

Determining values of reaction parameters of a reaction model
for a pyrolysis process

The invention relates to a computer-implemented method for determining values of reaction parameters of a reaction model for the pyrolysis of a plastic starting material into plastic products, a method for carrying out pyrolysis of a plastic starting material into plastic products, a system for data processing for carrying out the computer-implemented method, and a corresponding computer program product.

Europe alone generates several million tonnes of plastic waste every year, of which only a relatively small proportion is collected for recycling. Therefore, large amounts of plastic waste are incinerated, landfilled or shipped off. In order to increase recycling rates, for example, a deposit system can be introduced, plastic waste can be mechanically recycled or, for example, chemically reprocessed by depolymerization and repolymerization. A major challenge associated with plastic waste is the sorting of the different types of plastic and the contamination of the waste. Pyrolysis offers a relatively easy way to process mixed plastic waste or even plastic waste contaminated with other waste. In pyrolytic processes, valuable resources are generated from organic substances at high temperatures and in the absence of oxygen, which can be used as starting material for the reuse of plastic waste. In the course of pyrolysis, long-chain hydrocarbons from the plastic waste are split into molecules with a lower molecular weight by means of thermal energy. The products of the pyrolysis are liquid or gaseous and can be further processed in already existing infrastructure such as in a conventional petroleum refinery.

The chemical processes that take place during pyrolysis can hardly be described theoretically in detail due to their high complexity. In order to find suitable parameters, such as the pyrolysis duration and the pyrolysis temperature, of a planned pyrolysis, the pyrolysis can be modelled in a simplified form by means of a so-called lump model. The pyrolysis products are

typically classified into so-called lumps according to their boiling point. A lump includes pyrolysis products of a particular boiling point temperature range. Within the framework of known lump models, the individual lumps are typically connected to one another via monomolecular, irreversible reactions of the first order. Pyrolysis products of a lump with a high boiling point temperature range can decompose into pyrolysis products of any lump with a lower boiling point temperature range as part of the lump models. The reverse process, i.e. polymerization, is negligible in the context of pyrolysis and is typically not modeled in the context of lump models. Each of the reactions is modeled such that a rate or velocity of the respective reaction of a lump into another lump may be indicated. Experimental data from an experimental reactor are typically used to determine the parameters of the individual reactions.

For example, Lechleitner, A.E.; Schubert, T.; Hofer, W.; Lehner, M. Lumped Kinetic Modeling of Polypropylene and Polyethylene Co-Pyrolysis in Tubular Reactors. *Processes* 2021, 9, 34, <https://doi.org/10.3390/pr9010034>, shows a lump model for the pyrolysis of polypropylene and polyethylene in a tubular reactor. To describe the pyrolysis, a model with four lumps is used to classify the products resulting from the pyrolysis of plastic. All lumps are connected to each other by means of a monomolecular, irreversible first-order reaction. In addition, an initial process step is provided in which the starting material ("plastic"), which is not associated with a boiling point temperature range, is converted into products of the lump with the highest boiling point temperature range ("wax 420 °C"). According to the publication, this initial process step could not be evaluated (see Chapter 2.2.1, last paragraph). The total of six reactions k_i are modeled by means of the Arrhenius equation in order to detect the temperature dependence of the reactions. For each reaction k_i , an Arrhenius constant A_i and an activation energy $E_{A,i}$, i.e. a total of twelve parameters, are determined by means of experimental data.

Another model for the pyrolysis of LDPE ("low-density polyethylene") is known from Schubert, Teresa, et al. "4-Lump kinetic model of the co-pyrolysis of LDPE and a heavy petroleum fraction." *Fuel* 262 (2020): 116597. The model has four lumps, which in turn are each connected to one another by means of monomolecular, irreversible reactions of the first order.

According to Naik, Desavath V., et al. "Kinetic modeling for catalytic cracking of pyrolysis oils with VGO in a FCC unit." *Chemical Engineering Science* 170 (2017): 790-798, two problems typically occur in the calculation of kinetic parameters. On the one hand, there are problems with convergence when there are too many parameters. On the other hand, initializing the parameters can cause the optimization to reach a local minimum (which would calculate incorrect parameters). The publication shows a model with 5 lumps for the catalytic cracking of pyrolysis oils. The parameters of the 5-lump model were determined sequentially by means of a 3-lump and a 4-lump model in order to keep the number of parameters to be determined simultaneously low.

It is the object of the invention to alleviate or eliminate the disadvantages of the prior art. In particular, the object of the invention is to provide a computer-implemented method, a system for data processing and a computer program product for determining values of reaction parameters of a reaction model for the pyrolysis of a plastic starting material into plastic products, which allows simple, robust and efficient modeling of the pyrolysis without significantly impairing the accuracy of the modeling.

The object is achieved by a computer-implemented method for determining values of reaction parameters of a reaction model for the pyrolysis of a plastic starting material into plastic products, the method comprising the following steps:

- providing experimental data comprising a plurality of boiling point distributions of plastic products, wherein each boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration, wherein the boiling point

distributions are each binned into a number N lumps L_1 to L_N , wherein each lump is associated with a boiling point temperature range;

- determining a respective value of the reaction parameters by fitting the reaction parameters of the reaction model to the experimental data;

wherein the reaction model for each lump L_i from L_1 to L_{N-1} has a partial reaction determined by at least one reaction parameter for describing a conversion of plastic products of this lump into plastic products of a lump L_{i+1} lying below and adjacent with respect to the boiling point temperature range, wherein the reaction model has less than $N*(N-1)/2$ partial reactions.

The reaction models known hitherto from the prior art, as described, for example, in the abovementioned publication Lechleitner et al. (Processes 2021, 9, 34) comprise the partial reactions of each individual lump into all lumps lying below in the boiling point temperature range. As a result, the complexity of the model increases rapidly as the number of lumps increases, since $N*(N-1)/2$ partial reactions must be taken into account. The prior art therefore also strives to make do with as few lumps as possible. Lechleitner et al. Originally based on a 6-lump model, which was subsequently simplified to a 4-lump model (cf. Lechleitner et al., Chapter 2.2.1).

In the course of the present invention, it has now surprisingly been found that some partial reactions can be neglected without significantly impairing the accuracy of the reaction model. Compared to the prior art, the number of partial reactions is therefore reduced to less than $N*(N-1)/2$. By reducing the partial reactions, the convergence of the fit can be improved and, in general, the model complexity can be reduced for the same number of lumps - or the number of lumps taken into account can be increased for the same model complexity. The decisive factor here is the recognition of which partial reactions can be neglected and which can in no way be neglected without significantly worsening the accuracy of the reaction model. The most crucial partial reactions for the accurate description of

pyrolysis are those between adjacent lumps with respect to the boiling point temperature range. It has been found that partial reactions between lumps that are spaced apart with respect to the boiling point temperature range occur less frequently in pyrolysis and are less critical to the accuracy of the reaction model. Conversely, the reaction parameters of these less decisive partial reactions are more difficult to determine, since the experimental data only subordinate to these partial reactions and therefore the determination of the values of the reaction parameters in question are subject to greater experimental as well as statistical uncertainties. The modelling of such less frequent partial reactions can negatively influence the overall convergence of the fit. Therefore, it has turned out to be decisive in total that the reaction model for each lump L_i from L_1 to L_{N-1} has a partial reaction for describing a conversion of plastic products of this lump into plastic products of a lump L_{i+1} lying below and adjacent with respect to the boiling point temperature range, since these reactions are the most critical for describing the pyrolysis.

As part of a pyrolysis of a plastic starting material into plastic products, thermal energy is supplied to the plastic starting material, whereby long-chain molecules of the plastic starting material are split and plastic products are formed. For example, any type of plastic waste can be used as the plastic starting material. For example, the plastic starting material may comprise polypropylene or polyethylene. The plastic products may comprise, for example, (comparatively shorter-chain and/or lighter) hydrocarbons, such as, for example, heavy oils, spindle oils, gas oils, kerosene, naphtha, liquefied petroleum gas (LPG) or hydrocarbons which are gaseous under normal conditions.

Pyrolysis can be carried out in a pyrolysis reactor. For example, Lechleitner, A.E.; Schubert, T.; Hofer, W.; Lehner, M. Lumped Kinetic Modeling of Polypropylene and Polyethylene Co-Pyrolysis in Tubular Reactors. *Processes* 2021, 9, 34, <https://doi.org/10.3390/pr9010034> shows a pyrolysis reactor, which is designed as a tubular reactor. Decisive parameters of

the pyrolysis are the pyrolysis temperature, i.e. the temperature to which the plastic starting material is heated, as well as the pyrolysis duration, which indicates how long the pyrolysis temperature is maintained. In general, both a higher pyrolysis temperature and a longer pyrolysis duration lead to increased conversion into shorter-chain plastic products.

One step of the method relates to providing experimental data comprising a plurality of boiling point distributions of plastic products. The experimental data can be obtained, for example, by means of a plurality of pyrolysis runs, in the course of which pyrolysis is carried out in each case with the same plastic starting material in the same pyrolysis reactor at a pyrolysis temperature and a pyrolysis duration. Each pyrolysis run leads to plastic products that can be classified according to their boiling point. Each experimentally determined boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration. The experimental data preferably have boiling point distributions of a plurality of different pyrolysis temperatures and/or a plurality of different pyrolysis durations. The boiling point distributions are each binned into a number N lumps L_1 to L_N , each lump being associated with a boiling point temperature range. A measured boiling point distribution can, for example, originally exist continuously as a function of the boiling point temperature, into which lumps are binned and consequently exist in the form of a histogram. For example, nine lumps L_1 to L_9 may be provided, into which the individual boiling point distributions are each binned. The first lump L_1 may have, for example, the plastic starting material and a boiling point temperature range above 600 °C. The second lump L_2 may, for example, have a boiling point temperature range between 450 °C and 600 °C and may be referred to as a bottom product or heavy product. The third lump L_3 may have heavy oil and may have a boiling point temperature range between 400 °C and less than 450 °C. The fourth lump L_4 may have spindle oil and may have a boiling point temperature range between 350 °C and less than 400 °C. The fifth lump L_5 may have gas oil and may have a boiling point temperature range between 225 °C and

less than 350 °C. The sixth lump L6 may have kerosene, for example, and have a boiling point temperature range between 165 °C and less than 225 °C. The seventh lump L7 may have, for example, naphtha and have a boiling point temperature range between 20 °C and less than 165 °C. The eighth lump L8 may have, for example, liquefied petroleum gas (LPG) and a boiling point temperature range between -120 °C and less than 20 °C. In this example, the eighth lump L8 may predominantly comprise hydrocarbons having a number of hydrocarbon atoms between two and four (for example, ethene, ethane, propane, propene, butane, and/or butene). The ninth lump L9 may, for example, have gaseous hydrocarbons with a boiling point of less than -120 °C under normal conditions. In this case, the ninth lump L9 may predominantly comprise methane. Alternatively, more or fewer lumps may be provided. For example, two or more of the lumps exemplified above may be combined. For example, other lumps with other boiling point temperature ranges may be provided.

In the next step, a value of the reaction parameters is determined by fitting the reaction parameters of the reaction model to the experimental data. The reaction model describes the conversion of the plastic products and the plastic starting material of the respective lumps into plastic products of other lumps. According to the model, the lumps are preferably associated with first-order monomolecular, irreversible partial reactions. For example, lump L1 is connected to lump L2 with a partial reaction r_{12} , where the following relation applies: $r_{12} = k_{12} \cdot X_{\text{Lump1}}$. k_{12} is a reaction rate between lump L1 and lump L2. X_{Lump1} is a mass fraction of plastic products in lump L1 (relative to the total mass of all lumps). The individual partial reactions can be described by means of the Arrhenius equation in order to take into account the dependence of the pyrolysis temperature T :

$$k_{12} = k_{12} \times \exp\left(\frac{-E_{A12}}{RT}\right)$$

k_{12} is an Arrhenius constant (also known as a pre-exponential factor or frequency factor). E_{A12} describes the activation energy

of the respective conversion, in this case the activation energy for a conversion of plastic products from lump L1 to lump L2. R is the universal gas constant and T is the (absolute) pyrolysis temperature. In the event that each partial reaction is modeled by means of an Arrhenius equation, each partial reaction is consequently described by means of two reaction parameters. The reaction parameters per partial reaction from a lump L_i to a lump L_j in this case are k_{ij} and E_{Aij} .

For each lump L_i from L_1 to L_{N-1} , the reaction model has a partial reaction determined by at least one reaction parameter for describing a conversion of plastic products of this lump into plastic products of a lump L_{i+1} lying below and adjacent with respect to the boiling point temperature range. i is an index that can assume integer positive values between one and the number of lumps N . The reaction model refers to pyrolysis in a pyrolysis reactor. The experimental data are experimental data obtained by means of the pyrolysis reactor. The reaction model is a function of pyrolysis temperature and pyrolysis duration.

A pyrolysis model with three lumps $L1$, $L2$ and $L3$, in which a partial reaction from lump $L1$ to lump $L2$ and a partial reaction from lump $L2$ to lump $L3$ is taken into account, may have the following form, for example.

$$k_{12} = k_{12} \times \exp\left(\frac{-E_{A12}}{RT}\right)$$

$$k_{23} = k_{23} \times \exp\left(\frac{-E_{A23}}{RT}\right)$$

$$\frac{dX_1}{dt} = -k_{12} \times X_1$$

$$\frac{dX_2}{dt} = -k_{23} \times X_2 + k_{12} \times X_1$$

$$\frac{dX_3}{dt} = k_{23} \times X_2$$

X_1 , X_2 and X_3 denote the respective mass fraction in lump $L1$,

lump L2 and lump L3, respectively. t denotes the pyrolysis duration. The reaction rates k_{12} and k_{23} can be described by means of the Arrhenius equation, which also includes the pyrolysis temperature T . X_1 , X_2 and X_3 are in this case functions of the pyrolysis duration t and the pyrolysis temperature T , therefore, for example, $X_1 = X_1(t, T)$. In this simplified case, the pyrolysis model has a total of four reaction parameters: k_{12} and E_{A12} , and k_{23} and E_{A23} , the values of which can be determined by means of the method according to the invention.

The experimental data represent experimental data from pyrolysis runs for a single value pair of pyrolysis temperature and pyrolysis duration. By means of the reaction model, it is possible to interpolate between the experimental data on these value pairs or to extrapolate beyond them. By means of the reaction model, the boiling point distribution of plastic products of a pyrolysis with any pyrolysis temperature and any pyrolysis duration can be estimated. Typically, the pyrolysis temperature is between 300 °C and 650 °C. The pyrolysis duration is typically between a few minutes and up to a few hours. For example, the pyrolysis duration may have a value between 3 minutes and 100 minutes.

The values of the reaction parameters are determined by fitting the reaction parameters of the reaction model to the experimental data. In this case, fitting means that the values of the reaction parameters are selected in such a way that the reaction model reproduces the experimental data as accurately as possible. For example, a sum of least squares of the reaction model to the experimental data may take the smallest possible value (also known as the least squares method). For example, fitting may include minimizing a distance from the experimental data to the reaction model. The distance can be calculated, for example, by means of a target function. For example, the reaction parameters can be varied as part of the fitting, so that a minimum distance of the experimental data from the reaction model is found. The values of the reaction parameters determined in this way lead to the minimum distance of the

reaction model from the experimental data.

In the prior art, reaction models with $N*(N-1)/2$ partial reactions are known, i.e. partial reactions between all lumps are taken into account. Compared to the prior art, the number of partial reactions is reduced to less than $N*(N-1)/2$. By reducing the partial reactions, the convergence of the fit can be improved and the model complexity can generally be reduced. The decisive factor here is which partial reactions can be neglected and which can in no way be neglected without significantly worsening the accuracy of the reaction model. As described in more detail above, it is decisive in total that the reaction model for each lump L_i from L_1 to L_{N-1} has a partial reaction for describing a conversion of plastic products of this lump into plastic products of a lump L_{i+1} lying below and adjacent with respect to the boiling point temperature range, since these reactions are the most critical for describing the pyrolysis.

For example, the reaction model may not have a partial reaction r_{1N} for a reaction between the first lump L_1 and the last lump L_N . This partial reaction has the largest distance in the boiling point temperature range of the two lumps involved and is therefore particularly irrelevant for the description of the pyrolysis. Conversely, the reaction parameters of this partial reaction r_{1N} in particular cannot be easily initialized in the context of the fit and can also negatively influence the convergence of the fit.

In general, the reaction model may have N lumps and less than $N*(N-1)/M$ partial reactions, where M is a natural number greater than two that is less than the number of lumps N (i.e., $N > M$). For example, the reaction model may have a number N of at least 4 lumps and less than $N*(N-1)/3$ partial reactions.

The number N of lumps is preferably at least three, more preferably at least four, more preferably at least five, more preferably at least six, more preferably at least seven, more preferably at least eight, more preferably at least nine, more

preferably at least ten, more preferably at least eleven, more preferably at least twelve. The number N of lumps may be at least seven, for example. For example, the number of lumps may be at least twenty. Due to the reaction model with a smaller ratio of partial reactions or reaction parameters to the number of lumps compared to the prior art, it is possible to use a relatively large number of lumps without impairing the convergence of the fit. This allows to increase the granularity of the prediction without significantly degrading the prediction quality.

For example, the reaction model may have exactly $(N-1)$ partial reactions. In this case, the reaction model only considers partial reactions between adjacent lumps with respect to the boiling point temperature range. In this case, the reaction model can be referred to as a sequential reaction model and has only sequential partial reactions. In this case, the reaction model maps a single reaction path from the first lump L_1 to the last lump L_N . For example, conversion from a first lump L_1 to a third lump L_3 may occur only via conversion of lump L_1 to a second lump L_2 and further conversion of lump L_2 to lump L_3 , where lump 2 is between lump L_1 and lump L_3 with respect to the boiling point temperature range and is adjacent to both lump L_1 and lump L_3 . Alternative paths, for example a direct conversion from lump L_1 to lump L_3 (which are not contiguous with respect to the boiling point temperature range) are not provided in the context of the sequential reaction model and therefore not possible in the context of the reaction model. The sequential partial reactions are the most decisive partial reactions between the lumps in terms of an accurate description of the pyrolysis. By restricting the reaction model to the $(N-1)$ sequential partial reactions, convergence problems can be avoided as far as possible; furthermore, the fit and thus the values of the reaction parameters do not depend on initial starting values of the reaction parameters for the fit. The reaction model accurately maps the pyrolysis despite the simplification compared to known and more complex reaction models. In addition, the restriction of the reaction model to

the (N-1) sequential partial reactions makes it possible to take into account a significantly larger number of lumps without increasing the overall model complexity.

The invention further relates to a method for determining values of reaction parameters of a reaction model for pyrolysis of a plastic starting material into plastic products with a computer-implemented method according to the invention for determining values of reaction parameters of a reaction model for pyrolysis of a plastic starting material into plastic products, wherein the provision of experimental data comprises the following steps:

- carrying out a plurality of pyrolysis runs with different pyrolysis temperature and/or pyrolysis duration in a pyrolysis reactor;
- measuring a boiling point distribution of plastic products per pyrolysis run, wherein each boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration;
- binning of the individual boiling point distributions into the N lumps L_1 to L_N , wherein a boiling point temperature range is associated with each lump in order to obtain experimental data.

The experimental data were obtained by means of a plurality of pyrolysis runs, in which a pyrolysis was carried out in each case with the same plastic starting material in the same pyrolysis reactor at a pyrolysis temperature and a pyrolysis duration. Each pyrolysis run leads to plastic products that can be classified according to their boiling point.

For each pyrolysis run, the boiling point distribution of the plastic products is measured and thus the plastic products are classified according to their boiling point. Lechleitner, A.E.; Schubert, T.; Hofer, W.; Lehner, M. Lumped Kinetic Modeling of Polypropylene and Polyethylene Co-Pyrolysis in Tubular Reactors. *Processes* 2021, 9, 34. <https://doi.org/10.3390/pr9010034> shows, for example, an experimental reactor ("pilot plant") which has a

flash vessel (can also be referred to as an evaporator) downstream of the pyrolysis reactor (i.e. downstream of the pyrolysis reactor). With the help of the flash vessels, plastic products that are present in gaseous form can be separated. For this purpose, a temperature and a pressure in the flash vessel can be set in order to influence the separation (the so-called separation cut). Plastic products that are gaseous under the respective conditions (i.e. pressure and temperature) in the flash vessel can leave the evaporator and can be directed to one or more cold traps. The plastic products removed in this way can be weighed, cooled and mixed, for example, with a bottom product of the flash vessels to form a liquid end product, which can consequently be analyzed. Plastic products that are gaseous below 0 °C can be collected, for example, with a gas balloon and then further analyzed.

The gaseous plastic products can be analysed, for example, by means of gas chromatography in accordance with DIN 51666:2007-01. As a result, for example, the calorific value, the specific gravity and/or a detailed molecular composition of the plastic products can be determined. The boiling point distribution of the collected liquid plastic products and any carrier medium can be analyzed, for example, according to ASTM D7169-20e1 by means of simulated distillation. The boiling point distribution is weighted according to mass.

Each experimentally determined boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration of the respective pyrolysis run.

The boiling point distributions are each binned into a number of N lumps L_1 to L_N , each lump being associated with a boiling point temperature range in order to obtain the experimental data. Binning means a division or subdivision of the boiling point distribution into classes, where the classes in this case are the lumps.

The invention further relates to a method for carrying out a

pyrolysis of a plastic starting material into plastic products, comprising the following steps:

- determining values of reaction parameters of a reaction model of pyrolysis via the computer-implemented method according to the invention;
- specifying an intended boiling point distribution;
- determining a pyrolysis temperature and a pyrolysis duration by minimizing a distance of a boiling point distribution calculated by means of the reaction model and the previously determined values of the reaction parameters from the intended boiling point distribution; and
- carrying out the pyrolysis with the predefined pyrolysis temperature and the predefined pyrolysis duration.

The pyrolysis model is a function of pyrolysis duration and pyrolysis temperature. By means of the pyrolysis model with the previously determined reaction parameters of the partial reactions, a (theoretical) boiling point distribution of the plastic products can be calculated for each value pair from the pyrolysis duration and the pyrolysis temperature. The calculated boiling point distribution has the same lumps as the pyrolysis model.

In a subsequent step, an intended boiling point distribution is specified. The predetermined boiling point distribution can be continuous or in the form of a histogram. The predetermined boiling point distribution may, for example, have the same lumps as the reaction model. The specified boiling point distribution indicates which boiling point distribution the plastic products should ideally have after pyrolysis of a plastic starting material. The intended boiling point distribution can indicate into which lumps the plastic products should preferably be converted by the pyrolysis.

In the next step, the pyrolysis temperature and the pyrolysis duration are determined by minimizing a distance between a boiling point distribution calculated by means of the reaction model and the previously determined values of the reaction

parameters and the intended boiling point distribution. For example, the predetermined boiling point distribution and the calculated boiling point distribution can each be present as a histogram and have the same lumps. In this example, the distance can be a sum of the differences in each case of a predetermined accumulation value of a lump of the predetermined boiling point distribution from a corresponding calculated accumulation value of a lump of the calculated boiling point distribution. The distance can have a weighting, for example, one lump can be weighted more strongly than the other lumps, so that the model particularly accurately depicts the more heavily weighted lump. The pyrolysis temperature and the pyrolysis duration are each variables of the reaction model (and also of the pyrolysis). The predefined pyrolysis temperature and the predefined pyrolysis duration are those values of these variables that result in the minimum distance of the specified boiling point distribution from the calculated boiling point distribution.

In the last step, the pyrolysis is carried out with the predefined pyrolysis temperature and the predefined pyrolysis duration. For this purpose, the pyrolysis reactor is operated in such a way that the predefined pyrolysis temperature and the predefined pyrolysis duration are reached and maintained. For example, the same plastic starting material may be used as was used in the pyrolysis runs previously performed to determine the reaction parameters of the partial reactions. For example, the same pyrolysis reactor can be used for the pyrolysis as was used in the pyrolysis runs previously carried out to determine the reaction parameters.

A further method for carrying out pyrolysis of a plastic starting material into plastic products comprises the following steps:

- determining values of reaction parameters of a reaction model of pyrolysis via the computer-implemented method according to the invention;
- calculating a plurality of boiling point distributions by means of the reaction model and the previously determined values

of the reaction parameters, each calculated boiling point distribution being associated with a pyrolysis temperature and a pyrolysis duration;

- selecting one of the calculated boiling point distributions to determine the pyrolysis temperature and pyrolysis duration; and

- carrying out the pyrolysis with the predefined pyrolysis temperature and the predefined pyrolysis duration.

The calculated boiling point distribution can be selected, for example, on the basis of predefined criteria. For example, a boiling point distribution having a maximum in a predefined lump may be selected. Pyrolysis at the predefined pyrolysis temperature and predefined pyrolysis duration may result in a boiling point distribution of the plastic products substantially corresponding to the selected boiling point distribution.

The invention further relates to a system for data processing comprising means for carrying out the steps of the computer-implemented method according to the invention. For example, the data processing system may be a computer, such as a laptop. For example, the data processing system may include a processor and a hard disk.

The means of the data processing system may further be configured to perform the following step:

- calculating a pyrolysis temperature and a pyrolysis duration by means of the reaction model and the previously determined values of the reaction parameters, wherein the pyrolysis temperature and the pyrolysis duration are defined such that a distance of a boiling point distribution calculated by means of the reaction model from an intended boiling point distribution is minimized.

The invention further relates to a computer program product comprising instructions that, when the program is executed by a computer, cause the computer to perform the steps of the computer-implemented method according to the invention.

The present invention will be explained in more detail with reference to exemplary embodiments illustrated in the figures, to which, however, it is not intended to be limited.

FIG. 1 schematically shows the structure of a pyrolysis reactor

FIG. 2 schematically shows a reaction scheme between two lumps in the context of kinetic reaction modelling of lumps

FIG. 3 shows a schematic representation of a reaction model for pyrolysis with nine lumps

FIG. 4 shows a comparison of the kinetic decay rates of different plastic starting materials

FIGS. 5A-5I show the deviations of the individual lumps of the reaction model as a function of the mean pyrolysis temperature

FIG. 6 shows a measured boiling point distribution (dotted line) compared to a boiling point distribution calculated using the reaction model (solid line)

FIGS. 7A-7I show a parameter study of various pyrolysis temperatures and mass flows in the pyrolysis reactor

Example 1

Example 1 relates to a sequential reaction model with nine lumps for the co-pyrolysis of plastic mixtures with a heavy oil fraction and the determination of the reaction parameters of the sequential reaction model. The plastic starting material in this case is the plastic mixture with the heavy oil fraction.

In this example, a nine lump kinetic reaction model was used. The reaction model has exclusively sequential partial reactions without alternative reaction paths. This circumstance enabled an uncomplicated implementation of the reaction model. The reaction model was established based on experimental data collected in a

laboratory-sized pyrolysis reactor in the form of a tubular reactor with a maximum throughput of 2500 g/h.

For the determination of the reaction model, three different types of plastics, mixed with a heavy oil fraction of different composition, were used as plastic starting material for the pyrolysis reactor. The plastics were untreated polypropylene (PP), low density polyethylene (LDPE) and high density polyethylene (HDPE) in powder form (see Table 1). Due to the physical dimensions of the reactor, in particular the narrow inner diameter of the tubes, the maximum particle size of the plastic had to be less than 500 μm . For this reason, the plastic was ground under cryogenic conditions before use for the experiments. The maximum ratio of plastic to carrier medium that could be achieved by the design of the system was 30 % by weight. Higher proportions of plastic would have led to blockages in the feed system of the reactors.

The organic carrier medium used was a readily available by-product from the petroleum refining process. It is a predominantly aliphatic medium with an aromatics content of about 25 %, a density of 880 kg/m^3 and a calorific value of 45 MJ/kg. Since the carrier medium is also cracked under the conditions prevailing in the reactor, the (kinetic) reaction parameters were determined in preliminary experiments only for the carrier medium.

Table 1. Specifications of the plastic types used for the pyrolysis experiments (i.e. plastic starting products)

	Molecular mass (Mw)	Net calorific value	Gross calorific value	TGA inflection point
	(g/mol)	(kJ/kg)	(kJ/kg)	(°C)
Polypropylene	$3,624 \cdot 10^5$	44,510	47,343	484
LD Polyethylene	$2.3834 \cdot 10^5$	43,409	46,159	500
HD Polyethylene	$2.0275 \cdot 10^5$	43,525	46,409	509

Experimental set-up and experimental procedure

The experiments were carried out in a pyrolysis reactor 1 (also referred to as a laboratory reactor), which was built specifically for this process and is shown schematically in FIG. 1. Pyrolysis reactor 1 substantially corresponds to the reactor described in *Schubert T, Lehner M, Hofer W (2018) Experimental and modeling approach of LDPE thermal cracking for feedstock recycling, 14th MINISYMPOSIUM CHEMICAL & PROCESS ENGINEERING and 5th PARTICLE FORUM Book of Abstracts* with some adjustments to the experimental procedure.

The liquid carrier medium and the plastic powder were mixed manually before the experiment runs in predefined mass ratios between 0 and 30 % by weight of plastic. The mixture (i.e. the plastic starting material) was then filled into a storage container 2 and continuously stirred there. The plastic starting material is conveyed from the reservoir 2 by means of a pump 3 (in this case an eccentric screw pump). Two reactors 4 and 5 were arranged downstream of the pump 3. Reactors 4, 5 were coils 6, which were heated in sand baths 7 to the required temperature range of 400 °C to 550 °C. The length of each reactor coil 6 could be varied between 8 m and 24 m in order to further adjust the residence time (i.e. the pyrolysis duration) without changing the flow pattern. The actual pyrolysis took place in reactors 4 and 5. After the medium (i.e. the plastic products after pyrolysis) had passed the reactors 4, 5, it was cooled to about 90 °C by an air cooler 8 and an oil cooler 9. The pressure in the system could be regulated with a valve 10 (either with a manual valve or with an automatic diaphragm valve) to relax the products to atmospheric pressure. For all experiments, the pressure in the system was regulated to 15 bar. Following the oil cooler 9 and the valves 10, a flash vessel 11. The plastic products, which were gaseous under the conditions in the flash vessel 11, left the latter through a head part and were passed to a first cold trap 12 and a second cold trap 13. The first cold trap 12 was set to a temperature of 15 °C, while the second cold trap 13 was set to a temperature of 0 °C. Plastic products present at the bottom of the flash vessels 11 are referred to as

bottom products and have left the flash vessels through a bottom line 14. Plastic products collected by means of the first cold trap 12 are referred to as top products and have left the first cold trap 12 through a top line 15. Plastic products collected by means of the second cold trap 13 are referred to as light products and have left the second cold trap 13 through a light product line 16. The pyrolysis products (i.e. the plastic products), which were gaseous below 0 °C after the second cold trap 13, were sampled with a gas balloon (not shown). After product removal, all liquids were weighed, cooled in a freezer and mixed into the final liquid product that was analyzed.

The experimental conditions, i.e. the pyrolysis temperature and the pyrolysis duration, were mainly varied by the temperature of the sand baths 6, the length of the reactors 4, 5 and the output of the pump 3. The pump output regulated the mass flow in the reactors 4, 5 and has a minimum flow of 300 g/h and a maximum flow of 2500 g/h. This results in residence times (i.e. pyrolysis durations) in a range from 3 min to 60 min, depending on the operating conditions.

$$Residencetime = \frac{Reactorvolume}{Volume\,flow}$$

The residence time can be calculated and summed up differentially for each reactor volume element.

A main influence on the residence time (which corresponds to the pyrolysis duration) is the temperature of the reactor, since the vapor content of the medium and thus its average density depends strongly on it. With respect to the chemical reactions, the residence time and the temperature are independent parameters for the reaction rate. However, physical phenomena also occur in a flow tube, which can lead to a correlation of the two parameters. Due to the rising temperatures, for example, the boiling point could be partially exceeded, which is why vapors could form. In addition, reactions to lighter products (or low-boiling lumps) could also occur, which would increase the proportion of steam. This could reduce the average density. This

would increase the volume flow, which could lead to a shorter residence time with the reactor volume remaining the same.

The gaseous plastic product collected by means of the gas balloon was analysed by means of gas chromatography in accordance with DIN 51666:2007-01. The results are the calorific value, the specific gravity and the molecular composition of the gas phase. The true boiling point curve of the liquid products and the carrier medium was analyzed according to ASTM D7169-20e1 by means of simulated distillation (SIM-Dist).

Reaction model with 9 lumps

Kinetic modelling using lumps is a standard approach for modelling the kinetics of hydrocarbon cleavage. This approach is necessary because the typical starting material for hydrocarbon pyrolysis is a mixture of many different molecules and the consideration of each individual real reaction between each molecule is not feasible. In this method, each individual component of the plastic products is associated with a specific lump in a reaction network. The lumps were divided according to the boiling point. Alternatively, the division can also be made according to other material properties such as molecular structure or density. Each lump functions as a pseudo-component with representative material properties derived from the molecules contained therein. The cleavage reactions between the lumps were modeled as irreversible, single-stage, monomolecular reactions, as shown schematically in FIG. 2, with the reaction rate r (cf. Eq. (1)) following the Arrhenius law (cf. Eq. (2)).

$$r_{12} = k_{12} \cdot X_{Lump1} \quad (1)$$

$$k_{12} = k_{12} \cdot e^{\frac{-E_{A12}}{R \cdot T}} \quad (2)$$

In the reaction model in this example, the lumps were separated by the boiling point. First, the boiling point temperature ranges of interest to the refinery were defined, which led to the classification of gas to bottom products shown in Table 2. All components with a boiling point above 600 °C were defined as

plastic/wax lumps, which represents the end of the boiling point temperature range of the organic carrier medium. A complete reaction network with nine lumps (i.e., the number N of lumps is nine), in which each heavier lump (i.e., each of the lumps with a higher boiling point temperature range) reacts with each lighter lump (i.e., each of the lumps with a lower boiling point temperature range), would consist of $N*(N-1)/2$, i.e., 36 different reactions, each with two kinetic reaction parameters for each reaction. The sequential reaction model takes into account only one reaction for each heavier lump to the next lighter lump directly following with respect to the boiling point. This significantly reduces the number of reactions to eight unknown reactions with 16 kinetic parameters. The resulting reaction model is shown schematically in FIG. 3.

The sequential reaction model takes into account the decomposition of mixtures of plastics and carrier medium in such a way that there is no interaction between the materials. For the carrier medium and any plastic in the plastic starting material, the reaction model can be solved independently of each other. The final mass fraction of the lump j is the sum of all lumps with the same boiling point temperature range from n separate components (Eq. (3)).

Table 2. Boiling point temperature range and number of carbon atoms for the nine lumps of the reaction model

Lump Name	Lump No.	Boiling point temperature range	Number of carbon atoms
		(°C)	(-)
Plastic/Wax (P)	1	>600	>55
Bottom products (Res)	2	450 - 600	30-55
Heavy oil (HO)	3	400 - < 450	23-30
Spindle oil (SO)	4	350 - < 400	18-22
Gas oil (GO)	5	225 - < 350	13-17
Kerosene (Kero)	6	165 - < 225	10-12
Naphtha	7	20 - < 165	5-9
LPG	8	-120 - < 20	2-4
Gas	9	< - 120	1

$$X_j = \sum_{i=1}^n X_{j,i} \wedge \sum_{j=1}^m X_j = 1 \quad (3)$$

Simulation and fitting of reaction parameters

The reactor was programmed in PetroSim 7.2 as a custom operation unit in Visual Basic. For the simulation, the laboratory system was divided into nine parts according to their geometry. Each part was simulated as a tubular plug flow reactor and differs from the other parts in its geometry, ambient temperature and pipe insulation. For example, the first part is a horizontal tube, the second part is a vertical tube, and the third is a downward flowing coil. All these geometries have different formulas for the heat transfer coefficient and different ambient temperatures. The initial conditions for the integration of the first reactor part are the measured mass flow, the measured feed temperature and the concentration of the feed in lumps. The initial conditions of the following part are the solution of the differential equations of the preceding part.

In this model, the mass balance with the reaction of the lumps, the energy balance for the temperature of the fluid required for the reaction rates, and the pressure loss equation for a two-phase fluid were solved. The differential equations were discretized as a one-dimensional grid along the length of the reactor tube (cf. Eq. (4), (5), (6)). The Darcy coefficient of friction for the pressure loss calculation is calculated according to the correlation of Beggs and Brill for two-phase flows (cf. (1996) Standard handbook of petroleum & [and] natural gas engineering. Gulf Publ, Houston, TX).

$$\frac{\Delta X_i}{\Delta z} = \frac{-k_i \cdot X_i + k_{i-1} \cdot X_{i-1}}{v} \quad (4)$$

$$\frac{\Delta T}{\Delta z} = \frac{\sum \Delta H_R - \alpha \cdot \frac{4}{d_r} \cdot (T - T_{Environment})}{v \cdot \rho \cdot c_p} \quad (5)$$

$$\frac{\Delta p}{\Delta z} = \frac{\lambda \cdot \rho \cdot v^2}{d_r \cdot 2} \quad (6)$$

The kinetic parameters of the model were adjusted with Matlab and the surrogate optimization solver of the global optimization toolbox. Surrogate optimization is generally used for the global optimization of expensive cost functions for which no derivatives are available. For the adjustment, PetroSim was approached as a COM server by Matlab to write the experimental parameters and measurements into the case and obtain the results after the calculation. The simulation results are the composition of the lumps of the simulated products compared to the measured real composition of the lumps. The model itself is treated as a black box by the surrogate solver, which does not require a gradient for adaptation. The objective function *Obj* used in this study is the sum of the squared errors between the experimental and the calculated composition of the lumps according to equation (7).

$$Obj = \sum_{j=1}^m \sum_{i=1}^n (X_{i,j}^{cal} - X_{i,j}^{exp})^2 \quad (7)$$

Since it is assumed that there are no interactions between the components, the kinetic reaction parameters can be adjusted first for the carrier medium and then for each plastic individually by carrying out experiments only with the carrier medium or only with the individual plastic (i.e. a plastic starting material with only one plastic). The parameter ranges and number of experiments for each plastic composition are listed in Table 3. From each plastic starting material, two to three experiments were randomly selected for the evaluation of the kinetic parameters. These selected experiments and all experiments with mixed plastics were used only for the evaluation of the model parameters, but not for the training of the model.

Table 3: Data for adjusting the kinetic reaction parameters.

Mixed plastic runs were used to evaluate the results

	Number of experiments for		Temperature range	Mass flow range	Reactor length range	Plastic content
	Fitting	Evaluation				
	(-)	(-)	(°C)	(g/h)	(m)	(wt. %)
Carrier medium	21	3	410-520	600-2500	32-48	0
Polypropylene	10	2	440-520	600-2500	32-48	10-30
LD-	20	3	450-530	600-2500	48	10-30
Polyethylene						
HD-	20	3	450-540	600-2500	48	10-30
Polyethylene						
Plastic mixture	0	32	440-530	600-2500	32-48	30

Simulation and fitting of reaction parameters

The experimental results showed a significant influence of the process parameters and the composition of the plastic starting material on the boiling point distribution of the plastic products after the pyrolysis runs. An overview of the experimental process data is given in Table 4.

Table 4. Experimental parameters for the figures.

No.	Starting material	Plastic	Temperature reactor 4	Temperature reactor 5	Mass flow	Residence time
(-)	(-)	(wt. %)	(°C)	(°C)	(g/h)	(min)
257	Carrier (C)	0	450	450	1050	~17
	C+PP					
	C+LDPE					
	C+HDPE					
275	C+MIX	30	460	470	880	19.9

Decomposition kinetics of the different types of plastic

Since the heaviest lump (i.e. the lump with the highest boiling point temperature range and the longest hydrocarbons) consists of plastic and its heaviest wax products, the k1 partial reactions from the respective kinetic networks can be regarded as the decomposition rates of the plastics. Figure 4 shows that

polypropylene is broken much faster than low-density polyethylene and high-density polyethylene over most of the temperature range studied. The reaction rate of low-density polyethylene is twice as fast as that of high-density polyethylene over the investigated temperature range. At 500 °C, the reaction rates of all plastics approach a similar value and the differences become smaller. The activation energies and frequency factors of the reactions are shown in Table 5.

Table 5. Activation energy and frequency factor of the k_{12} decomposition reactions of PP, LDPE and HDPE.

Reaction	Frequency factor (1/s)	Activation energy (kJ/mol)
k_{12} - PP	1.84E+09	167,318
k_{12} - LDPE	3.21E+19	316,124
k_{12} - HDPE	7.16E+20	338,287

Accuracy of the reaction model

The calculated kinetic parameters (i.e. the reaction parameters) were evaluated with experimental data that were not used for fitting the reaction parameters. The criterion for a good fit of the model was that the maximum deviation from the simulated data to the experimental values is less than 0.05 kg/kg (cf. Eq. (8)) and no obvious systematic error can be observed. Figures 5A to 5I show the deviation between the simulated and the measured mass fraction for each evaluation experiment, plotted over the average temperature in the reactor. No systematic error can be detected across all lumps and the entire temperature range. It can also be seen that the accuracy for most lumps is within the accuracy criterion defined above. The least accurately imaged lump is the plastic/bottom product lump. In this lump, two of the experiments show a slightly higher deviation than the threshold with a maximum deviation of 0.07 kg/kg. Despite the higher deviation, no systematic error is discernible, so the kinetic parameters are well suited despite these two outliers. The higher deviation from the heaviest lump can be explained by the measurement inaccuracy of SimDist, which is less accurate at higher boiling points. Figure 6 shows that the boiling point distributions of the simulation (solid line) match well compared

to the measured boiling point distribution (dotted line).

$$\Delta X_{Max} = Max \quad (9) \quad (8)$$

Experimental series with a laboratory reactor

The kinetic model was used in a case study to find optimal experimental parameters for the laboratory reactor (which in this case is the pyrolysis reactor). The case study was carried out with a plastic starting material consisting of 20 % by weight LDPE, 10 % by weight PP and 70 % carrier medium. A separate reaction model was determined for each of the different plastic starting materials. The individual models can be summed (weighted according to the respective proportion of plastic starting material). Figures 7A to I show the yield of the lumps of the reactor over the entire temperature and mass flow range. It can be clearly seen that temperatures above 470 °C have a positive impact on the yield of plastic products from more valuable lumps with intersections below 350 °C. Above this temperature, almost all of the plastic breaks down into the lighter fractions (or lumps) of kerosene and gas oil, which have a clearly visible maximum yield of 0.14 % by weight and 0.25 % by weight, respectively.

Example 1 Summary

Pyrolysis processes for the chemical recycling of plastics are a necessary technology for a complete circular economy. In this example, it has been shown that a simple kinetic reaction model based on lumps, which has nine lumps and exclusively sequential partial reactions, can model the decomposition of polyolefins in a carrier medium with very good accuracy. The resolution of the boiling points of the plastic products is more precise than other reaction models with fewer lumps, with the number of unknown reaction parameters for fitting being limited. The maximum deviation of the modelled mass fraction from the experimental results is less than 0.05 kg/kg for most lumps, with the exception of the plastic residue lump, which has a

maximum deviation of 0.07 kg/kg. This accuracy has been demonstrated to be detectable in the relevant temperature range for slow pyrolysis above 400 °C and below 500 °C. A case study for the laboratory plant showed that there was a clear temperature window between 470 °C and 520 °C for a maximum yield of kerosene or gas oil.

List of abbreviations

C	Carrier medium
Cal	Calculated value
Exp	Experimental measured value
GO	Gas oil
HDPE	High-density polyethylene
HO	Heavy oil
HTC	Heat transfer coefficient
IBP	Initial boiling point
Kero.	Kerosene
LDPE	Low-density polyethylene
LKM	Reaction model with lumps
LPG	Liquefied petroleum gas
Obj	Target function
P	Plastic
PP	Polypropylene
Res	Bottom products
SO	Spindle oil
TBP	Actual boiling point

List of Symbols

C	Number of carbon atoms
C_p	Heat capacity
d_r	Diameter of the reactor
$E_{a_{ij}}$	Activation energy for the conversion of lump i to lump j
k^*_{ij}	Arrhenius constant (frequency factor) for the partial reaction from lump i to lump j
k_{ij}	Velocity constant for the partial reaction from lump i to lump j
p	Pressure
R	Gas constant (J/molK)
r_{ij}	Partial reaction of lump i to lump j
T	Temperature
v	Flow velocity
X_i	Mass fraction of lump j
X_{ij}	Mass fraction of the lump j of component i
z	Reactor length
α	Heat transfer coefficient

ΔH_R

Reaction enthalpy

 λ

Darcy friction factor

 ρ Density

Claims:

1. A computer-implemented method for determining values of reaction parameters of a reaction model for the pyrolysis of a plastic starting material into plastic products, the method comprising the following steps:

- providing experimental data comprising a plurality of boiling point distributions of plastic products, wherein each boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration, wherein the boiling point distributions are each binned into a number N lumps L_1 to L_N , wherein each lump is associated with a boiling point temperature range;

- determining a respective value of the reaction parameters by fitting the reaction parameters of the reaction model to the experimental data;

wherein the reaction model for each lump L_i from L_1 to L_{N-1} has a partial reaction determined by at least one reaction parameter for describing a conversion of plastic products of this lump into plastic products of a lump L_{i+1} lying below and adjacent with respect to the boiling point temperature range, wherein the reaction model has less than $N*(N-1)/2$ partial reactions.

2. The computer-implemented method according to claim 1, characterized in that the number N of lumps is at least seven.

3. The computer-implemented method according to any one of claims 1 or 2, characterized in that the reaction model has exactly $(N-1)$ partial reactions.

4. A method for determining values of reaction parameters of a reaction model for the pyrolysis of a plastic starting material into plastic products with a computer-implemented method according to one of the preceding claims, characterized in that the provision of experimental data comprises the following steps:

- carrying out a plurality of pyrolysis runs with different pyrolysis temperature and/or pyrolysis duration in a pyrolysis

reactor

- measuring a boiling point distribution of plastic products per pyrolysis run, wherein each boiling point distribution is associated with a pyrolysis temperature and a pyrolysis duration;

- binning of the individual boiling point distributions into the N lumps L_1 to L_N , wherein a boiling point temperature range is associated with each lump in order to obtain experimental data.

5. A method of carrying out pyrolysis of a plastic starting material into plastic products comprising the steps of:

- determining values of reaction parameters of a reaction model of pyrolysis via the computer-implemented method according to any one of claims 1 to 3 or the method according to claim 4;

- specifying an intended boiling point distribution;
- determining a pyrolysis temperature and a pyrolysis duration by minimizing a distance of a boiling point distribution calculated by means of the reaction model and the previously determined values of the reaction parameters from the intended boiling point distribution; and

- carrying out the pyrolysis with the predefined pyrolysis temperature and the predefined pyrolysis duration.

6. A system for data processing, characterized by means for carrying out the steps of the computer-implemented method according to any one of claims 1 to 3.

7. The data processing system according to claim 6, characterized in that the means are further adapted to perform the following step:

- calculating a pyrolysis temperature and a pyrolysis duration by means of the reaction model and the previously determined values of the reaction parameters, wherein the pyrolysis temperature and the pyrolysis duration are defined such that a distance of a boiling point distribution calculated by means of the reaction model from an intended boiling point distribution is minimized.

8. A computer program product comprising instructions that, when the program is executed by a computer, cause the computer to perform the steps of the computer-implemented method according to any one of claims 1 to 3.