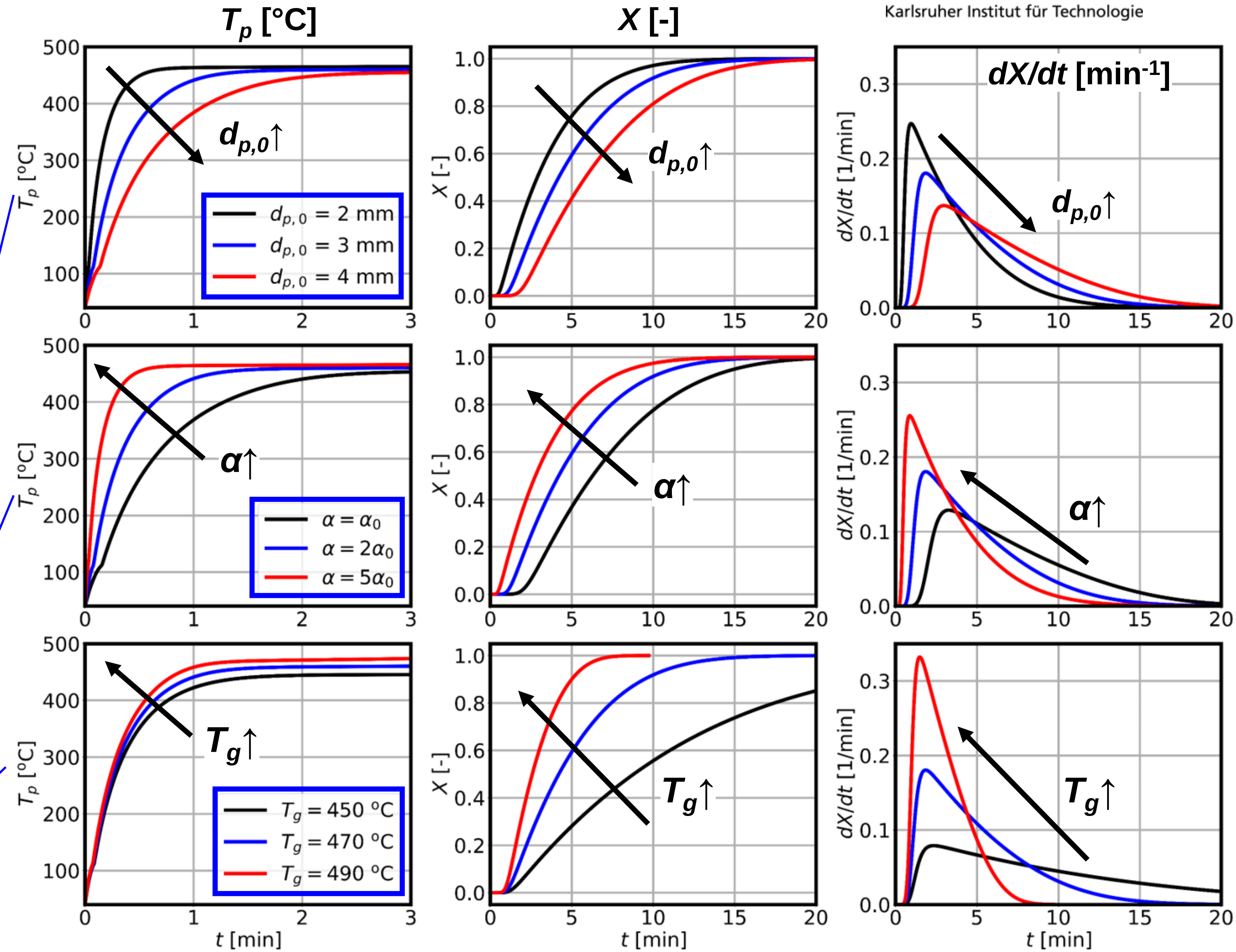
Simulation of plastic pyrolysis at isothermal conditions

Effect of operating parameters

- Variations of particle diameter $d_{p,0}$ and heat transfer coefficient α at given gas temperature T_g
- Study of interactions between heat transfer and pyrolysis reaction
- Faster heating and pyrolysis process when $d_{p,0}\downarrow$, $\alpha\uparrow$, $T_g\uparrow$

		Ref.	
$d_{p,0}$ [mm]	2	3	4
α/α_0 [-]	1	2	5
T_g [°C]	450	470	490

LDPE

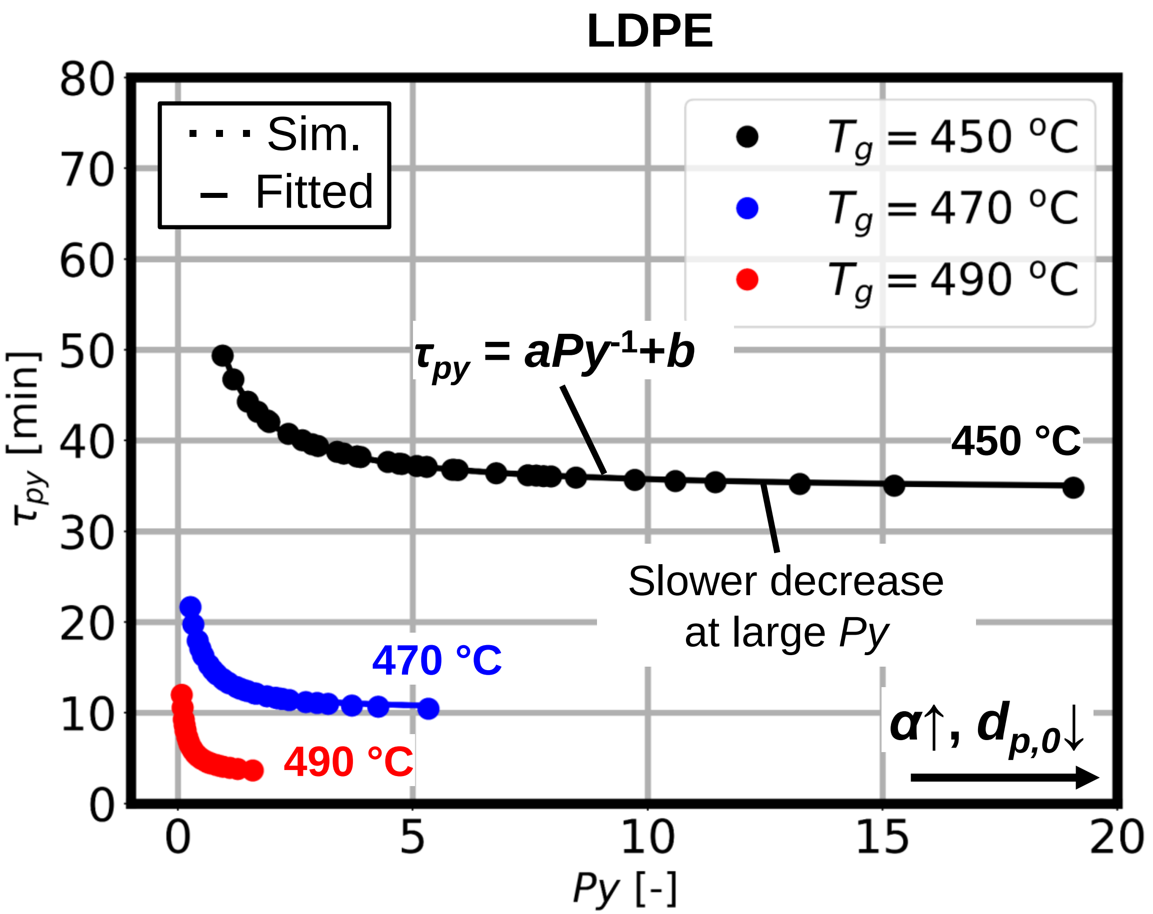


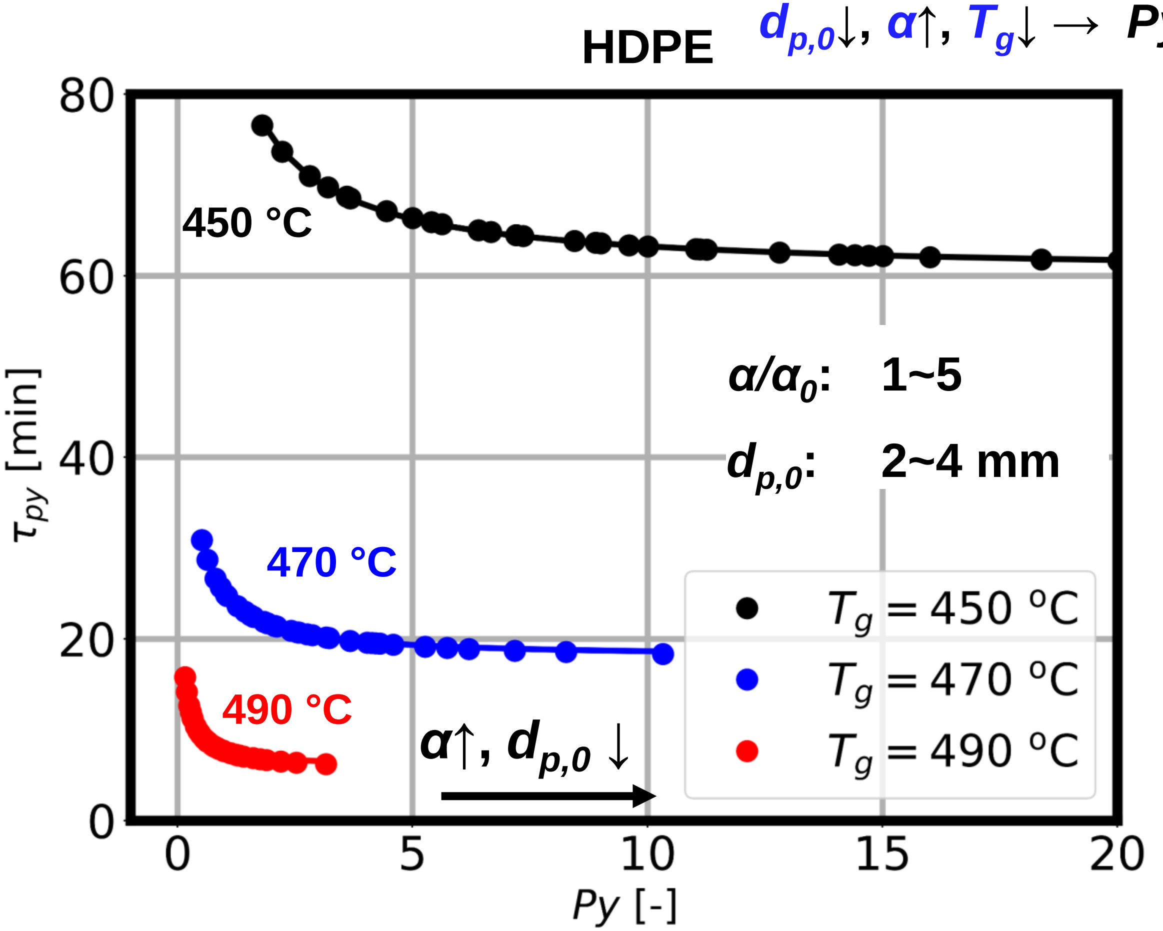
Correlation of pyrolysis time with pyrolysis number

- *Py*: ratio of characteristic time scales for chemical reaction and heat transfer
- Almost <u>inversely proportional</u> correlation between τ_{py} and *Py*

$$Py = \frac{t_c}{t_h} = \frac{\alpha}{k_r \rho_p c_p d_{p,0}}$$

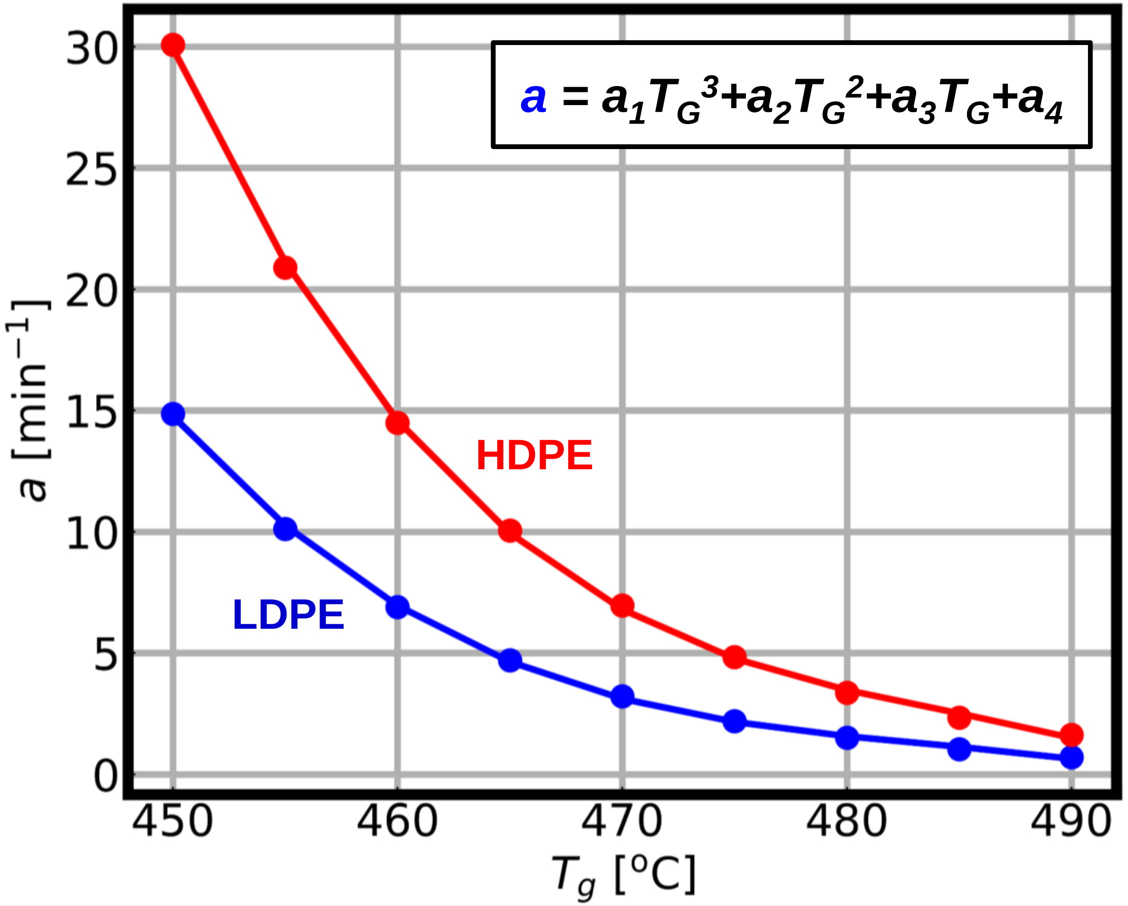
$d_{p,0}\downarrow,\ \alpha\uparrow,\ T_g\downarrow \rightarrow Py\uparrow$

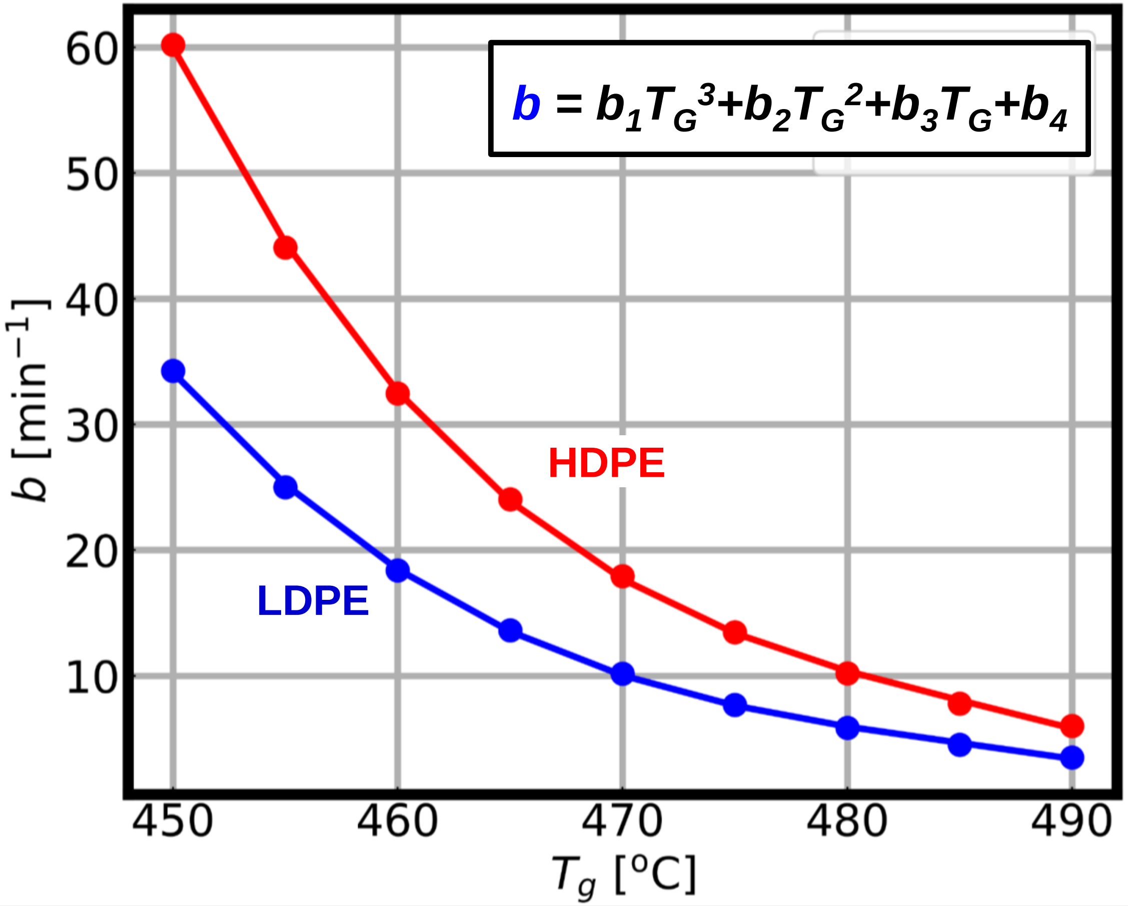




Correlation of pyrolysis time with pyrolysis number

- Polynomial fitting of a and b in $\tau_{py} = aPy^{-1}+b$ as functions of T_g
- Prediction of τ_{py} at given reactor temperature for design of pyrolysis process

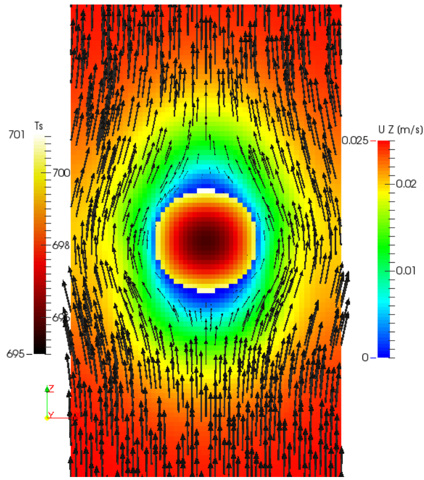




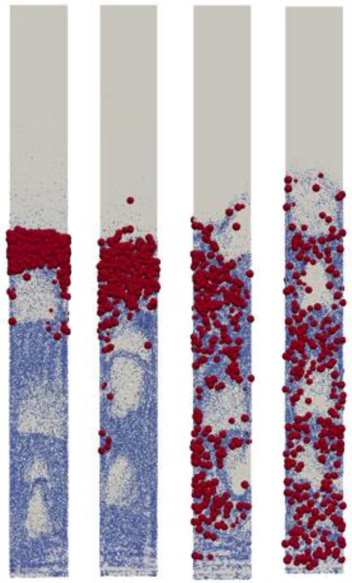
Summary

- Numerical study of pyrolysis process of LDPE and HDPE particles
  - Model validation via TG experiments
- Competition between heat transfer and chemical reaction
  - Significant impact of convective heat transfer at small *Py* on τ_{py}
  - Subordinate influence of heating at large *Py* on τ_{py}
  - Quasi-inversely proportional correlation of τ_{py} with *Py*
  - Assessment of optimal process conditions
- Future task: real condition, plastic pyrolysis in fluidized bed

Particle-resolved simulation



Plastic pyrolysis in fluidized bed



Thank you for your attention!

Backups

Simulation conditions

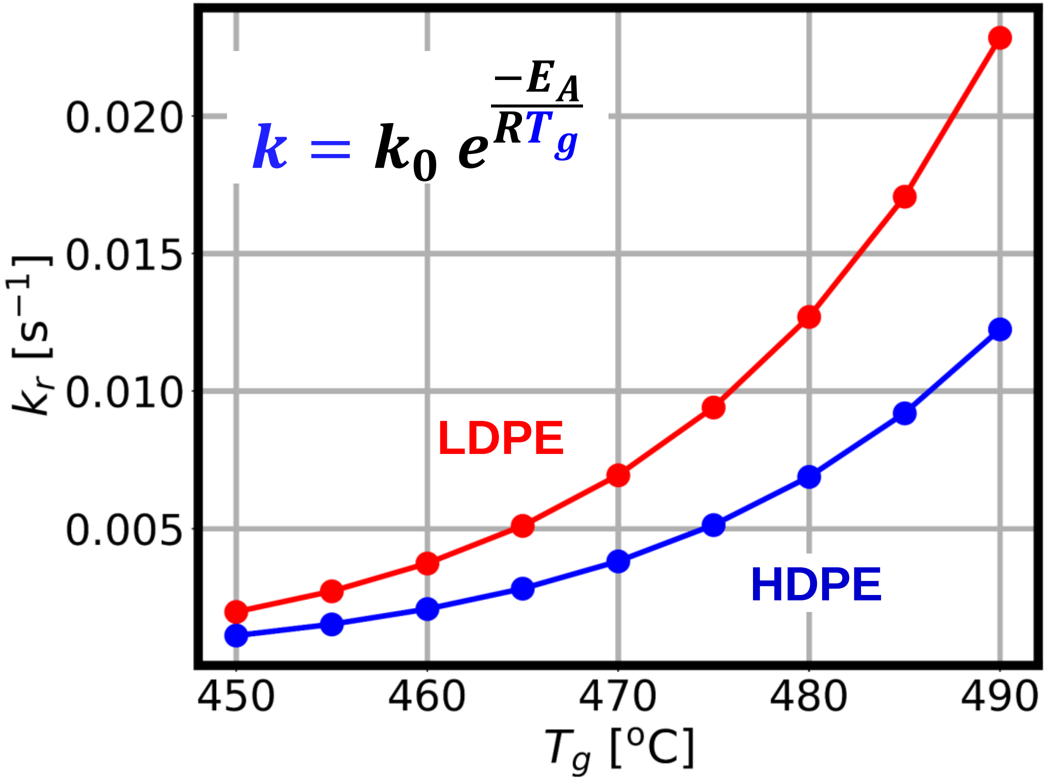
Pyrolysis number

$$Py = \frac{t_{py}}{t_\alpha} = \frac{\alpha}{k_r \rho_p \, c_p \, d_p}, \; k_r = k_0 \, e^{\frac{-E_A}{RT_g}}$$

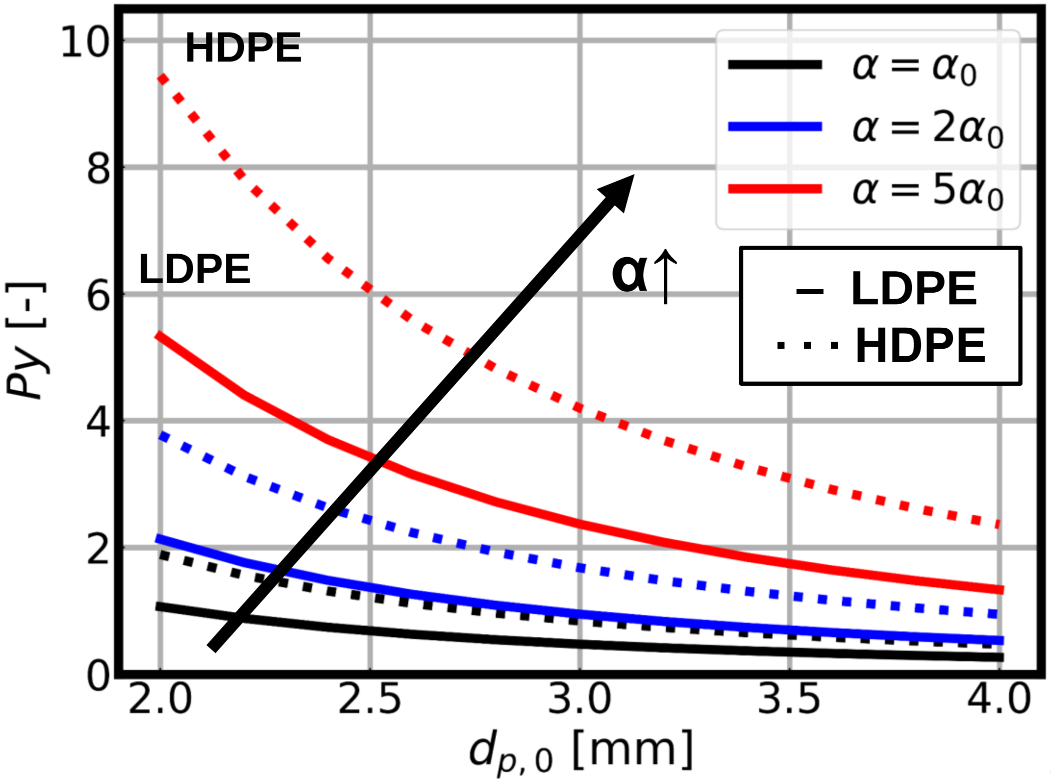
$T_g \uparrow \rightarrow Py \downarrow$

$d_p \uparrow \rightarrow Py \downarrow$

$\alpha \uparrow \rightarrow Py \uparrow$



T_g = 470 °C



Effect of particle diameter

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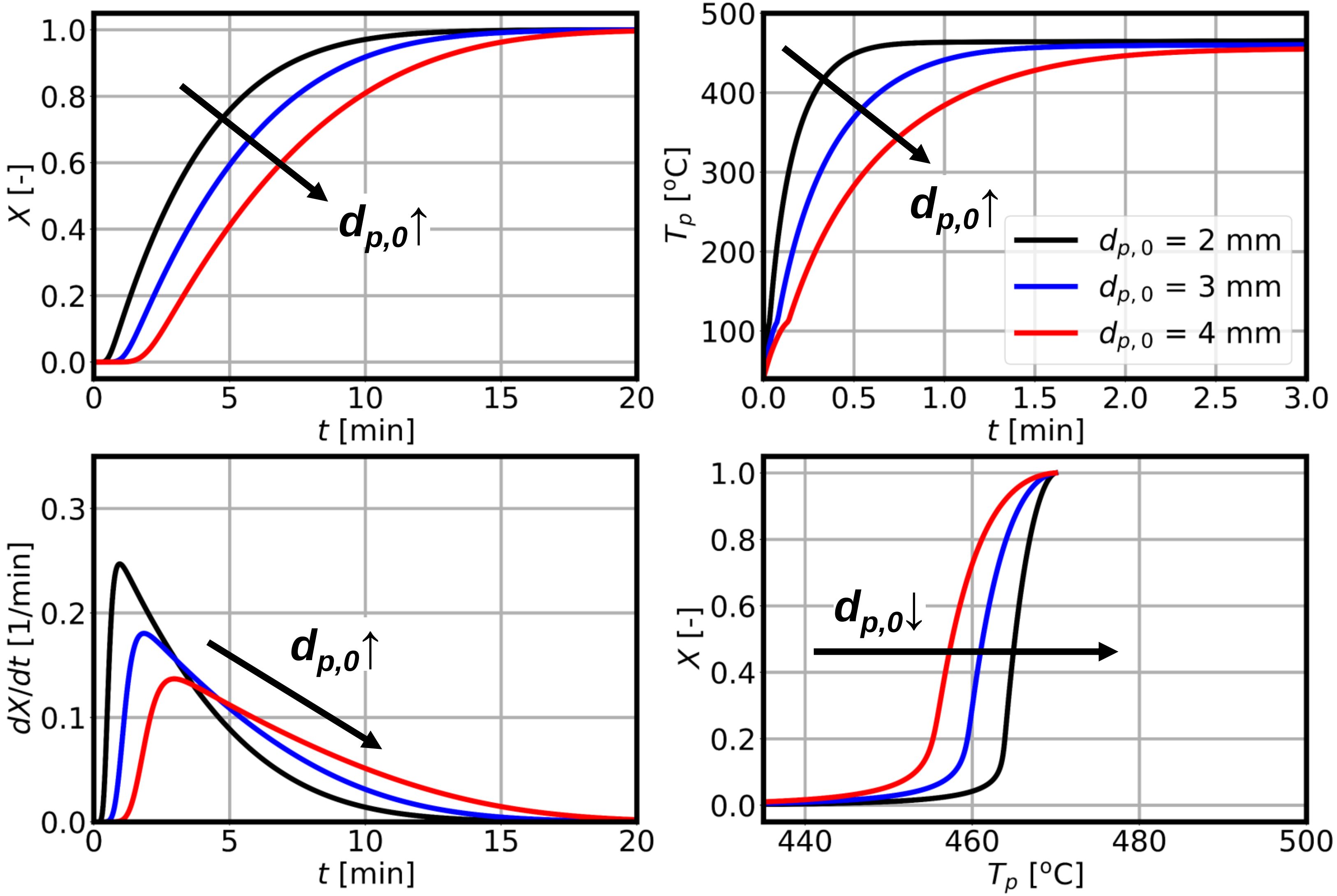
Increase of particle diameter

- Slower heating of particle
- Slower pyrolysis conversion
- Lower particle temperature
- Smaller reaction rate
- Lower pyrolysis temperature

$d_{p,0}$ [mm]	2	3	4
T_g [°C]	450	470	490
α/α_0 [-]	1	2	5

LDPE



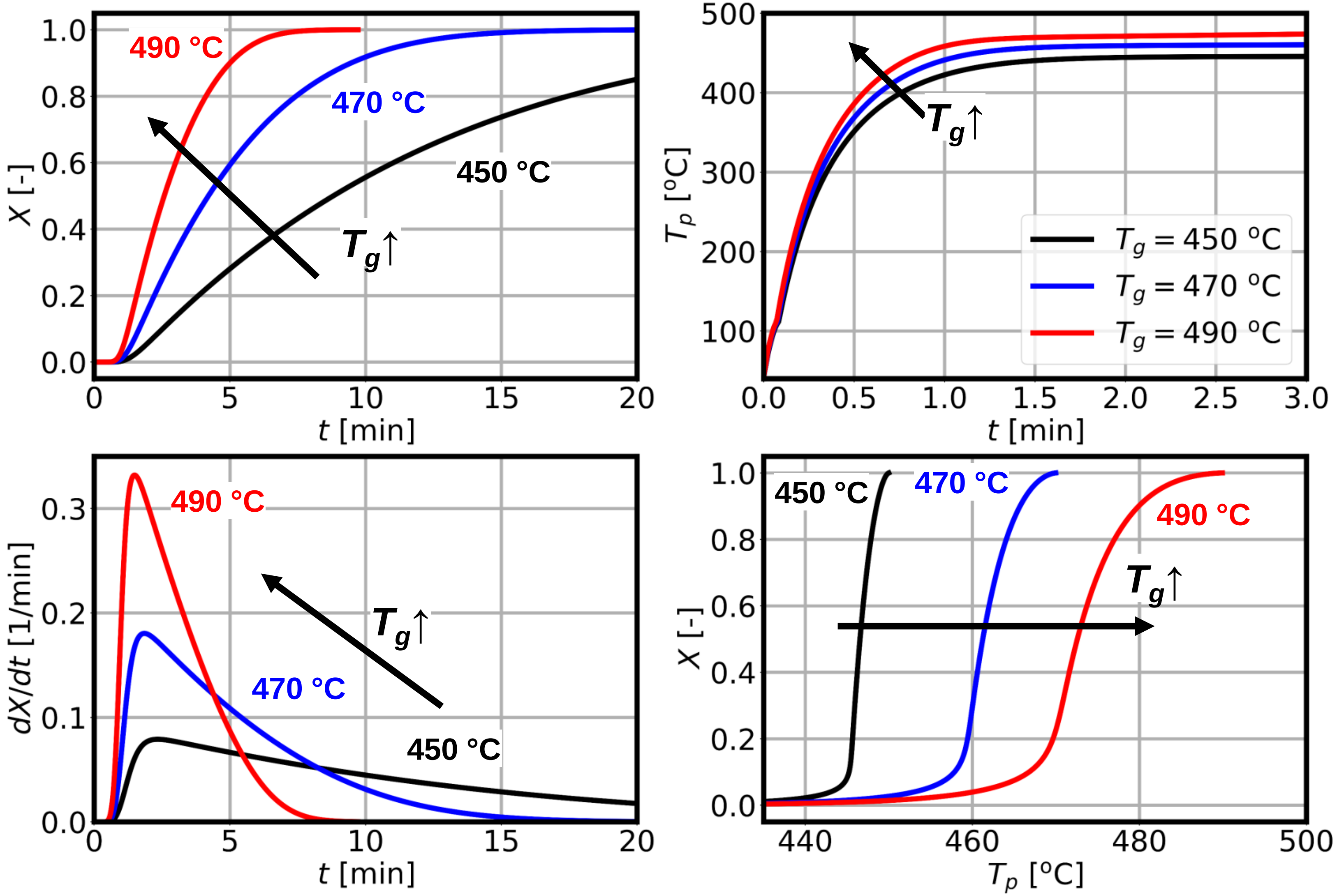
Effect of gas temperature

Increase of reactor temperature

- Faster heating of particle
- Faster conversion
- Higher particle temperature
- Increase of reaction rate
- Higher pyrolysis temperature

$d_{p,0}$ [mm]	2	3	4
T_g [°C]	450	470	490
α/α_0 [-]	1	2	5

LDPE



Effect of heat transfer coefficient

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Enhanced heat transfer

- Faster heating of particle
- Faster conversion
- Higher particle temperature
- Increase of reaction rate
- Higher pyrolysis temperature

$d_{p,0}$ [mm]	2	3	4
T_g [°C]	450	470	490
α/α_0 [-]	1	2	5