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# Reactor Modeling for Up Scaling a Plastic Pyrolysis Process

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## Abstract

For upscaling of a carrier fluid based plastic pyrolysis process, a model is needed, which can predict the conversion of different plastics at different operating conditions in a pipe reactor, but also correctly reproduces both reaction and physical mechanisms of the thermal cracking. For this reason, a pilot plant was built to generate data for the development of a kinetic model. In order to simplify the complex chemical reaction system, lumped kinetic modelling is used which combines product species to four pseudo components with a certain boiling cut. The heat transfer is described analogical to flow boiling (VDI Wärmeatlas). In this work, the modelled kinetic data of Polypropylene and Polyethylene high density cracking as well as the blank value test with pure carrier fluid are presented.

## Introduction

The European commission compiled a strategy for a circular economy. For this reason recycling of post-consumer plastics (PCP) has to be expanded (European Commission 2018). Therefore, feedstock recycling can be an option, aiming on products of lighter hydrocarbons, which can be reprocessed in petrochemical plants or used as fuels.

For this purpose, a solvent-based thermal cracking process has been developed in previous works. A highly aromatic and high boiling by-product of the refinery is used as carrier fluid. Thereby mechanical and thermal properties of plastics are improved to enhance processability. (Lederer 2013)

To investigate the complex reaction scheme of plastic pyrolysis, lumped kinetic modeling is used. For this reason, pseudo-components are defined as lumps, classified in boiling cuts, which simplifies the reaction systems. The exemplary mapping of a four-lump irreversible reaction system with no recombination to heavier products is shown in **Error! Reference source not found.** 1.

## Materials and Methods

A pilot plant with a maximal turnover of 600 grams plastics per hour generates the data for the kinetic model (Figure 2). The setup consists of two serial electrical heated plug flow reactors, which can be operated at temperatures between of

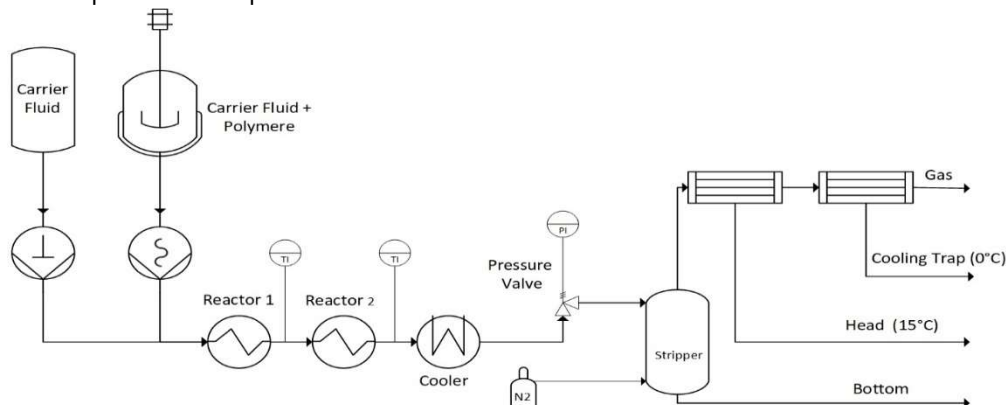


Figure 2: Scheme of the carrier fluid-based, thermal cracking pilot plant. (Schubert et al. 2018)

300-500°C, pressures up to 15 bar and residence times up to 15 minutes. The feed is a mixture of plastic and the carrier fluid in a ratio up to 1:4.

The pilot plant was used in previous works to build up a first model for polyethylene low density (PE-LD) (Schubert et al. 2018; Lechleitner et al. 2019). The experimental data base has been enlarged with polypropylene (PP) and polyethylene high density (PE-HD). Because of technical reasons a plastic conversion of 100% has to be achieved in the pilot plant. Therefore, it is not possible to find direct kinetic parameters of the plastic pyrolysis with this setup. Hence literature data from plastic pyrolysis is used to describe the reaction rate of the plastic to wax conversion,  $k_{Lit}$  in the model, as shown in Figure 3. For both plastics, PE-HD and PP, data from Bockhorn et al. (1999) is used. Bockhorn et al. (1999) found a preexponential factor of  $10^{17.78} \text{ min}^{-1}$  and an activation energy of 268 kJ/mol for PE-HD and a preexponential factor of  $10^{15.06} \text{ min}^{-1}$  and an activation energy of 220 kJ/mol for PP. However, the remaining reactions  $k_1$  to  $k_6$  have to be determined by fitting the experimental data.

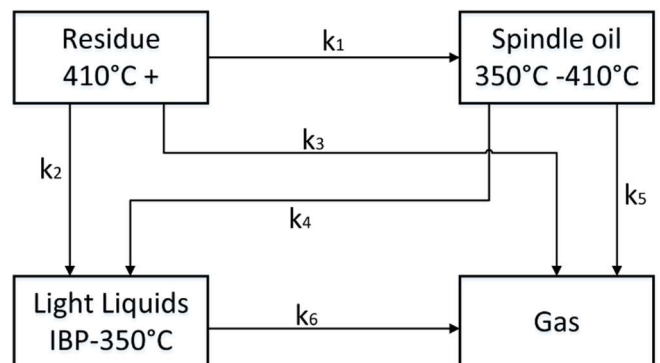


Figure 1: Four lump model with six possible irreversible, monomolecular, first order reactions for the carrier fluid.

First, a test campaign with pure carrier fluid is done and the kinetic parameters for a four lump system are determined (Figure 1). The carrier fluid consists out of Residue and Spindle Oil at the beginning and react to a mixture of all four lumps after passing the reactor.

In additional test campaigns, certain mixtures of carrier fluid and plastic are used to evaluate the reaction rate constants  $k_{1,P}$  to  $k_{6,P}$  in the lump system shown in Figure 3.

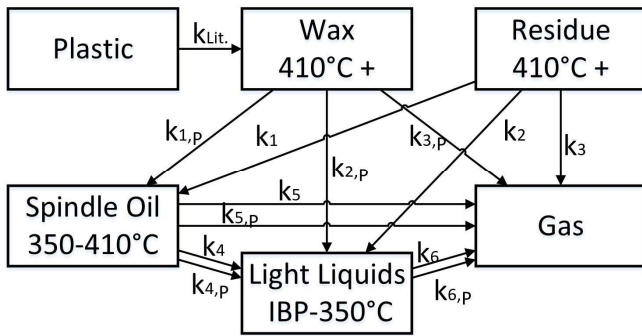


Figure 3: Six lump model with twelve possible irreversible, monomolecular, pseudo first order reactions.

Compared to the basic lump system of Figure 2, the advanced lump system of the carrier fluid with plastic species is extended with two new lumps: Wax and Plastic. It turned out to be sufficient to add these two lumps, however, the valuable products lumps do not distinguish between products originating from plastic or products originating from carrier fluid. With this approach the complex interactions between the two reactants are reflected in the model but have not be considered in mechanistic details. The character of the highly radical reaction sequences makes it practically impossible to assign the products to plastic or carrier fluid origin. All reaction rate constants  $k_i$  are described by the Arrhenius equation (1).

$$k_i = k_{\infty,i} \cdot e^{-\frac{E_{A,i}}{RT}} \quad (1)$$

Whereas  $k_{\infty,i}$  is the preexponential factor,  $E_{A,i}$  the activation energy,  $R$  the ideal gas constant,  $T$  the temperature and  $i$  the number of the reaction shown in

Figure 3.

To improve the accuracy of the Arrhenius constants also a heat balance was implemented in the model. The heat transfer coefficients are derived from "VDI Wärmeatlas" (Kabelac 2006) analogous to flow boiling. Thus, the heat transfer and the flow in the pipe reactors are described. In order to solve the model with simultaneous link between mass and heat balances, a reduction of the number of unknown parameters has to be carried out. The heat balance consists of the heat transfer into the reactor, the heats of vaporizing and the reaction enthalpies. Assuming paraffin cracking the difference of the heat of formation of paraffinic educts and grouped products stays nearly the same based on the mole increase for each product group. Product groups are aromatics, paraffins, olefins and naphthene's. The reaction enthalpy was determined based on the mean composition of the products.

However, to calculate the heat transfer, vaporizing of products, etc. it is necessary to know the properties of all species in the reactor. This is one big advantage of lumped systems, because it is possible to generate pseudo components in software's such as PetroSim based on the analytic data. So, each lump has its own physical properties and its condition can be evaluated in every environment.

The use of Arrhenius equations at a temperature changing system makes it necessary to evaluate the Arrhenius constants (preexponential factors) and the activation energies simultaneously. For this purpose, the optimization toolbox from Matlab has been used. This tool needs a high computational capacity and is speeded up with parallel

computing. Values from first, older models as well as the plastic kinetic data from literature are used as initial values for calculating the modeling. The optimization toolbox then calculates the mean squared error between modeled and measured data. Afterwards the algorithm minimizes the mean squared error by changes of the kinetic data until the predefined accuracy of the error is reached.

### Results

The first results show that there are reaction pathways which are much slower than other paths. Thus these reactions are neglected, and the outcome is a reduced six lump system as shown in Figure 4.

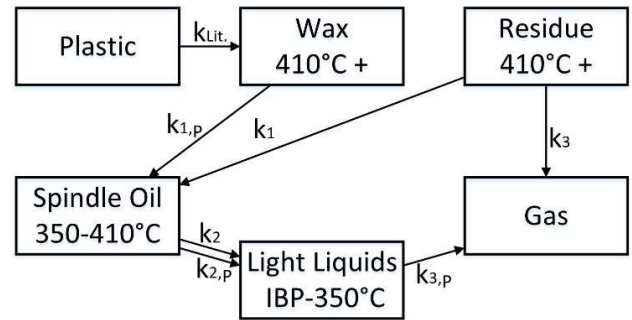


Figure 4: Reduced six lump model with seven possible irreversible monomolecular, pseudo first order reactions.

The reaction rates of this model are given in Table 1.

Table 1: Activation energies ( $E_A$ ) and reaction rates at 480°C of carrier fluid, PP and HDPE in the reduced six lump model.

	Carrier Fluid		PP		HDPE			
	k at 480°C [10 <sup>-4</sup> /s]	$E_A$ [kJ/mol]	k at 480°C [10 <sup>-4</sup> /s]	$E_A$ [kJ/mol]	k bei 480°C [10 <sup>-4</sup> /s]	$E_A$ [kJ/mol]		
$k_1$	38.7	202	$k_{1,P}$	217.6	233	$k_{1,P}$	538.8	228
$k_2$	113.7	226	$k_{2,P}$	120.4	231	$k_{2,P}$	64.9	233
$k_3$	7.2	240	$k_{3,P}$	22.9	267	$k_{3,P}$	8.4	274

The activation energies are in the same range as the used data from Bockhorn et al. (1999). The carrier fluid also can be pyrolyzed at these conditions and has another path than the plastics. The carrier fluid can crack directly to the Gas lump via reaction three (Figure 4). Furthermore, PP produces the fastest way light products (Light Liquid lump) via reaction two and the PE-HD pyrolysis yield is mainly heavy product (Spindle Oil lump) via reactions one at the pilot plant conditions.

However to determine the accuracy of the model, the deviation of the modeled kinetic data from the measured values is shown in Figure 5 to 7. If all points would lay on the diagonal in these diagrams, there would be a perfect fit. The absolute 5°C or 5 kg/kg deviation is also plotted in dashed lines.

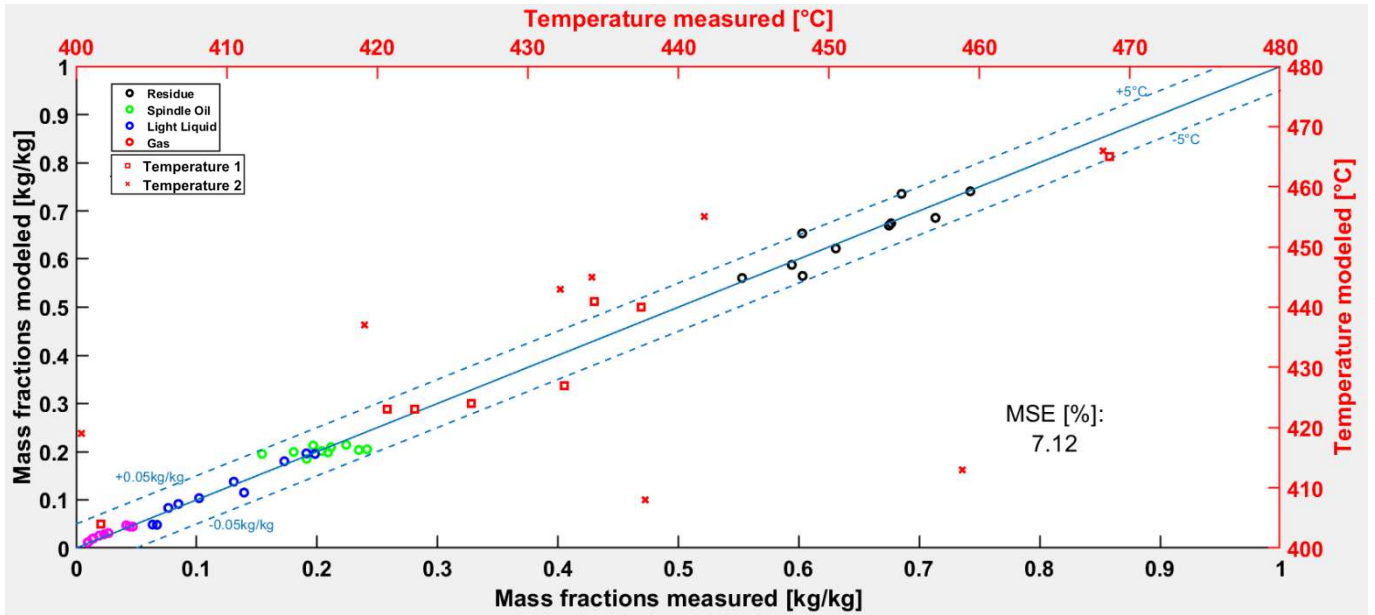


Figure 5: Measured and modeled temperatures (red) and mass fractions (circles) at the reactor outlet of test runs with pure carrier fluid. The ideal line is at the diagonal and the  $\pm 5$  kg/kg or  $\pm 5^\circ\text{C}$  deviation is marked with dashed lines.

The mean squared error (MSE) for the test campaign with pure carrier medium is 7.12%, in which the mass fractions have a very good consistency with the measured values. The temperatures have bigger deviations due to the pointwise measurements of the temperatures over the whole reactor coil.

In Figure 6 and 7 the MSE of the test campaign of PP and HDPE, 8.43% and 9.12% respectively, can be seen. These values have to be higher than the one with pure carrier fluid, because the results from the carrier fluid are needed to determine the kinetic constants of the plastics. Even though the test runs with plastics are done with different mixtures of plastic, the data fits very well. However, it can be concluded that the model also respects the interaction between the carrier fluid and the plastic.

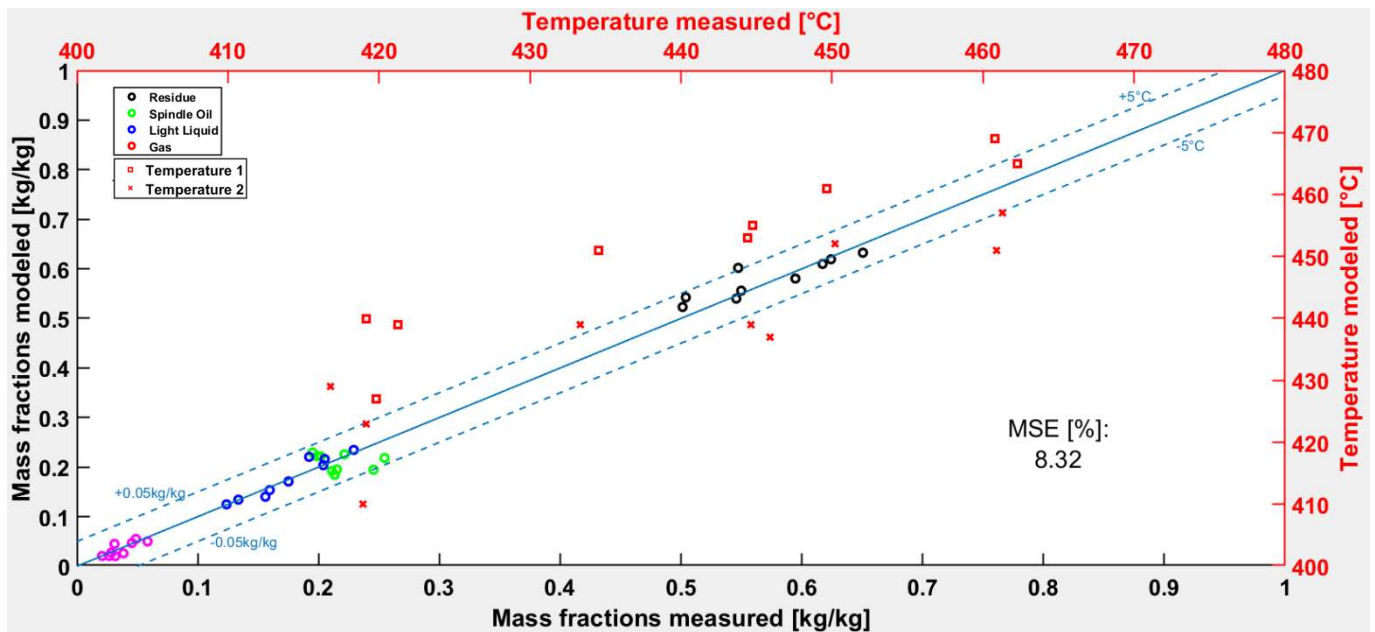


Figure 6: Measured and modeled temperatures (red) and mass fractions (circles) at the reactor outlet of test runs with carrier fluid mixed with 10 and 20% PP. The ideal line is at the diagonal and the  $\pm 5$  kg/kg or  $\pm 5^\circ\text{C}$  deviation is marked with dashed lines.



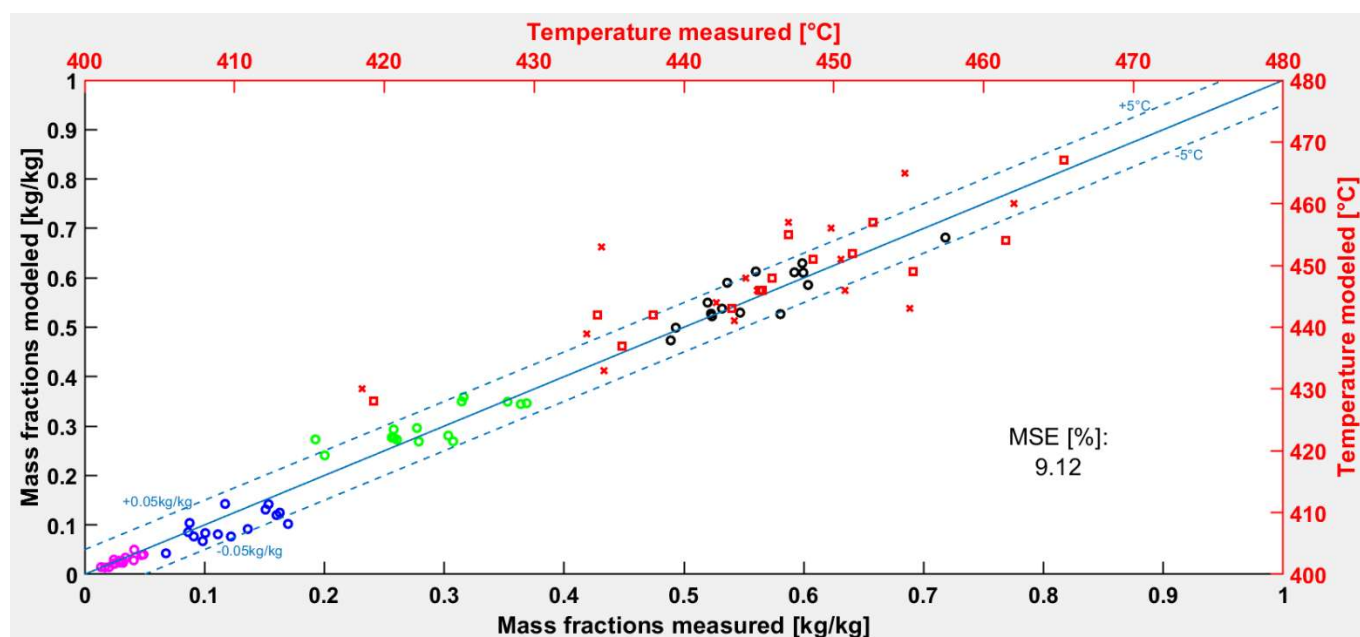


Figure 7: Measured and modeled temperatures (red) and mass fractions (circles) at the reactor outlet of test runs with carrier fluid mixed with 5 and 10% HDPE. The ideal line is at the diagonal and the  $\pm 5$  kg/kg or  $\pm 5^\circ\text{C}$  deviation is marked with dashed lines.

### Conclusion

The developed model describes the co-pyrolysis of the thermal cracking process with just a few lumps, although different sorts of polymers produce different kind of products at certain conditions. The model shows that HDPE yields in heavier products than PP, which has to be considered at a producing plant.

Hence a feedstock monitoring for such a chemical recycling process will be suggested. Furthermore, the carrier medium reacts directly to gas. The hydrogen content of the gas is very high, which results to lower hydrogen contents in the liquid products. This can lead to unwanted, higher coking rates, which is a common phenomenon in cracking processes, but have to be considered in commercial plants.

The performance of the model is improved by the more detailed evaluation of the temperature trend, but also the interactions between the carrier fluid and the polymers have a significant impact.

### Outlook

The experimental data will be further expanded to include more data points at different temperature-residence time couples and different pressures. The test runs shown in this work are done at 5 barg, at which products can be vaporized. At higher pressures, the vaporization can be inhibited in the pipe reactor, what results in longer residence times. In contrast the principle of Le Chatelier says that the pyrolysis should be enhanced with lower pressures. The physical impact of the pressure should already be considered by calculating the properties of species, but the potential chemical effect will be further investigated.

Additionally, also more common plastics and different carrier fluids will be tested to achieve a bigger data pool.

Moreover, the pilot plant will be improved to get advanced information of the pressure drop and reactor wall temperatures to get a more accurate temperature trend.

In addition, polycondensation reactions should be introduced in the model to evaluate the coking rate of different mixtures. Such an approach could quantify the runtime of a producing plant between cleaning stops.

Finally, the lumped kinetic model will be used to scale up an industrial plant.

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