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Chemical Recycling of Thermoplastic Mixtures: Superposition Modeling and Experimental Validation

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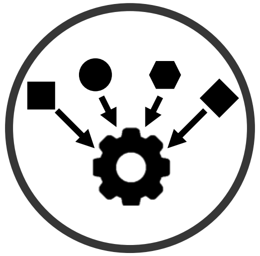
Modeling for plastic pyrolysis - Why?

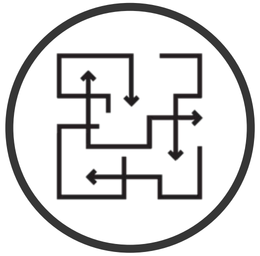
Substitution of fossil feedstocks by pyrolysis products of plastic waste

→ Reliable process design, optimization, and evaluation by simulation

Time-consuming and cost-intensive experimental work



Feedstock influence in plastic mixtures

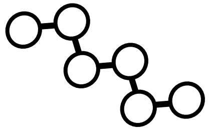


Polymer-dependent and complex degradation mechanism

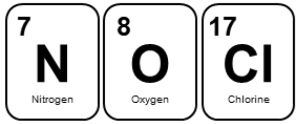
Superposition of mixture:
Linear combination of the single polymer behavior
→ **Simple access, but valid in applicability?**

Polymer selection

Selection criteria for investigated material:



Representative polymer types



Replication of key contamination sources

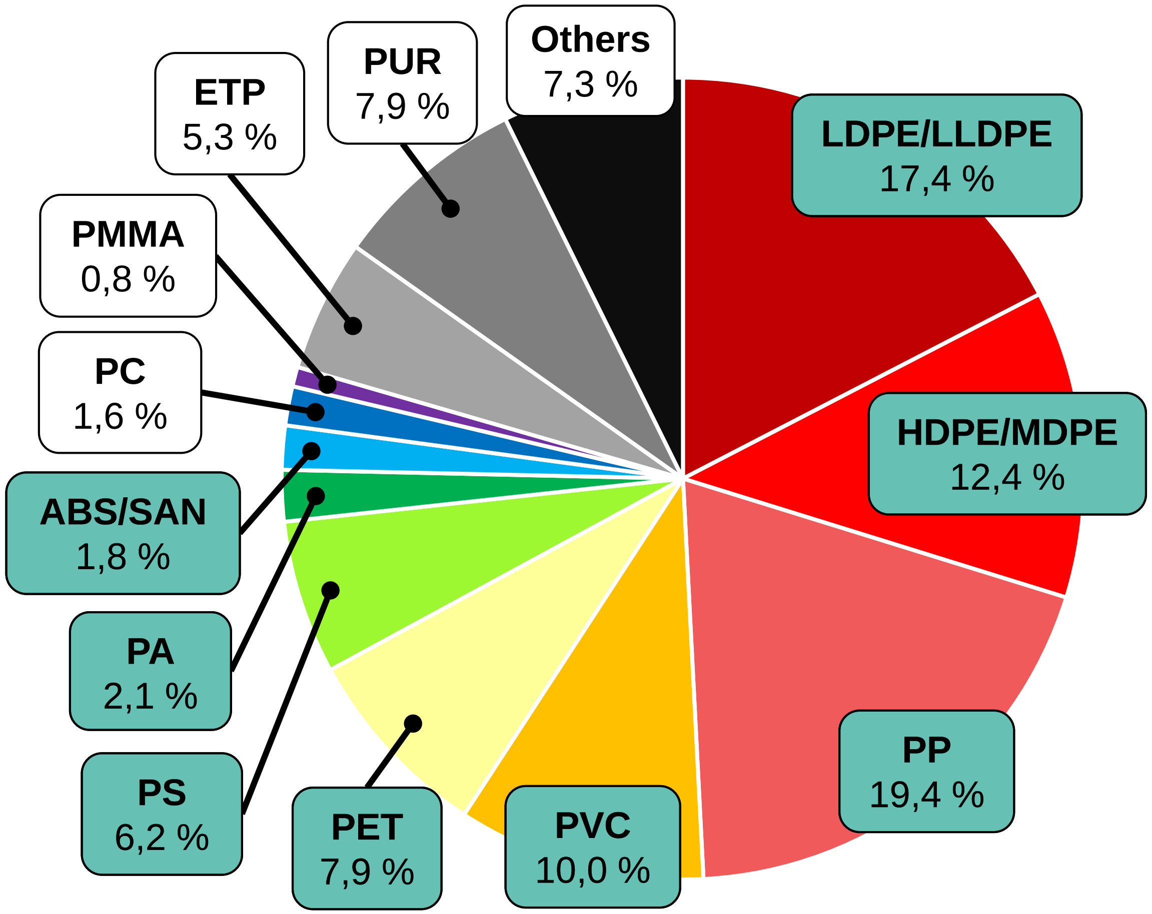
Prevention of additional feedstock influence

- **Thermoplastics** including main **heteroatom contaminants**:

Hydrocarbons:	LDPE, HDPE, PP, PS
O-containing:	PET, PA6
N-containing:	ABS, PA6
Cl-containing:	PVC

- Polymers free of additives (= **virgin polymers**)

Plastics production EU28+NO/CH in 2019:



PlasticsEurope (2020): Plastics – The facts.
Link: https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/

Pyrolysis energy demand: Modeling methodology

Karlsruhe Institute of Technology

Prediction of minimal process energy demand for mixed plastics pyrolysis

→ Superposition of experimentally accessible **pure polymer data** for mixed plastic behavior

Model equation

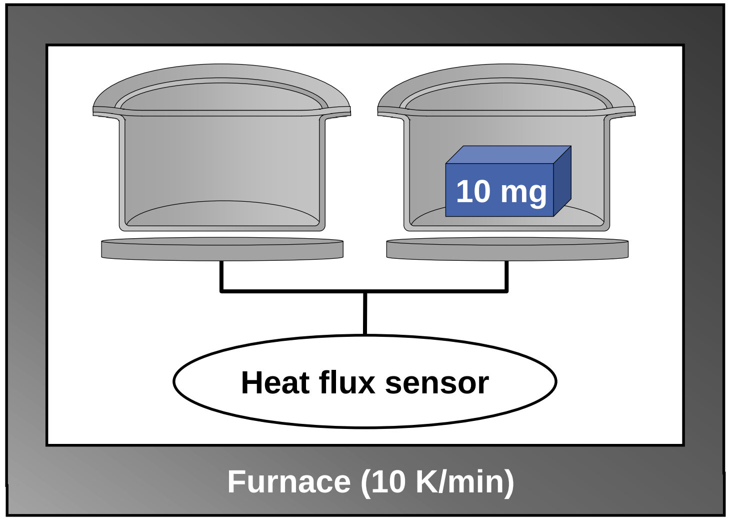
$$h_{py,min} = \sum_i x_i \left(h_{solid,i} + h_{f,i} + h_{melt,i} + h_{R,i}\right)$$

Superposition

(related to mass fraction)

Heating of solids	$c_{p,solid,i}$	via DSC
Heat of fusion	$h_{f,i}$	
Heating polymer melt	$c_{p,melt,i}$	
Reaction enthalpy	$h_{R,i}$	

Differential scanning calorimetry (DSC)



Netzsch 214 Polyma
Netzsch 204 F1 Phoenix

x_i Mass fraction polymer i in mixture

h Enthalpy

c_p Heat capacity

Validity of superposition approach
Transferability to processes in technical scale

Netsch et al. (2024), ACS Sustain. Resour. Manage.
doi: 10.1021/acssusresmgt.4c00109

Pyrolysis energy demand: Pilot-scale validation

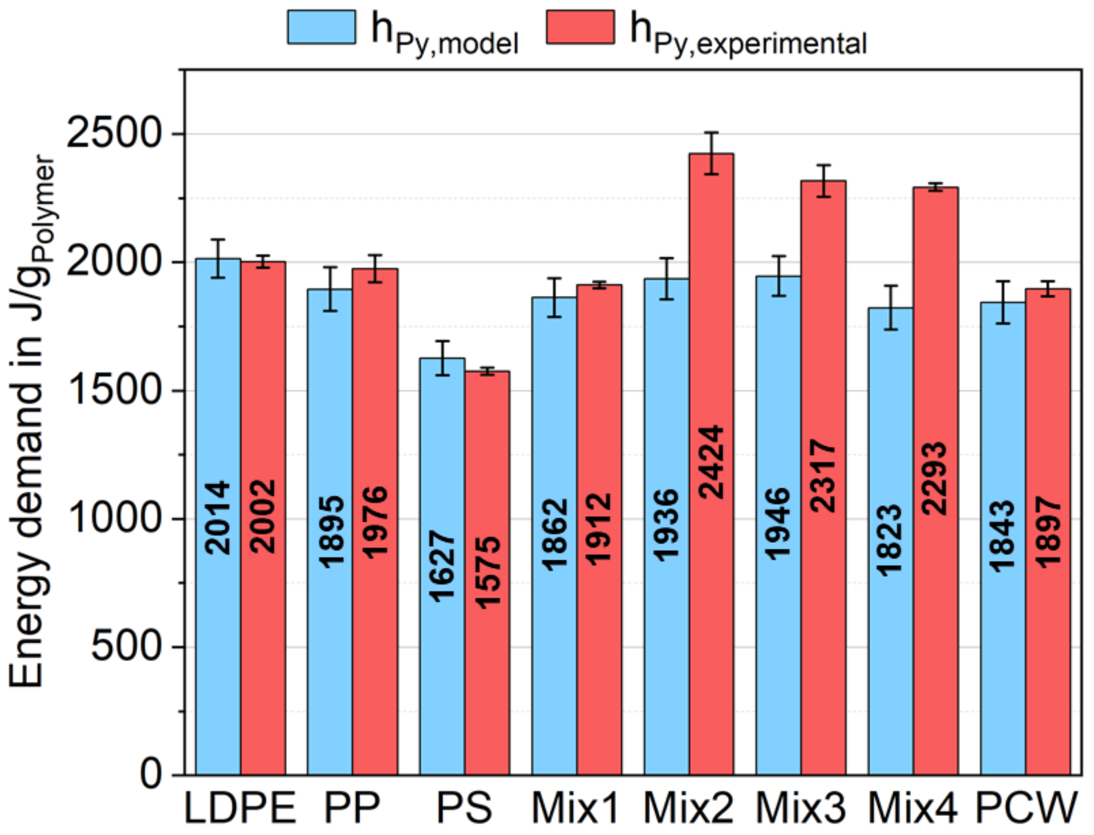
Composition of feedstock mixtures in m.%

Polymer	Mix 1	Mix 2	Mix 3	Mix 4	PCW
LDPE	40	70	72	50	30
HDPE	-	-	-	-	17
PP	30	20	20	15	25
PS	30	2	2	10	4
ABS	-	-	-	5	4
PET	-	4	4	10	10
PA6	-	2	2	5	6
PVC	-	2	-	5	4

PCW = Post-consumer waste

→ C-C-backbone
→ Heteroatom-free

→ O-, N-, and Cl-containing polymers



✓ Successful model validation

✗ Energy demand underestimated

Netsch et al. (2024), ACS Sustain. Resour. Manage.
doi: 10.1021/acssusresmgt.4c00109

Pyrolysis kinetics: Modeling methodology

Karlsruhe Institute of Technology

Prediction of degradation kinetics for mixed plastics pyrolysis

→ Superposition of experimentally accessible **pure polymer data** for mixed plastic behavior

Model equation

$$\frac{d\alpha_{Mix}}{dt} = \sum_i x_i \cdot \left(f(\alpha_i) \cdot k_{0,i} \cdot exp\left(-\frac{E_{A,i}}{RT}\right)\right)$$

Superposition

(related to mass fraction)

Conversion rate of volatilization

Arrhenius approach

n^{th} order kinetic model

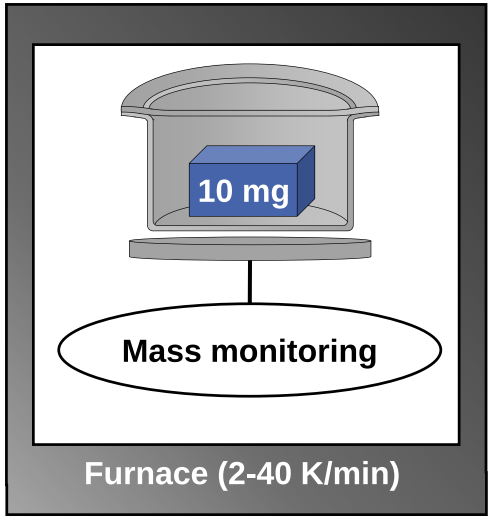
$k_{0,i}$

$E_{A,i}$

via TGA

- α Conversion of volatilizaton
- $f(\alpha)$ Kinetic model
- k_0 Pre-exponential factor
- E_A Activation energy

Thermogravimetry



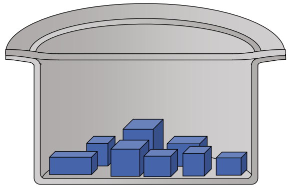
Netzsch TG 209 F1 Libra

Validity of superposition approach
Polymer-specific **interactions** during pyrolysis

Netsch et al. (2024), SSRN (under review).
doi: 10.2139/ssrn.4757121

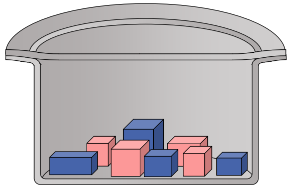
Pyrolysis kinetics: Experimental procedure

Temperature-dependent determination of volatile pyrolysis products formation and evaporation



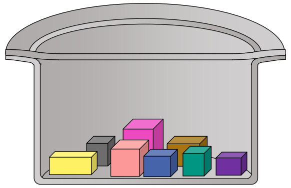
Virgin Polymer

Determination of individual kinetic parameters



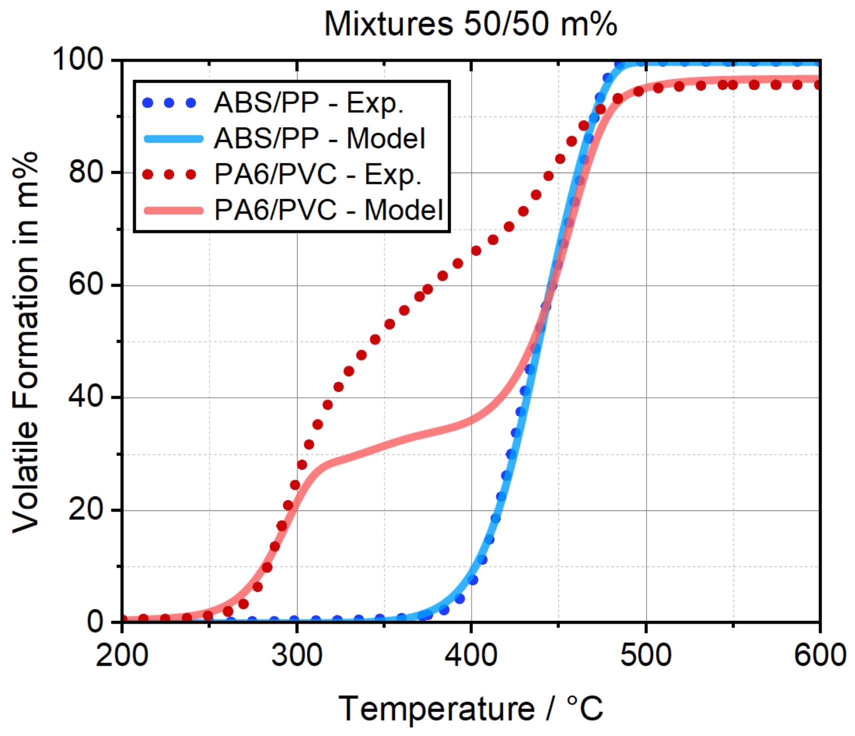
Binary mixtures

Systematic parameter variation in mixture
- Polymer types
- Mass fractions



Complex mixtures

Validation of identified interactions



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Kinetic analyses: Occurance of Interactions

Hydrocarbon Mixture

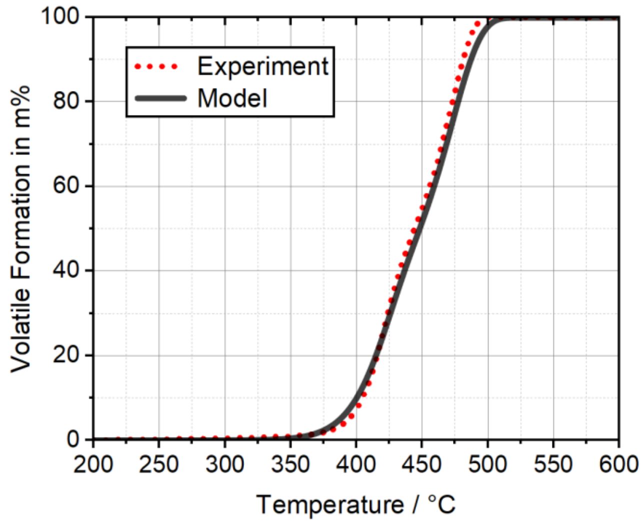
20% of each **LDPE, HDPE, PP, PS, ABS**

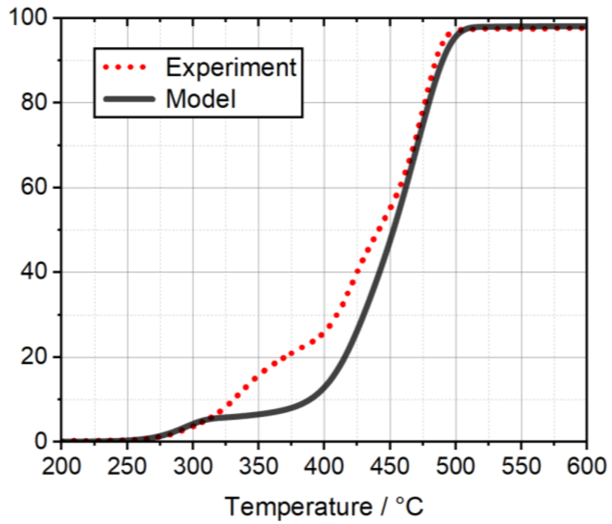
→ **Minor interactions**

Heteroatom-containing Mixture

20% of each **LDPE, HDPE** + 10% of each **PP, PS, ABS**, **PET, PA6,** and **PVC**

→ **Intensive interactions**

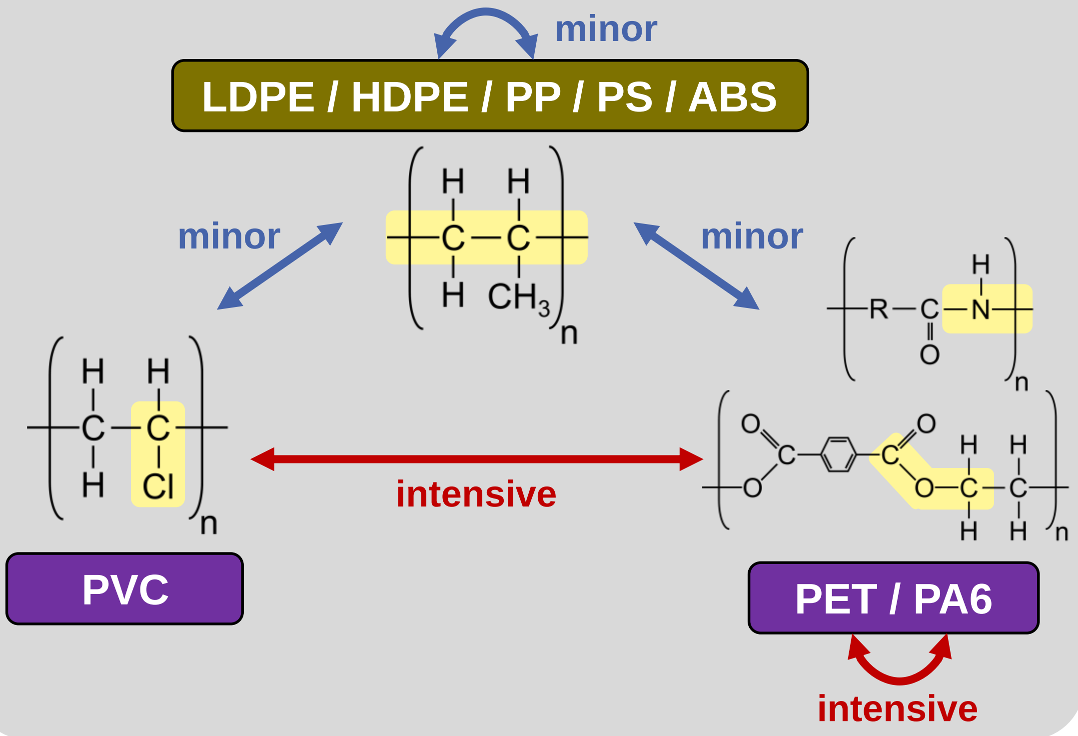




Polymer type dependence of interactions

→ **Minor** and **intensive** degradation interactions

→ Important role of heteroatoms and polymer backbone



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Wrap Up and Outlook:

Chemical Recycling of Thermoplastic Mixtures: Superposition Modeling and Experimental Validation

Karlsruhe Institute of Technology

Validity

Transferability

- Energy demand prediction
- Degradation kinetics reveals volatile formation
- Virgin polymers and simple mixtures:

LDPE / HDPE / PP / PS / ABS

Interactions

- Superposition-based modeling not applicable when interactions occur
- Complex mixtures including heteroatom-containing polymers

PVC | **PET / PA6**

- **Pending research questions**
  - → In-depth study of interactions
  - → Influence of additives
- **Model adaptions**
  - → Implementing further polymers or other waste components

Institute for Technical Chemistry

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