

KINETIC MODELLING OF SCAVENGER REACTIONS: PARAMETER ESTIMATION FOR A GALLIC ACID-BASED OXYGEN SCAVENGER

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ABSTRACT

The software-based design of active packaging requires mathematical models of oxygen scavenger reactions. In this study we present a simple approach for describing such reactions with a second-order kinetic model and for determining the corresponding kinetic parameters. For the example of a gallic acid-based oxygen scavenger stored at 21°C and 0% RH, 75% RH and 100% RH, the model was fitted to oxygen absorption data using a downhill simplex-based algorithm for numerical optimization. As expected, the optimization results depended on the choice of the starting values. To identify the global optimum of the given parameter space, the results of multiple optimization runs with varying starting values were analyzed quantitatively. For the scavenger reactions at 75% RH and 100% RH unambiguous minima could be found. The reaction rate constants are $1.347 \cdot 10^{-7} \text{ m}^3/(\text{mol} \cdot \text{s})$ and $1.496 \cdot 10^{-6} \text{ m}^3/(\text{mol} \cdot \text{s})$ and the stoichiometric coefficients are 1.639 and 2.534 for 75% RH and 100% RH, respectively. However, at 0% RH, there was no detectable scavenger reaction and fitting the noisy experimental data led to ambiguous solutions without physical meaning. The analyzed method for the estimation of kinetic parameters can be applied for any scavenger reaction, thereby providing necessary information for active packaging design.

INTRODUCTION

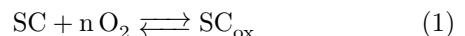
In food packaging technology, oxygen (O_2) scavengers are used to prevent sensitive foods or food components from oxidation. O_2 scavengers are based on substances that easily react with O_2 , e.g. iron, sulfite, oxidizable polymers or natural antioxidants (Vermeiren et al. 2003, Rooney 2005). In packaging applications, O_2 scavengers can fulfill different tasks: They are used to remove O_2 from the packaging headspace and/or for improving the O_2 barrier function of polymeric packaging films.

In the last few years there has been a strong trend towards software-based packaging design. Gas transfer models have been developed that are now used to optimize packaging designs in terms of tailor-made barrier properties, e.g. packaging for fresh produce or modified atmosphere packaging (Cagnon et al. 2013, Van Bree et al. 2010, Sousa-Gallagher and Mahajan 2013). For modelling active packaging systems including O_2 scavengers, a quantitative description of the reaction kinetics of the scavenger related to typical storage parameters (e.g. relative humidity and temperature) is necessary. Thus, novel approaches for modelling scavenger kinetics have to be developed.

In this study we have a closer look at kinetic models of scavenger reactions and we focus on the determination of kinetic parameters from experimental data obtained for a gallic acid-based oxygen scavenger.

OXYGEN SCAVENGER KINETICS

The function of O_2 scavengers relies on the chemical reaction between the active substance (SC) of the scavenger and O_2 , leading to the formation of oxidation products (SC_{ox}). The overall reaction of an O_2 scavenger can be written as follows:



where n is a stoichiometric factor.

O_2 scavengers are characterized by (a) their absorption capacity, i.e. the amount of O_2 that can be absorbed by a given amount of the scavenger and (b) the time-dependent absorption of O_2 , i.e. the rate of the scavenger reaction. This information is obtained from O_2 absorption measurements. In such experiments, a defined amount of the scavenger is stored in a closed vessel under defined conditions, i.e. temperature, relative humidity (RH) and initial O_2 concentration. The decrease in O_2 concentration due to the scavenger reaction is monitored during storage. Figure 1 shows the results of an O_2 absorption experiment with a gallic acid-based scavenger.

Different approaches for modelling scavenger kinetics

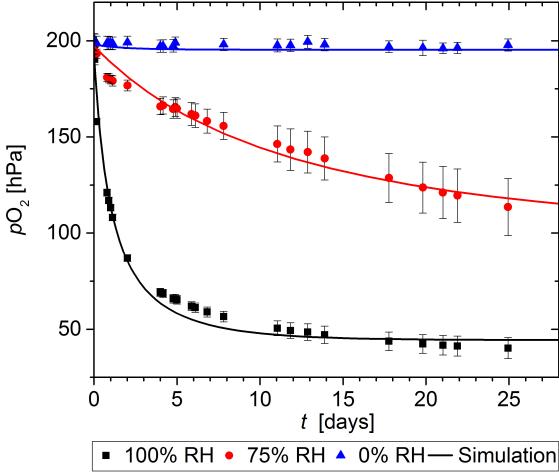


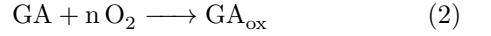
Figure 1: Oxygen Absorption of a Gallic Acid-based Scavenger at various Relative Humidities (RH)

can be found in literature. In recent years, the most common approach was to approximate scavenger kinetics with the kinetic law of a first-order elementary reaction. This approach often results in a good fit of the experimental data and is easy to apply as there are analytic solutions readily available (Charles et al. 2003, Galotto et al. 2009). However, it is based on the assumption that the reaction rate solely depends on the concentration of one reactant, i.e. O₂ or SC. This is a reasonable approximation when there is large excess of either O₂ or SC (pseudo first-order reaction). In most packaging applications, however, this assumption is not valid (i.e. there are low concentrations of O₂ and SC) so that first-order kinetic parameters cannot be transferred to other packaging systems.

For the software-based design of active packaging including O₂ scavengers, kinetic parameters independent from initial reactant concentrations are needed. Recently, some research groups have successfully applied second-order kinetic models to scavenger reactions: Dombre et al. (2015) and Di Maio et al. (2017) described the O₂ absorption of polymer-based scavengers with the kinetic law of a second-order elementary reaction. However, in these publications the method of fitting kinetic models is not discussed in detail so that there is still little knowledge about how to generate kinetic information from scavenger experiments in a way that is advantageous for packaging design and development. Whenever models with two or more free parameters have to be fitted to experimental data, manual fitting methods may fail to find optimum solutions. In this context, we closely evaluate the fitting of a second-order kinetic model to experimental data from O₂ absorption measurements in order to distinguish between different local and global minima of the objective function of the fit.

MODEL DEVELOPMENT

The active substance of the O₂ scavenger used in this study is gallic acid (3,4,5-trihydroxybenzoic acid, GA), a simple polyphenol that can be found in many plants. For the application as a scavenger, it is combined with the base sodium carbonate (Na₂CO₃) which serves as a catalyst for the oxidation. The reaction is triggered by humidity (Pant et al. 2017). Equation (1) was therefore rewritten as follows:



GA_{ox} denotes all oxidation products that are formed in this reaction, e.g. larger polyphenols. The reaction mechanism is not yet fully understood and may include a multi-step polycondensation (Tulyathan et al. 1989). The overall reaction is therefore assumed to be irreversible.

In this study, we used the kinetic law of a second-order elementary reaction as the minimal viable approximation to describe the reaction rate *r*:

$$r = k \cdot [GA] \cdot [O_2] \quad (3)$$

Here, *r* depends on the concentrations of both reactants, [GA] and [O₂], and *k* is the reaction rate coefficient. Based on this kinetic law, the net rates of consumption of GA and O₂ were described with a system of ordinary differential equations (ODE):

$$\frac{d[GA]}{dt} = -k \cdot [GA] \cdot [O_2] \quad (4)$$

$$\frac{d[O_2]}{dt} = -n \cdot k \cdot [GA] \cdot [O_2] \quad (5)$$

The net rate of production of GA_{ox} is the same as Equation (4) but with inverted sign (mass conservation).

EXPERIMENTAL DATA

Experimental data from O₂ absorption measurements with a gallic acid-based scavenger at 21°C and various relative humidities was used (Figure 1). In these experiments, 0.06 g of the scavenger were stored in closed cells with a free headspace volume of 88 cm³ or 108 cm³ and the O₂ absorption (i.e. the decrease of the O₂ partial pressure) was measured non-destructively during storage. To allow for homogenous oxygen exposition, the scavenger powder was spread in a thin layer on a glass plate. A more detailed description of the method is given by Pant et al. (2017). For all measurements, a fourfold determination was made. The experimental data (O₂ partial pressure in hPa) was transferred to O₂ concentrations [O₂] in mol/m³ using the ideal gas law. The mean square deviation for each experimental condition was then calculated as follows:

$$MSE_{exp} = \sqrt{\frac{1}{N} \sum_{i=1}^m \sum_{l=1}^q ([O_2]_{exp} - [O_2]_{mean})^2} \quad (6)$$

where N is the total number of observations, m is the number of parallel experiments, q the number of observations in one experiment, $[O_2]_{\text{exp}}$ the observed oxygen concentration and $[O_2]_{\text{mean}}$ the arithmetic mean of all m observations for each l .

PARAMETER ESTIMATION

The ODE system given in Equations (4) and (5) was solved in MATLAB R2014a (The MathWorks, Inc., Natick, MA, USA) using the multistep solver `ode15s` with the default tolerances $\text{AbsTol} = 10^{-6}$ and $\text{RelTol} = 10^{-3}$. The model was fitted to the available experimental data sets reflecting different relative humidities from 0% RH to 100% RH. The fit was optimized based on the minimization of the sum of squared residuals (SSQ) to be calculated according to the following equation:

$$\text{SSQ} = \sum_{i=1}^m \sum_{l=1}^q ([O_2]_{\text{sim}} - [O_2]_{\text{exp}})^2 \quad (7)$$

where m is the number of parallel experiments, q the number of observations in one experiment, and $[O_2]_{\text{sim}}$ and $[O_2]_{\text{exp}}$ the predicted and the observed O_2 concentrations, respectively.

For the minimization of the SSQ objective function, the MATLAB function `fminsearch` was used - a function based on the Nelder-Mead downhill-simplex algorithm for local optimization as described by Lagarias et al. (1998). The termination tolerance of the function value (`Tolfun`) was 10^{-4} and the lower bound on the size of a step (`TolX`) was 10^{-4} (MATLAB default settings). `Fminsearch` terminates when both stopping criteria are fulfilled.

The stoichiometric coefficient n is a measure for the O_2 absorption capacity and gives the number of absorbed molecules O_2 per molecule GA. Therefore, n must not be negative. Tulyathan et al. (1989) found an O_2 absorption capacity of 4.9 O-atoms per molecule GA. The reaction rate coefficient k , by definition, must also not be negative, but there was no previous knowledge about its order of magnitude. Thus, the parameter space was investigated in the range of $n = 0..10$ and $k = 10^{-10} \text{ m}^3/(\text{mol} \cdot \text{s}) .. 10^{10} \text{ m}^3/(\text{mol} \cdot \text{s})$. To enable an effective search for k in this broad range of 20 orders of magnitude, a logarithmic scaling of k was chosen. Thereby, equal importance was attached to all possible solutions for k , regardless of their order of magnitude. For the optimization procedure, k was therefore replaced by $k = 10^{k'}$ in Equation (2).

Since the downhill-simplex optimization is known to be sensitive to the chosen starting values, the initial k and n values were varied systematically in equidistant steps over the whole parameter space so that in total 231 different combinations of k and n were tested. For all optimization results, the root mean square error (RMSE)

was calculated as a measure of the goodness of fit:

$$\text{RMSE} = \sqrt{\frac{\text{SSQ}}{N - p}} \quad (8)$$

where N is the total number of experimental observations and p the number of fitted parameters.

The results (combinations of k and n) were then sorted by their RMSE values, starting with the lowest value RMSE_{min} . All solutions with RMSE below a $\text{RMSE} = \text{RMSE}_{\text{min}} + \text{MSE}_{\text{exp}}$ were considered optimum solutions, where MSE_{exp} is the experimental error of the respective experimental data set (Equation 6). With this threshold, the experimental error was taken into account.

To validate the optimization results, the k - n -parameter space was mapped out in terms of the SSQ objective function in order to visually identify minimum and maximum regions.

RESULTS

In this study, the reaction of a gallic acid-based O_2 scavenger was described with a second-order kinetic model. The model was fitted to experimental data obtained at 21°C and various relative humidities to determine the model parameters, i.e. the reaction rate coefficient k and the stoichiometric factor n .

The simulated curves based on the best-fit sets of model parameters are shown in Figure 1. All experiments could be sufficiently described with the chosen model. The goodness of fit was adequate in relation to the experimental error; the results are given in Table 1. These results show that the GA-based scavenger is activated by humidity. While there was no detectable O_2 absorption at 0% RH, the values of k and n were significantly higher at 75% RH than at 100% RH. This may be explained by the mechanism of the scavenger reaction which includes the deprotonation of the GA and a subsequent multi-step oxidation. The availability of water, in presence of a base, is a prerequisite for the proton transfer as an initiating step. Both, the velocity of the reaction and its extent (i.e. the absorption capacity) appear to be affected by the level of RH. To determine the optimum reaction conditions of a GA-based scavenger, further research should therefore focus on analyzing the combined effect of humidity and the base on the reaction kinetics.

For a closer analysis of the fit, the complete k - n -parameter space was mapped in terms of the SSQ objective function. In the simple case of a model with two parameters, this results in a 3-D plot of the parameter space. Figure 2 shows the contour plots of the different parameter spaces for 0% RH, 75% RH and 100% RH, respectively. The SSQ values describe a mathematical surface that is defined by the model equation and the experimental data set. Parameter estimation from ex-

Table 1: Optimization Results for Experimental data at 21°C and various Relative Humidities (RH)

| | MSE _{exp} mol/m ³ | RMSE _{min} mol/m ³ | n | | | k m ³ /(mol · s) | | | |
|---------|--|---|---------|---------|---------|--------------------------------|----------------------------|----------------------------|---------------------------|
| | | | median | min | max | median | min | max | |
| | 0% RH | 0.116 | 0.038 | 0.06301 | 0.05165 | 3.64178 | 7.54668 · 10 ⁻⁷ | 1.75341 · 10 ⁻⁹ | 9.71062 · 10 ⁹ |
| 75% RH | 0.286 | 0.347 | 1.63914 | 1.63908 | 1.63924 | 1.347524 | 1.34741 · 10 ⁻⁷ | 1.3476 · 10 ⁻⁷ | |
| 100% RH | 0.117 | 0.256 | 2.53430 | 2.53423 | 2.53439 | 1.49632 · 10 ⁻⁶ | 1.49584 · 10 ⁻⁶ | 1.49651 · 10 ⁻⁶ | |

perimental data, formulated as a nonlinear least-squares problem, may bear the risk of multiple local optimum solutions. The related plateau phenomenon has been discussed in literature (e.g. Choi and Chiang (2009)) and was also observed in our study: The 100% RH plot shows regions with very high SSQ at low values of $\log k$ and n and a large SSQ plateau at high values of $\log k$ and n . In between these, a minimum can be presumed around $\log k = -6$ and $n = 2.5$. Although less pronounced, similar features can be observed for 75% RH. Here, a minimum can be presumed in the area of $\log k = -7$ and $n = 1.5$. At 0% RH, in contrast, there is no clearly defined minimum region; all SSQ values for $\log k < -7$ and $n < 1$ appear to be equivalent minima forming another plateau.

The described features of the k - n -parameter space are also reflected in the optimization results shown in Figure 3. For all experimental conditions it was shown that the optimization results depended on the chosen starting values, leading to apparent groups of results with different RMSE (Figure 3). This can be explained with the characteristics of the parameter space: Whenever the downhill simplex algorithm started at the plateau regions, no downhill movement was observable within the given tolerances so that the algorithm stopped, resulting in k - n -combinations with high RMSE as best-fit results (numerical local minimum). Additionally, the algorithm got stuck in other local minima (Figure 2) in the form of trenches at $n = 2$ and $\log k = -6$. Without any previous knowledge about k and n , the total minimum of the defined parameter space could only be found by multiple runs of the downhill simplex algorithm with varying initial values.

All solutions below a RMSE threshold of 0.155 mol/m³, 0.633 mol/m³ or 0.373 mol/m³ for 0% RH, 75% RH and 100% RH respectively, were considered optimum solutions. The thresholds are derived from the experimental error as described above. Table 1 gives an overview of the found optimum values for k and n . To show the distribution of the found optimum values, the median, minimum (min) and maximum (max) values are presented.

At 100% RH, there was an unambiguous minimum at $n = 2.534$ and $k = 1.496 \cdot 10^{-6}$ m³/(mol · s), which can be regarded as the global minimum given the constraints on n and k discussed above. The minimum

and maximum solutions only differed in the 3rd or 4th decimal (Table 1). Accordingly, an unambiguous minimum for 75% RH could be found at $n = 1.639$ and $k = 1.347 \cdot 10^{-6}$ m³/(mol · s).

For 0% RH, already from the experimental data it could be seen that $k = 0$ m³/(mol · s) and $n = 0$ since there was no detectable O₂ absorption. A fit of these data, however, resulted in n and k values differing by several decimal powers although characterized by similar RMSE. This example illustrates the sensitivity of the model to noisy data. The experimental data lack meaningful information, so that the issue of multiple local solutions arises. In such cases, the downhill simplex-based method fails to determine the values of the kinetic parameters.

CONCLUSION

A second-order kinetic model was developed and fitted to O₂ absorption data of a gallic acid-based O₂ scavenger. It could be shown that this model was suitable for describing oxygen absorption and the kinetic parameters could be obtained. Both, the rate coefficient k and the stoichiometric factor n were affected by the storage relative humidity. Thus, gallic acid belongs to the group of humidity-activated scavenger systems and should be used for food products with high water activity. The applied method for determining the kinetic parameters includes (a) a multiple-run local optimization and (b) a subsequent quantitative analysis of the results based on an acceptance threshold derived from the experimental error. Independent from the model to be fitted, this method can be used for searching a predefined parameter space for a global optimum. In the context of an increasing demand for active packaging solutions, the applied method provides meaningful kinetic information - a prerequisite for software-base packaging design.

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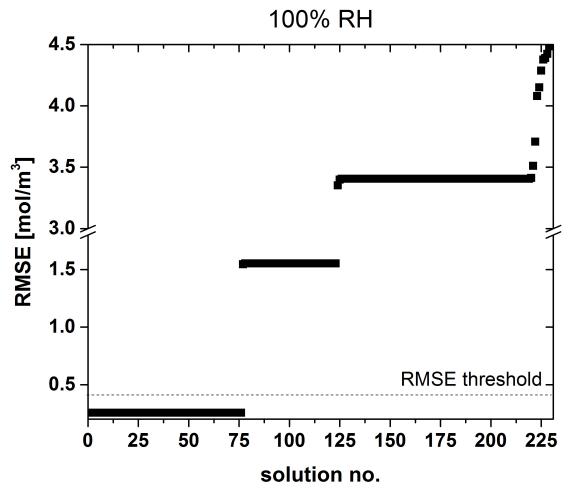
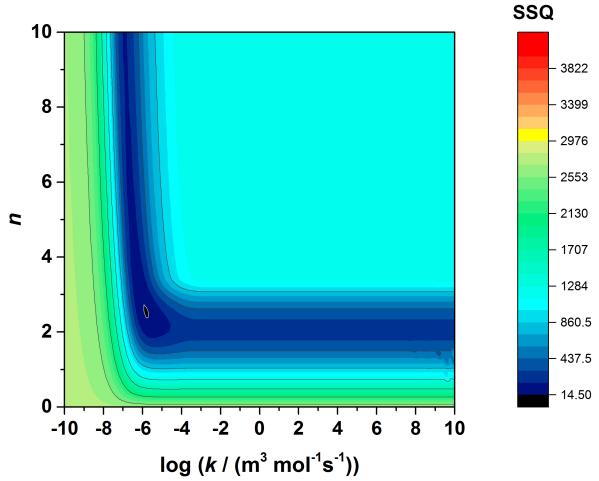
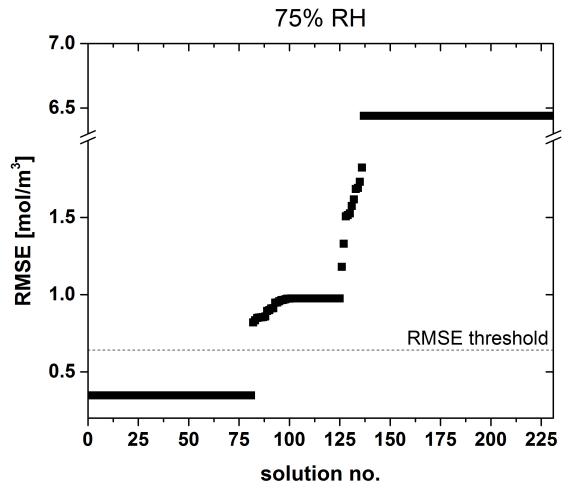
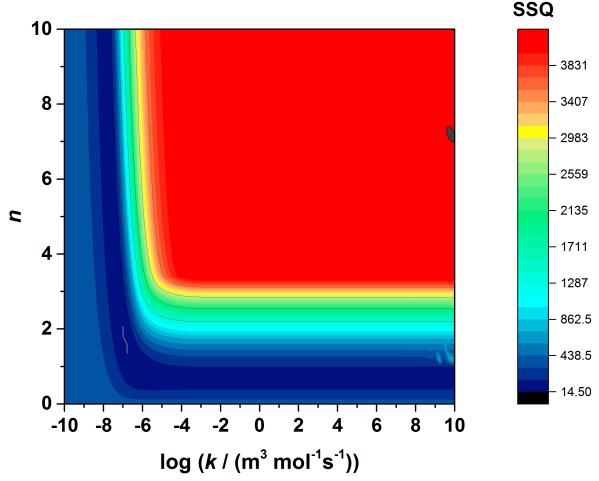
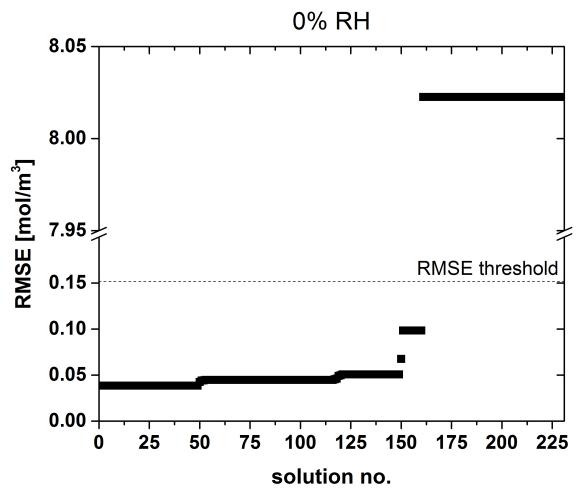
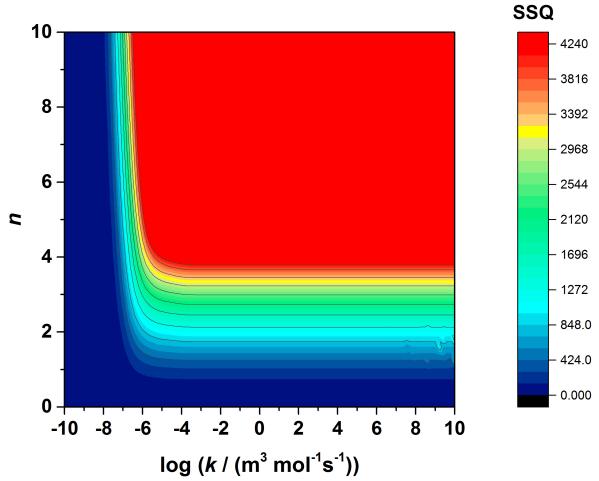


Figure 2: Contour Plots of the Parameter Spaces at various Relative Humidities (RH)

Figure 3: RMSE Values of the Optimization Results for various Relative Humidities (RH)

AUTHOR BIOGRAPHIES

ASTRID PANT studied food technology at the University of Bonn, Germany, and at the Swedish University of Agricultural Sciences in Uppsala, Sweden. Since 2010, she has been working at Fraunhofer IVV in the field of active packaging and food packaging. Currently she is pursuing her PhD studies at the Technical University of Munich with a focus on oxygen scavenger kinetics.

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