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Reaction Kinetics of Gallic-Acid-Based Oxygen Scavengers for Packaging Applications

Dipl.-Ing.

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INTRODUCTORY REMARKS

This thesis was prepared during my time as a research associate at the Fraunhofer Institute for Process Engineering and Packaging (IVV), Freising, at the Department of Materials Development.

Part of the results were generated within the project ”NextGenPack - Next generation of advanced active and intelligent bio-based packaging for food” in the framework of the ”Programme Inter Carnot Fraunhofer PICF 2011”.

The following **peer-reviewed publications** comprise the main results of this thesis:

1. Pant, A. F., Sängerlaub, S. and Müller, K. (2017). Gallic Acid as an Oxygen Scavenger in Bio-Based Multilayer Packaging Films. Materials, 10(5), 489.
2. Pant, A. F. and Reinelt, M. (2018). Kinetic Modelling of Scavenger Reactions: Parameter Estimation for a Gallic Acid-Based Oxygen Scavenger. Paper presented at the FOODSIM'18, Leuven, Ghent, Belgium.
3. Pant, A. F., Dorn, J. and Reinelt, M. (2018). Effect of Temperature and Relative Humidity on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid. Frontiers in Chemistry, 6:587.
4. Pant, A. F., Özkasikci, D., Fürtauer, S. and Reinelt, M. (2019). The Effect of Deprotonation on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid. Frontiers in Chemistry, 7:680.

The doctoral candidate is the main author of all listed publications. This means that the conception and design of the scientific studies, the experimental setup, and the data analysis were essentially the work of the doctoral candidate. The manuscripts were principally written by the doctoral candidate.

The following **scientific textbook contributions** are related to the introduction of this thesis:

1. Pant, A. F., Sängerlaub, S., Müller, K. and Thielmann, J. (2017). Technologie aktiver und intelligenter Verpackungen. In: J. Hennig (Ed.), Verpackungstechnik. Mittel und Methoden zur Lösung der Verpackungsaufgabe (Vol. 2017-12 Loseblattwerk). Berlin: Beuth Verlag.
2. Pant, A. F. and Thielmann, J. (2018). Active Packaging for Fresh and Fresh-Cut Fruit and Vegetables. In: M. W. Siddiqui, M. S. Rahman and A. A. Wani (Eds.), Innovative Packaging of Fruits and Vegetables - Strategies for Safety and Quality Maintenance. Oakville, ON, Canada: Apple Academic Press.

Results of this thesis were also part of the following **oral presentations**:

1. Pant, A. F., Reinelt, M., Dorn, J., Sängerlaub, S. and Stramm, C. (2014). Gallic acid as oxygen scavenger in bio-based packaging materials. Advances in Food Processing - Challenges for the future, 5.-7.11. Campinas, Sao Paulo, Brazil.
2. Pant, A. F. and Sängerlaub, S. (2018). Sauerstoff-Absorber verstehen und Haltbarkeitsverlängerung vorhersagen. Paper presented at the Flexible Packstoffe im Verpackungsprozess. VVD-Workshop meets Freisinger Tage, 01.02.18, Freising, Germany.

The following publications continue the work of this thesis and present potential applications:

1. Apicella, A., Pant, A. F., Staebler, A., Leistl, D., Incarnato, L. (2019): Antioxidant properties of olive pomace extract. 3rd Innovations in Food Packaging, Shelf Life and Food Safety. 8-10 Oct. Munich, Germany.
2. Laridon, Y., Kurek, M., Pant, A. F., Reinelt, M., Stramm, C., Guillard, V.: Inclusion of O_2 scavenger to enhance barrier properties of PLA: application to packed food systems (to be submitted).

CONTENTS

ABBREVIATIONS

CO_2	carbon dioxide
DoD	degree of deprotonation
EFSA	European Food Safety Authority
EU	European Union
EC	European Commission
GA	gallic acid, 3,4,5-trihydroxybenzoic acid
GA^{x-}	gallate ion, x times negativly charged
GAE	gallic acid equivalents
H_3O^+	hydronium ion
HAT	hydrogen atom transfer
$HO^\bullet$	hydroxyl radical
HPLC	high pressure liquid chromatography
MA	modified atmosphere
MAP	modified atmosphere packaging
O_2	molecular oxygen
OH	hydroxy group
OH-	hydroxy ion
PhOH	phenol
$PhO^{\bullet +}$	phenoxy cation
$PhO^\bullet$	phenoxy radical
PE-LLD	linear low density polyethylene
PHA	polyhydroxyalkanoates
PLA	polylactic acid
$R^\bullet$	radical

RH	relative humidity
SC	scavenger
SC_{ox}	oxidized scavenger
SET	single-electron transfer
STP	standard temperature and pressure (0 °C, 1 bar)
UV	ultraviolet

SYMBOLS

[A], [B]	$\mathrm{mol\,m^{-3}}$	concentration of substance A or B
D	$\mathrm{m^2\,s^{-1}}$	diffusion coefficient
k	$\mathrm{mol\,m^{-3}\,s^{-1}}$	reaction rate coefficient (zero order reaction)
	$\mathrm{s^{-1}}$	reaction rate coefficient (first order reaction)
	$\mathrm{m^3\,s^{-1}\,mol^{-1}}$	reaction rate coefficient (second order reaction)
n	mol	absorption capacity
p	Pa	partial pressure
r	$\mathrm{mol\,m^{-3}\,s^{-1}}$	reaction rate
R	$\mathrm{J\,mol^{-1}\,K^{-1}}$	gas constant
S	$\mathrm{mol\,m^{-3}\,Pa^{-1}}$	solubility constant
T	K or °C	temperature
t	s	time
V	$\mathrm{m^3}$	volume

1. INTRODUCTION

1.1 Motivation

The preservation of food has always played an important role in people's everyday life. Once manufactured, a food product will continiously lose quality, a process which is commonly referred to as spoilage [56]. Thus, it has always been a major concern to protect food products from harmful external influences, such as oxygen or humidity, in order to slow down the spoilage processes and to maintain food quality [83]. Basically, modern packaging technology has evolved to meet these challenges. Nowadays, a multitude of technical approaches for the protection of food products is available.

Active packaging holds a special position in packaging technology as it actively interferes with the product and/or the environment surrounding the product: So-called active components are used in active packaging to absorb substances or to release substances in order to extend the shelf life of packaged food products [34, 58]. The concept of active packaging introduces enormous possibilities to packaging development and has gained a lot of attention in packaging research during the past years, leading to increasing numbers of publications.

Oxygen scavengers, i.e. substances that are used to absorb oxygen, are well-established active components and there are many examples for commercial applications [80, 86]. Recently, oxygen scavengers based on renewable resources have gained attention and among them gallic acid, a hydroxyphenol, stands out due to its high capacity for oxygen absorption [108].

However, the application of oxygen scavengers poses new challenges to the packaging design process. To provide optimum protection to the packed product, the active function has to be tailored to the packaging system. This involves several design decisions that, in many cases, are reached as the result of a "trial and error" process [77]. This means that an immense effort has to be put into application tests to decide upon e.g. the type and quantity of the active component, the packaging material and the type of product that can be packed.

Moving forward from the “pack and pray” approach, mathematical models have been presented to support the packaging design process [45, 81, 106]. However, only few modeling tools have reached industrial application, and they are still lacking the description of active functions.

In this context, this thesis aims at studying the scavenger reaction of gallic acid in oxygen absorption experiments and, based on these results, to develop an application-oriented approach for modeling the scavenger reaction. Here, the model should be used to identify potential applications and to facilitate the design of active packaging incorporating oxygen scavengers based on gallic acid.

The following sections introduce the concept of active packaging with a particular emphasis on the technology of oxygen scavengers. A special focus is put on functional packaging design and current approaches for describing scavenger kinetics. Gallic acid is reviewed in terms of current applications in packaging and regarding the physical and chemical properties that are the basis for the scavenger reaction.

1.2 Active packaging

Generally, food packaging fulfills several functions [4, 83]:

- Protection: Packaging protects food products from environmental influences such as light, oxygen, moisture, dust, microorganisms, and mechanical stress.
- Containment: Packaging facilitates food handling and distribution
- Information: Packaging provides necessary product information, such as shelf life, ingredients, nutritional value and can also be used for marketing purposes.
- Convenience: Packaging features such as reclosable caps and sprays can make a product usable and convenient.

The protective function of food packaging is crucial for maintaining the quality and thereby for the shelf life of the product. Traditionally, product protection has been achieved by providing a sufficient (passive) barrier to external influences.

Active packaging, in contrast, “is designed to correct deficiencies which exist in passive packaging” [84]. It may be defined as “packaging which performs some desired function other than merely providing a barrier to the external environment” [85]. This broad definition was introduced by Labuza in the late 1980s [58]. It includes all kinds of packaging with additional functions such as microwave susceptors, self-heating or self-cooling functions, and other widgets (e.g. for gas generation)[85].

In EU legislation, “active food contact materials and articles” are defined in the Regulation (EC) No. 450/2009. These materials are “intended to extend the shelf life or to maintain or improve the conditions of packaged food. They are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food” [34].

The incorporated component refers to “an individual substance or a combination of individual substances which cause the active [...] function of a material or article, including the products of an in situ reaction of those substances; it does not include the passive parts such as the material they are added to or incorporated into”.

The Regulation (EC) No. 450/2009 differentiates between “absorbing/scavenging systems”, “releasing systems” and “systems with substances grafted or immobilized on wall of the packaging”. Materials that are intended to function as an active oxygen barrier, i.e. polymers incorporated with oxygen scavengers to improve the barrier function of the polymer, do not fall under the definition as these materials are designed to interact with the oxygen coming from the environment, not with the oxygen inside the package [35].

Active packaging must not be confused with intelligent packaging. According to the Regulation (EC) No. 450/2009, intelligent materials or articles “monitor the condition of packaged food or the environment surrounding the food” [34]. This definition highlights the extended communication function of intelligent packaging, i.e. the ability to provide information on food quality. This function can be achieved by integrating indicators (e.g. time-temperature indicators, gas indicators, freshness indicators) into the packaging [4, 62]. Barcode labels and radio frequency identification tags are also often considered intelligent packaging [62]. Such data carriers provide an extended communication function by storing additional product information. However, they are not able to monitor food quality if not coupled with the respective indicator. Detailed reviews about intelligent systems and their applications have been presented by HAN ET AL. [46] and more recently by REALINI ET AL. [80].

Active packaging systems can be classified as absorber/scavenger systems or release/emitter systems according to their mode of action. These two groups can be further divided according to the substances that are being absorbed or released. Figure 1.1 shows the classification of common active packaging systems. Absorber systems include oxygen scavengers, water vapor absorbers, ethylene scavengers, and carbon dioxide scavengers. Antimicrobial systems, antioxidant systems, ethylene emitters and carbon dioxide emitters are the most important release systems [105, 107].

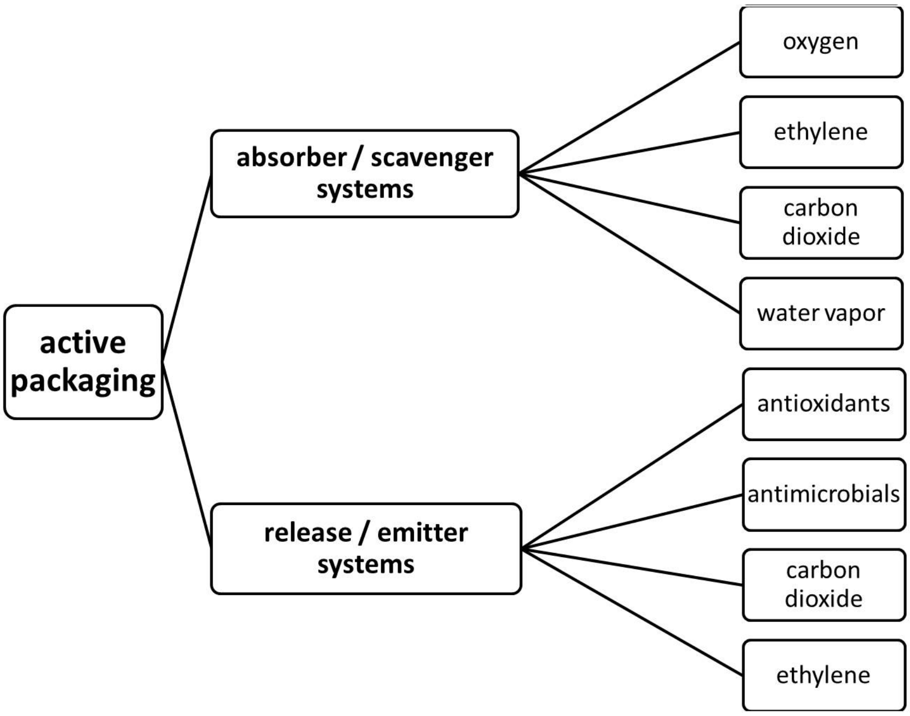

Figure 1.1: Classification of active packaging systems

Several reviews give an overview of published and/or commercialized active packaging systems and their properties [80, 107, 112]. The different types of active packaging are designed to provide packaging solutions that fit to the needs of certain food products. In recent years, many storage studies with different food products in active packages have been published. The results have been summed up in thorough reviews, e.g. for meat products [80, 91] and fruit and vegetables [77]. In general, these studies highlight the importance of tailoring the active function to the involved packaging system which comprises several parts: The packaging material, the active component(s), the product and the environment (i.e. storage conditions) [77].

1.3 Oxygen scavengers

1.3.1 General functionality and application

Oxygen has a detrimental effect on the quality of many sensitive food products. The oxidation of lipids is one of the major quality concerns [21, 101], but also food components such as proteins, polyphenols, colorants and vitamins are susceptible to oxidation. These reactions can lead to a loss of nutrients such as vitamin C [15] and to undesired changes in color [43, 49] and aroma [51, 52]. Moreover, the presence of oxygen enables the growth of microorganisms such as moulds and aerob bacteria [61].

Many packaging techniques aim to remove oxygen from the package (e.g. during filling) or to prevent oxygen ingress from the environment in order to protect the packed product [4, 83]:

In vacuum packages air is removed during the packaging process.

In modified atmosphere packaging (MAP), gas flushing is used during the filling process to replace air (and thereby oxygen) with gases such as nitrogen or carbon dioxide. However, 100% removal of oxygen from the packaging headspace is technically challenging and uneconomical, since it would require long processing times and high volumes of gas [83]. Hence, a residual oxygen content of 0.5-2% is common in MA packages [43, 78]. The oxygen content may further increase during storage due to dissolved oxygen that is released from the product [43].

Barrier packaging aims to prevent or limit oxygen permeation during storage and can be combined with MAP or vacuum packaging. The oxygen barrier properties of packaging films are determined by the oxygen permeability of the material or the combination of materials used. Multilayer films combining different polymers and inorganic layers are a common approach to improve the oxygen barrier of packaging films [59, 83].

Oxygen scavengers have been developed to overcome some of the mentioned shortcomings of passive packaging and can be combined with passive packaging strategies [86]. Nowadays, oxygen scavenging is the most widespread active packaging technology which is not only used in food packaging, but also for packaging of drugs, cosmetics, etc. [82]. Due to an increased awareness for food safety and food quality, high growth rates are expected for oxygen-scavenging packaging [97].

Oxygen scavengers are substances or mixtures of substances that readily react with oxygen and therefore can be used to remove oxygen from the package headspace and/or to improve the oxygen barrier properties of a packaging material [86]. They can be divided into insert types, e.g. sachets or labels, and polymer structure types, i.e. monolayer and multilayer materials incorporating the oxygen scavenger [62].

Scavengers are further classified by their active component, i.e the substance that actually binds oxygen. Usually, this effect is based on a chemical reaction. Examples include rusting of iron [37, 71], metal-catalyzed oxidation of synthetic polymers such as unsaturated hydrocarbon dienes [26, 39] or nylon MXD6 [42, 96], oxidation of tocopherol [89] or ascorbic acid [67], palladium-catalyzed oxidation of hydrogen [108, 113] and autoxidation of phenols

[108]. Additionally, scavengers based on biochemical processes, e.g. enzymatic conversion of oxygen [6, 53, 110] or respiration of microorganism have been described [8]. Recent reviews give an overview of different substances that can be used as oxygen scavengers [107, 112].

The mechanism of the scavenger reaction determines the conditions that are necessary to initialize the scavenging reaction (trigger). This is a determining criterion for the application of a scavenger. Many scavengers are triggered either by humidity or UV-light [86].

1.3.2 Functional packaging design

From a design perspective, an active packaging system comprises several parts: The packaging material, the active component, the packaging headspace, the packed product and the storage environment [81]. Thus, all these parts have to be considered during packaging design. Two examples for active packaging systems involving oxygen scavengers are shown in Figure 1.2: Insert-type systems and polymer-type systems. Here, a schematic overview of all processes affecting the overall oxygen balance of the system is given. Oxygen transport is indicated with arrows.

The packaging material provides an oxygen barrier towards the environment and is characterized by its diffusion coefficient $D_{\mathrm{O2,pack}}$ and solubility coefficient $S_{\mathrm{O2,pack}}$.

The packed product interacts with oxygen, i.e. oxygen can dissolve into the product and also diffuse within in the product ($S_{\mathrm{O2,prod}}$, $D_{\mathrm{O2,prod}}$). Furthermore, oxygen can be consumed by chemical reactions which are characterized by their reaction rate constants $k_{\mathrm{O2,prod}}$.

The oxygen scavenger actively contributes to the oxygen balance of the system by binding oxygen in a chemical reaction k_{scav}.

In insert-type packaging systems (Figure 1.2 A), the oxygen scavenger and the product compete for oxygen that is present in the packaging headspace. This can also be the case in polymer-type systems (Figure 1.2 B) if the scavenger is incorporated in the inner layer of the packaging film. For active barrier applications, the scavenger should be fast enough to bind oxygen during diffusion through the packaging material so that the oxygen is hindered from entering the packaging headspace (Figure 1.2 B).

These examples highlight the importance of tailoring the scavenger function to the target packaging system. This includes decisions on the type of scavenger, the quantity of scavenger used and the way of integrating the scavenger into the packaging systems.

In the past few years, mathematical models and simulation tools have been introduced to packaging design in order to facilitate complex design decisions and to reduce the number of tests needed compared to the traditional “trial and error” approach [44, 81]. To describe

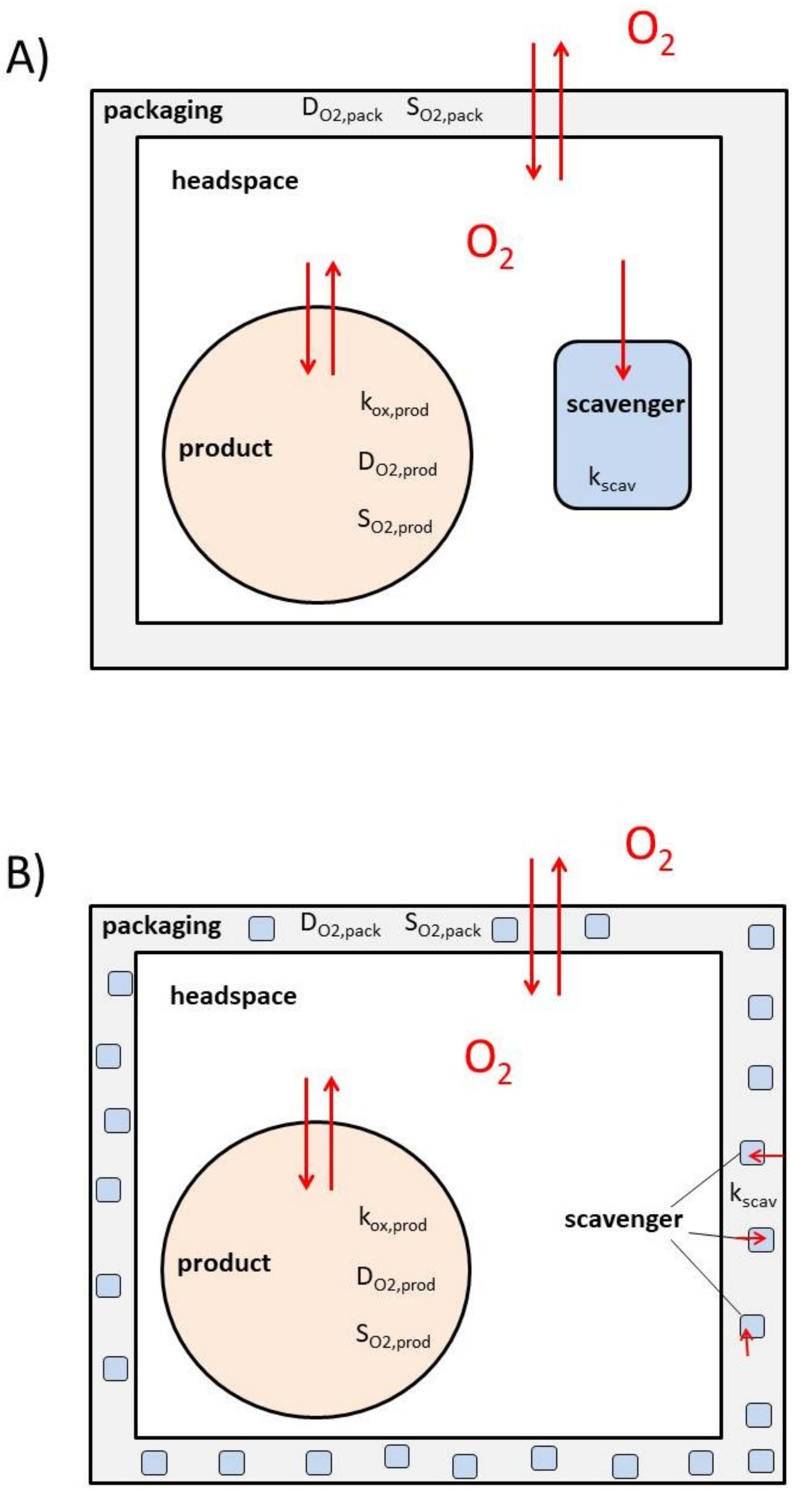

Figure 1.2: Oxygen exchange in oxygen-scavenging packaging systems. A) Insert-type scavenger: Package containing a scavenger sachet or scavenger label. B) Polymer-type scavenger: The scavenger is incorporated into the packaging film.

a full packaging system, all relevant processes related to the different parts of the system have to be included in the model.

There are several simulation tools, also commercially available, that describe gas transport through packaging materials and that can be used for the design of passive barrier packages and modified atmosphere packages [99, 106]. Some of these tools also include certain features of packed products, e.g. the respiration of fresh fruit and vegetables [45, 99] or microbial growth [18].

For active packaging systems, which require also the mathematical description of the active function, there are first modeling approaches available, e.g. for humidity absorbers [88], antimicrobial release [57] and oxygen scavengers in packaging films [27, 28]. Current models describing the oxygen absorption by oxygen scavengers are reviewed in the following section.

1.3.3 Scavenger kinetics

Oxygen scavengers are usually characterized in oxygen absorption experiments. Samples of the oxygen scavenger (e.g. sachet, powder sample, film sample) are stored in gastight vessels with a defined initial oxygen content in the headspace. The decrease in headspace oxygen content caused by the scavenger reaction is monitored during storage until a plateau is reached, i.e. until the scavenger is saturated and the headspace oxygen content remains constant. The storage conditions in terms of humidity and temperature can be adjusted by salt solutions in the vessel and/or by storage in a climate chamber.

This type of experiment results in an oxygen absorption curve. An example is given in Figure 1.3 A. From the absorption curve, the oxygen absorption can be calculated using the ideal gas law (Figure 1.3 B)

A main characteristic of oxygen scavengers that is determined in such an experiment is the oxygen absorption capacity or **scavenger capacity** $n_{\mathrm{O_2,\mathbf{max}}}$, which is the maximum oxygen uptake per unit scavenger, i.e. the amount of oxygen that has been consumed when the scavenger is saturated, usually normalized to the scavenger mass. In practice, common units for the scavenger capacity are cm^3(STP) O_2/g scavenger or mg O_2/g scavenger [1]. The scavenger capacity depends on temperature, and for many scavengers also on humidity [13, 14, 36].

Besides the scavenger capacity, the oxygen absorption experiment also provides information on the time-dependent oxygen uptake, which can also be affected by external factors such as temperature and humidity [14, 36, 41]. Some time-related parameters can be directly read from the absorption curve: The **scavenger half-life** refers to the point of time when

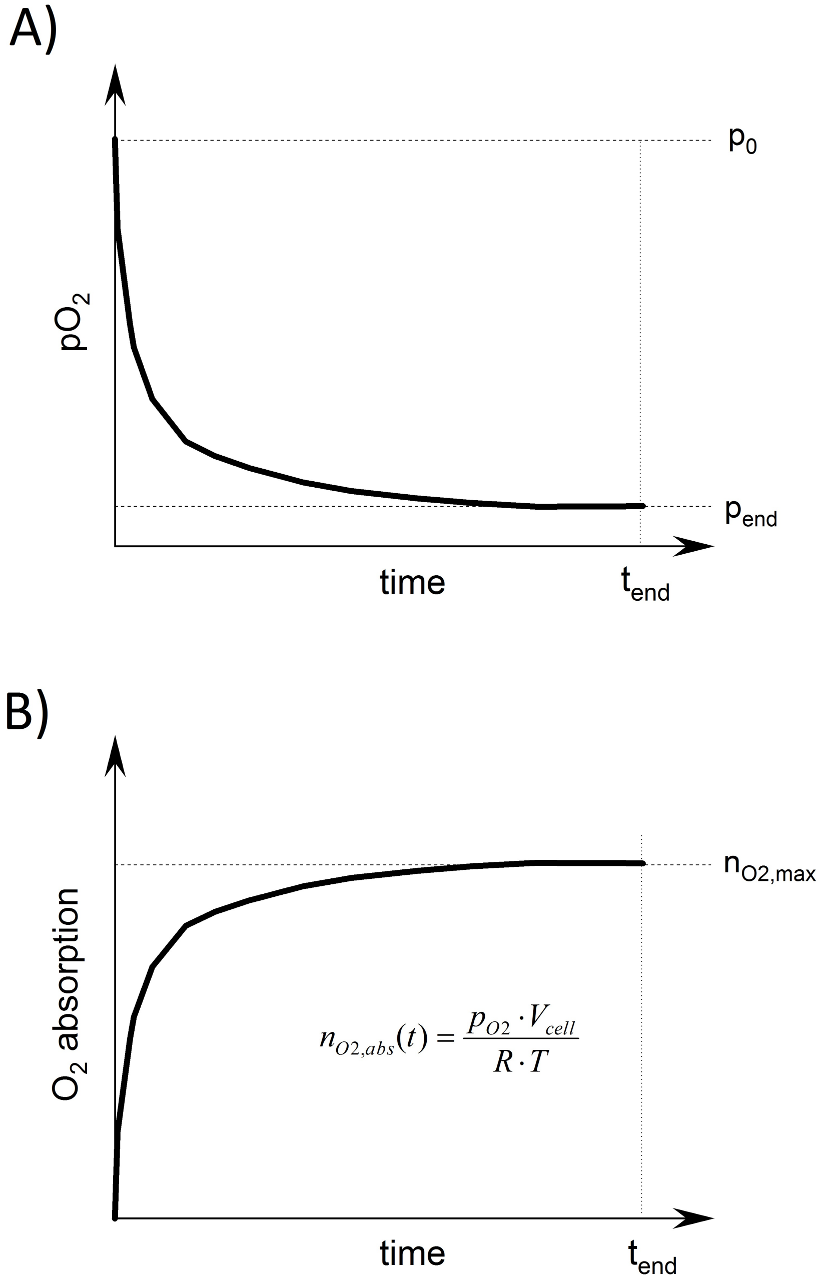

Figure 1.3: Typical data from oxygen absorption measurements. A) Evolution of the headspace oxygen partial pressure p_{O_2} in the measurement vessel, where p_0 and p_{end} are the initial and final oxygen partial pressure, respectively. B) Calculated oxygen absorption n_{O_2}, where $n_{\mathrm{O}_2,\mathrm{max}}$ is the absorption capacity, V_{cell} the volume of the measurement vessel, is the temperature and R the ideal gas constant.

the initial headspace oxygen content has been reduced to 50% [100]. Similarly, scavengers are compared regarding their **oxygen uptake after x days**, where x is the point of time when the measurement was stopped or any other point of time during the experiment [3]. The **exhaustion time** refers to the point of time when the scavenger capacity has been reached (t_{end} in Figure 1.3) [39]. All these parameters refer to single points on the absorption curves and can only be compared for experiments using the same initial headspace oxygen content and the same quantity of scavenger. Sometimes, a **scavenger rate** is given by normalizing the scavenger capacity to the exhaustion time [16]. Again, this value is highly dependent on the experimental setup and can only be seen as a rough estimate of the time-dependent oxygen absorption as it implies a linear absorption curve, which is not a valid assumption for most scavenger experiments (see Figure 1.3 A).

To provide information about the evolution of the scavenger reaction over time, a kinetic model is needed. Common approaches are based on kinetic models describing chemical elementary reactions.

By definition, "an elementary reaction is assumed to occur in a single step and to pass through a single transition state" [69], i.e "an elementary reaction takes place exactly as written" [68]. According to VAN'T HOFF, elementary reactions are classified by the number of participating reactant molecules, i.e. $\mathrm{A} \longrightarrow \mathrm{B}$ is a monomolecular reaction (first-order), described by the kinetic law $r = k \cdot [A]$, and $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$ is a bimolecular (second-order) reaction described by the kinetic law $r = k \cdot [A] \cdot [B]$ [104].

Many chemical reactions, which are no elementary reactions, can be approximated by such simple kinetic laws [68]. Usually, the order of the reaction is determined experimentally and the observed rate law does not necessarily correspond to the classification of elementary reactions [10]. Zero-order kinetics can be observed when the reaction rate is independent from the reactant concentrations so that $r = k$. This can be the case if there is a limiting factor, such as the number of reactive sites during an enzyme-catalyzed reaction [10]. Pseudo-first-order kinetics can be observed if there are two reactants A and B, but B is present in high excess so that the reaction rate depends mainly on the concentration of A and the kinetics can therefore be describe as $r = k \cdot [A]$.

Figure 1.4 gives an overview of the kinetic modeling approaches that have been used for describing scavenger kinetics.

Zero-order approaches were used for the examples given in Figure 1.4 A and B, where linear models were fitted to the initial part of the absorption curve or to different parts of the curve, respectively. Here, the reaction rate is equal to the rate coefficient and can easily be calculated by a linear regression.

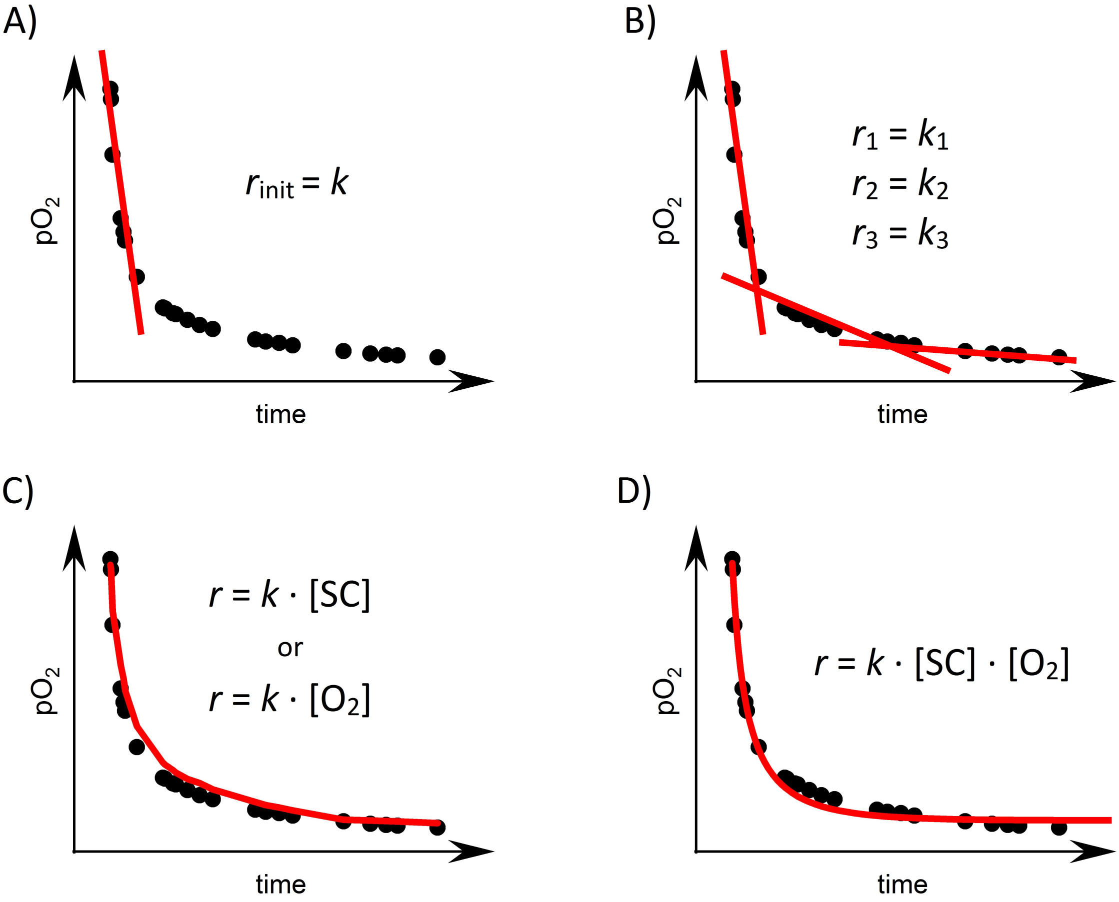

Figure 1.4: Kinetic modeling approaches for oxygen absorption. A) Zero-order kinetics: Initial absorption rate r_{init} [108]. B) Zero-order kinetics: Different regions of the absorption curve [39]. C) First-order kinetics [2, 13, 19] D) Second-order kinetics [29, 31]

Wanner defined the initial absorption rate as the linear decrease of the oxygen partial pressure from the beginning of the reaction ($t = 0$) to day one of the measurement. It was assumed that during this initial stage of the reaction the changes in oxygen concentration and scavenger concentration can be neglected, thereby justifying the zero-order approximation [108]. This model allows for a description of the initial period of the reaction, which, for many applications, is an important period because a fast reduction of the oxygen content after packaging is desired.

Galdi et al. extended this approach by identifying three different regions in the absorption curve and fitting linear models to each of the regions, resulting in three different reaction coefficients [39]. Thereby, the whole absorption curve is described. However, the choice of the regions is subjective which may complicate the comparison of different experiments.

Pseudo-first-order kinetic models, as shown in Figure 1.4 C, have been used in many studies on oxygen scavengers [13, 19, 28, 41]. Here, the reaction rate is proportional to the scavenger concentration, while the oxygen concentration is assumed to be constant (or vice versa), so that it is implicitly included in the rate coefficient. One major advantage of this approach is that there is a simple analytic solution of the rate law describing the absorption curve (Equation 1.1).

$$V_{\mathrm{O}_2} = V_{\mathrm{O}_2,\mathrm{max}} - V_{\mathrm{O}_2,\mathrm{max}} \cdot e^{-kt} \tag{1.1}$$

where V_{O_2} is the absorbed volume of oxygen at time t [mL]; $V_{\mathrm{O}_2,\mathrm{max}}$ is the maximum absorption capacity [mL]; k is the rate coefficient of absorption [h^{-1}] and t is the time [h].

Using this model for the evaluation of scavenger experiments, many authors reported good agreement between model and experimental data [13, 19]. Galotto et al. improved the fit of the model by introducing an additional model parameter, a so-called shape factor, that modifies the shape of the initial part of the absorption curve [41].

Pseudo-first-order kinetic models are included in current industry standards for oxygen scavenger measurements and the rate constant k can be easily determined from experimental data [2]. k can be used for comparison of different scavengers. However, it is important to note, that due to the pseudo-first-order assumption k can only be compared for experiments that were made under the same conditions regarding the initial oxygen concentration.

Second-order kinetic models, as shown in Figure 1.4 D, describe the reaction rate as a function of both reactant concentrations and have recently also been used to describe scavenger reactions [29, 31]. The major advantage of this approach is that the rate coefficient k is independent from the reactant concentrations. Therefore, the second-order kinetic model allows for comparison of scavenger experiments made under different initial conditions and thereby also allows for simulating different packaging scenarios. However, there is no simple analytical solution of the corresponding differential equations so that numerical methods have to be used.

Considering all discussed approaches, there is a variety of models available to describe scavenger reactions. Each model is based on a certain idea of how to describe the scavenger reaction, thus bringing its own strengths and weaknesses. In some cases there is also a trade-off between a "good fit" of the experimental data and usability aspects. However, each model is to be judged in the context of its desired application.

1.4 Gallic acid

1.4.1 Occurence and use

Gallic acid (GA) belongs to the group of plant secondary metabolites and is derived from the shikimate pathway [92]. As a free acid, GA can be found e.g. in raspberry, black currant, blackberry, gallnuts and oak bark [11]. More often, GA is part of hydrolyzable tannins (gallotannins and ellagtannins), i.e. polyphenolic galloyl ester derivatives of sugar-type polyols [79, 92].

Polyphenols, in general, are part of the protective system of plants providing resistance against microbes, insects, solar radiation and reactive oxygen species [79]. The term "tannin" refers to the tanning capacity of these substances, which are therefore used for the production of leather [79]. Further applications of GA include iron gall ink [72].

In chemical analytics, GA is used as a reference standard for the total phenol content determined by the Folin-Ciocalteu assay, i.e. the polyphenol content is expressed a gallic acid equivalents (GAE) [5].

GA is produced from tannins by acidic or alkaline hydrolysis [12] or by enzymatic hydrolysis by tannase [55].

1.4.2 General chemical and physical properties

GA (3,4,5-trihydroxybenzoic acid, $C_7H_6O_5$) is a yellowish-white crystalline powder. The molecular weight of GA is $172.12\,\mathrm{g\,mol^{-1}}$, the density (anhydrous) is $1.694\,\mathrm{g\,cm^{-3}}$ and the solubility (anhydrous) is $11.9\,\mathrm{g\,l^{-1}}$ at 20 °C. Pyrolysis occurs at 253 °C with the formation of pyrogallol and CO_2 [12].

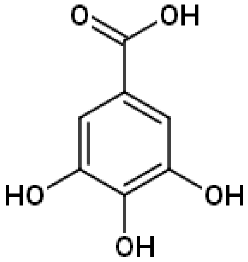

Figure 1.5: Gallic acid (3,4,5-trihydroxybenzoic acid)

Due to its structure including a carboxy group and three adjacent hydroxy groups on the phenyl ring, GA (or the galloyl moiety of larger polyphenols) can take part in various chemical reactions.

Proton transfer

GA is a weak polyprotic acid with the potential of donating four acidic protons, one carboxylic and three phenolic protons. An aqueous solution of GA therefore involves the equilibria shown in Equations (1.2)-(1.6), each characterized by the respective equilibrium constant K_a or K_w:

$$\mathrm{GA} + \mathrm{H_2O} \rightleftharpoons \mathrm{GA^-} + \mathrm{H_3O^+} \qquad K_{a1} = \frac{[\mathrm{GA^-}][\mathrm{H_3O^+}]}{[\mathrm{H_4A}]} \tag{1.2}$$

$$\mathrm{GA^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{GA^{2-}} + \mathrm{H_3O^+} \qquad K_{a2} = \frac{[\mathrm{GA^{2-}}][\mathrm{H_3O^+}]}{[\mathrm{GA^-}]} \tag{1.3}$$

$$\mathrm{GA^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{GA^{3-}} + \mathrm{H_3O^+} \qquad K_{a3} = \frac{[\mathrm{GA^{3-}}][\mathrm{H_3O^+}]}{[\mathrm{GA^{2-}}]} \tag{1.4}$$

$$\mathrm{GA^{3-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{GA^{4-}} + \mathrm{H_3O^+} \qquad K_{a4} = \frac{[\mathrm{GA^{4-}}][\mathrm{H_3O^+}]}{[\mathrm{GA^{3-}}]} \tag{1.5}$$

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \qquad K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{1.6}$$

where GA^-, GA^{2-}, GA^{3-} and GA^{4-} denote the different negatively charged gallate anions. The acidity constants of gallic acid $\mathrm{pK_a} = -\log K_a$ are given in table 1.1.

Metal chelation

Generally, phenols with at least two adjacent OH-groups on the phenyl ring can act as metal chelators due to the interactions between the positively charged metal cations and the

Table 1.1: Acidity constants of gallic acid

pK_{a1} carboxylic OH	pK_{a2} phenolic OH	pK_{a3}	pK_{a4}	Temperature °C	Reference
–	8.68	11.4	> 13	20°C	[94]
–	8.73	12.4	–	20°C	[54]
4.4	8.5	–	–	n.a.	[95]
4.26	8.7	11.45	–	n.a.	[23]
4.39	8.5	10.38	–	24 ± 0.5	[50]

negative charge concentration at the oxygen atom [79]. However, the availability of other functional groups such as carboxy groups have a major influence on the chelating abilities. Phenols bearing the catechol moiety (benzene-1,2-diol, i.e. a phenyl ring with two adjacent OH-groups) or the galloyl moiety were shown to have chelating effects towards ferrous iron (Fe^{2+}) whereas gallic acid had a medium chelating ability [7]. Metal chelation plays an important role for several reactions of polyphenols.

Radical scavenging reactions

Phenols and phenolate anions are prone to oxidation reactions due to the comparably weak bond dissociation energy of the phenolic OH-bond [79]. This feature makes phenols such as tocopherol, hydroxytyrosol and GA potent antioxidants [64]. There are two main mechanisms that have been described for the antioxidant action of phenols in aqueous solution: Single-electron transfer (SET), H-atom transfer (HAT) and their combinations [70, 79, 114].

During SET (Equation 1.7), the radical $R^\bullet$ is scavenged by an electron transfer from the phenol PhOH to the free radical, resulting in a stable phenoxy cation $PhO^{\bullet+}$.

$$R^\bullet + PhOH \longrightarrow R^- + PhO^{\bullet+} \tag{1.7}$$

During HAT (Equation 1.8), the phenol PhOH donates a hydrogen atom to a free radical $R^\bullet$, thereby terminating the radical chain reaction. The phenol itself becomes a phenoxy radical $PhO^\bullet$ which, however, is more stable than the scavenged free radical so that further reactions are prevented.

$$R^\bullet + PhOH \longrightarrow RH + PhO^\bullet \tag{1.8}$$

Which of the mechanisms is preferred depends on several factors, e.g. the reaction medium, type and position of the substituents of the phenol rings and the deprotonation of the phenolic OH groups [79]. For GA, HAT is the preferred antioxidant mechanism due to the high stability of the resulting phenoxy radical which is stablilized by hydrogen-bonding interactions of the adjacent hydroxy groups [64].

Several studies were dedicated to studying the antioxidant behaviour of GA towards free radicals: Using density functional theory calculations, DOROVIC ET AL. showed that the OH-group in para-position is the preferred site for oxidation during the reaction of GA with several radicals [30]. YOSHIOKA ET AL. confirmed the formation of this neutral neutral phenoxy radical by ESR measurements under acidic conditions [114]. The mechanism and the reaction rate coefficient of this radical scavenging reaction changes with increasing pH due to the higher deprotonation of the gallate ion [32]. The resulting phenoxy radicals may undergo further reactions, e.g. form dimers or quinones, depending on the pH of the solution [17, 76].

However, phenols, as redox systems, can also show prooxidant effects depending on the environmental conditions and the availability of redox partners that are readily reduced, e.g. iron(III) or copper(II) ions [79]. For example, GA showed pro-oxidant effects in experiments with deoxyribose. The pro-oxidant activity was attributed to the strong electron-donating and the weak metal chelating ability [9, 111].

Autoxidation

The oxidation of GA in the presence of oxygen (e.g. in air) is called autoxidation. This reaction is highly pH-dependent and involves the formation of GA radicals as well as hydrogen peroxide H_2O_2.

The initial step of polyphenol autoxidation in aqueous solution is the transfer of a single electron (SET) from a phenolic hydroxy group to dissolved oxygen. Figure 1.6 gives an example for a SET from the trianion GA^{3-} to O_2 at pH 11 [114].

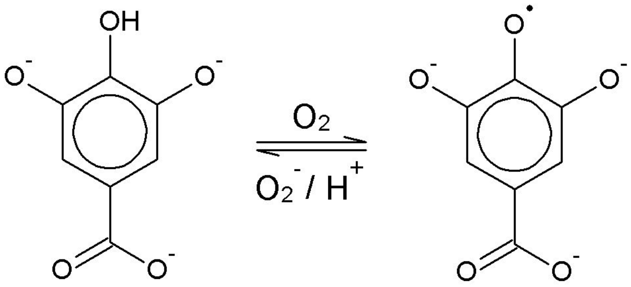

Figure 1.6: Single electron transfer from a gallate anion to dissolved oxygen at pH 11 [114].

In this reaction, a gallate radical and hydrogen peroxide are formed. Depending on the pH, different gallate ions are present in the solution. Thus, also the type of radical formed depends on the solution pH. In general, gallate ions with higher deprotonation are more readily oxidized [32, 33]. The resulting radicals are stabilized by electron delocalisation over the ring π system [32].

In alkaline solution, the by-product hydrogen peroxide is stabilized in the form of the hydroperoxide ion HOO^- [103]. A maximum yield of 1 mol H_2O_2 /mol GA obtained from the reaction with air in the pH range of 7.5 to 8.5 was reported. In this pH range the dianion GA^{2-} is the predominant species [23].

Experimentally it was shown that the initial oxidation step is followed by further reactions, first of all further oxidation: TULYATHAN ET AL. reported an oxygen uptake of 4.9 oxygen atoms per GA molecule for oxygen absorption experiments under alkaline conditions [103]. HOTTA ET AL. found "unusually high numbers of electrons" tranferred during the autoxidation of polyphenols under alkaline conditions, i.e. the number of transferred electrons and therefore the degree of polyphenol oxidation was high compared to what could be expected from the number of available polyphenolic hydroxy groups [48]. The high oxygen uptake was explained by further reactions which may be summarized as "oxidative polymerization". These reactions lead to the formation of additional oxidizable hydroxy groups, e.g. by dimerization and ring opening reactions [48, 103].

However, information on the mechanism and therefore also on the intermediates and products of oxidative polymerisation is scarce. FRIEDMANN ET AL. observed the irreversible formation of several reaction products during autoxidation of GA (pH 7 to 11) by UV spectroscopy. However, the nature of the changes was not further examined [38]. In the study by TULYATHAN ET AL., ellagic acid was identified as one oxidation product by paper chromatography. HPLC revealed two major reaction products and five minor reaction products, all with a higher polarity than GA. However, these reaction products were neither isolated nor identified [103]. More recently, additional autoxidation intermediates have been identified (Figure 1.7): C-O dimers [76], C-C dimers [17] and ellagic acid [75]. The dimers may undergo further polymerization and ring-opening reactions (Figure 1.7) and finally build high-molecular polyphenolic polymers that are similar to polymeric structures that can be found in humic substances [102] or red wine [93, 109].

Kinetic studies showed that the autoxidation of GA is highly dependent on the solution pH and on temperature. TULYATHAN ET AL. studied the oxygen uptake at different pH in the range of 10.36 - 14 and described it as first-order kinetics. The reaction rate coefficient had a maximum at pH 12. The increase from pH 10 to 12 was explained by increasing phenolate ion concentrations. The decrease at higher pH values was attributed to the deprotonation of the third phenolic OH group. This loss of the last OH group was assumed to

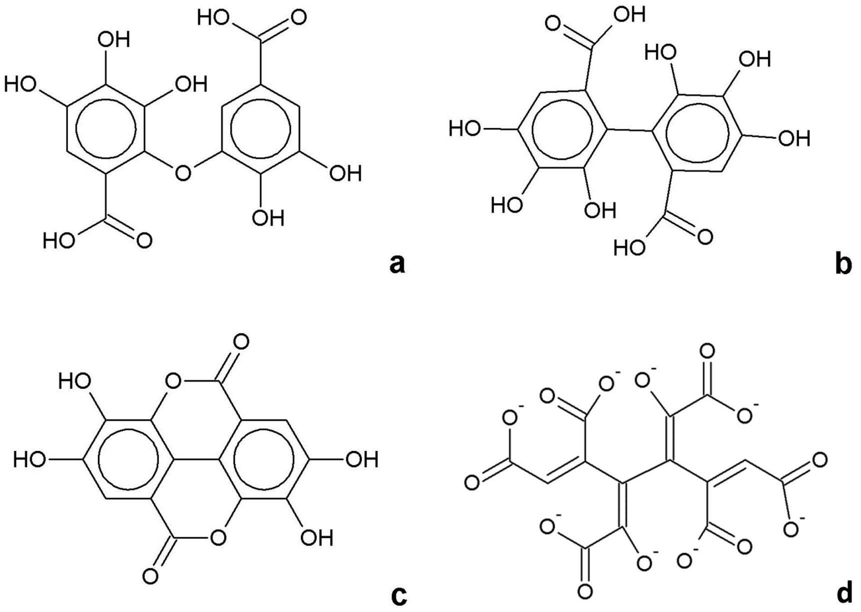

Figure 1.7: Gallic acid autoxidation intermediates: a) C-O dimer [76] b) C-C dimer [17] c) ellagic acid [75] d) open-ring product [103].

reduce the capability of the phenolate moiety for hydrogen bonding and thereby impeding the initial oxidation step [103]. Regarding the capacity for oxygen uptake it was found that the maximum capacity was lower when gallic acid is oxidized under acidic conditions (such as in wine) than under alkaline conditions [103].

Cilliers et al indicated that the mechanism of phenol autoxidation changes depending on the solution pH. They studied the autoxidation kinetics of caffeic acid (3-(3,4-dihydroxyphenyl)-2-propenoic acid), another phenolic acid, in the range pH 4-8 and found that the reaction rate coefficients increased in line with pH and temperature. HPLC analysis revealed the formation of different intermediates and products over time, but these products were not identified. For some reaction products, the pH affected the rate of formation, but not the total amount while for others the total amount was significantly influenced by pH. The reaction products led to a browning of the solution and the development of brown colour was directly correlated with caffeic acid consumption. The intensity of brown also changed with pH, with the solution of pH 6 showing the highest intensity [22].

1.4.3 Applications in active packaging

Taking advantage of the chemical properties, GA (or chemical compounds incorporating the galloyl moiety) could be used for different active packaging applications, e.g. antimicrobial, antioxidant and oxygen-scavenging packaging.

Antimicrobial properties have been reported for different materials containing GA. Rui et al. produced cast films consisting of chitosan and gelatin with incorporated or grafted GA. The films had an antimicrobial effect against *B. cereus, S. aureus, E. coli* and *S. typhimurium* [87]. Moreno-Vasquez et al. showed that extruded PLA-based films containing 10% (w/w) epigallocatechin gallate inhibited the growth of *S. aureus* and *Pseudomonas spp.*[73]. The antibacterial effect of polyphenols containing the GA moiety can be attributed to the metal chelating properties and the interaction with membrane proteins [24].

Antioxidant properties were reported for chitosan-based films grafted with GA. Rui et al. observed a scavenging effect on ABTS (2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) radicals [87]. Schreiber et al. reported a 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging ability. Furthermore, in storage test with peanuts the GA-grafted chitosan film reduced oxidation as shown by reduced level of thiobarbituric acid reactive substances (TBARS) formation, peroxide formation, and conjugated trienes formation [90].

When combined with a base, GA can also be used as an oxygen scavenger. The oxygen-absorbing function is activated by humidity [60]. Table 1.2 gives an overview of studies reporting the application of GA as an oxygen scavenger.

Table 1.2: Oxygen scavenger capacity of gallic acid (GA) in packaging applications

Scavenger composition	Application	Scavenger capacity mg O_2/g GA*	Test conditions	Ref.
10 mg GA + 5.4 mg Na_2CO_3 + 7.4 mg K_2CO_3 + 5.3 mg K_2CO_3	powder mixture	445 724 73	25°C 100% RH	[108]
GA + CaO**	multilayer film active layers: PE+CaO/Adh+15% GA	204	25°C 100% RH	[108]
GA + K_2CO_3 (mass ratio 2:1)	monolayer film PE+3% (w/w) Scav PE+5% (w/w) Scav PE+10% (w/w) Scav PE+20% (w/w) Scav	 103*** 138*** 123*** 84***	23°C 95% RH	[3]

* values recalculated from values given in the respective publication

** GA and CaO were incorporated in seperate layers

*** after 7 days; maximum absorption capacity may not have been reached

Wanner prepared different powder mixtures consisting of GA and potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3) or calcium oxide (CaO), respectively, and studied their oxygen absorption behaviour (Table 1.2). The type of base affected the absorption capacity and the initial reaction rate of the scavenger. Furthermore it was stated that a pH higher than 8 is necessary to start the reaction [108]. GA and CaO were also used for the manufacture of oxygen-scavenging multilayer films, where the scavenger was incorporated either in the coating layer or in an adhesive layer. Oxygen absorption measurements revealed that the initial oxygen absorption rate was ~4.5 times higher when the initial O_2 partial pressure was 202.6 mbar compared to 20.3 mbar. A variation of temperature showed that the initial oxygen absorption rate was ~10 times higher at 25°C compared to 5°C [108].

More recently, Ahn et al. produced monolayer packaging films based on polyethylene which contained up to 20% of a GA-based scavenger. The scavenger mixture contained GA and K_2CO_3 in a 2:1 mass ratio. For oxygen absorption measurements at 23°C and 95% RH, the films absorbed 0.130-0.709 mL O_2/m^2 [3]. This is equal to 84-138 mg O_2/g GA during 7 days (Table 1.2). A temperature-dependence of the oxygen uptake was also reported. However, only results from the first seven days of storage were reported and there was no evaluation of the kinetics.

Considering these results, GA is a polyphenol with a high potential for the application as an oxygen scavenger in active packaging: GA is available from natural resources, has a high oxygen absorption capacity and there are preliminary results showing the usability in packaging applications. However, in order to design oxygen-scavenging packaging materials, the following topics have to be evaluated:

- The processing of GA-based scavengers in an extrusion process has to be studied in more detail, especially the effect of processing on the oxygen scavenging properties.
- The oxygen absorption kinetics (i.e. the autoxidation kinetics) have to be studied in order to provide information on the time-dependent oxygen uptake, not only the scavenger capacity. Here, the influence of external factors such as temperature and humidity, which are relevant for packaging application should also be considered.
- The effect of the base on the autoxidation has to be evaluated in order to optimize the scavenger mixture.

2. OBJECTIVES

Oxygen scavengers are used in packaging to prevent sensitive products from oxidation [86]. Depending on the packaging design, oxygen scavengers can either serve at removing residual oxygen from the packaging headspace or they can be used to improve the barrier function of a packaging material [62]. Commercial examples of oxygen scavengers include scavengers based on iron, sulfite or oxidazable polymers [107, 112].

Gallic acid (GA) is a natural hydroxyphenol that is present in many plants either in a free form or as a part of larger compounds such as tannins [11, 92]. Under alkaline conditions, GA is readily oxidized with a high capacity for binding oxygen [79, 103]. Therefore, the combination of GA and a base has been proposed as an oxygen scavenger [60, 108]. First application tests in packaging showed that GA is a promising bio-based oxygen scavenger [3, 108]

However, to date there is only little knowledge about the oxygen absorption kinetics of GA-based oxygen scavengers and how the reaction can be tailored to packaging applications in order to achieve optimum scavenger performance.

Thus, the first objective of this thesis is to experimentally study the oxygen absorption reaction of GA-based oxygen scavengers and to analyze the main factors that affect the reaction.

For this, several factors that are important for packaging applications have to be considered: First of all, the effect of the external storage conditions, temperature and humidity, on the scavenging reaction has to be determined in oxygen absorption experiments. Similarly, as the scavenger reaction takes place under alkaline conditions, the effect of adding different types of bases on the scavenger reaction has to be analyzed in order to derive optimum scavenger mixtures. Furthermore, the production of active films containing GA in an extrusion process has to be studied in order to determine the effect of processing on the scavenger activity.

Besides experimental studies a thorough description of the scavenger reaction also requires a kinetic model, i.e. a mathematical description of the time-dependent oxygen absorption. Especially in the context of software-based packaging design, mathematical models describing active packging functions are necessary to guide and to facilitate the design process [45, 77].

Although different modeling approaches have been proposed for scavenger reactions, current simulation tools used in packaging design still lack descriptions of oxygen scavenger functions [45, 81, 106]. To date, there is no kinetic model for the oxygen uptake by GA-based scavengers that can be applied in packaging design.

Thus, the second objective of this thesis is to develop and to validate an application-oriented modeling approach for the reaction kinetics of GA-based oxygen scavengers.

For this, the complex autoxidation reaction of GA, which is the basis for the oxygen-scavenging effect, has to be described in a way that allows for the application in current laboratory practice. This means keeping it simple in terms of the analytical and computational effort on the one hand while maximizing the applicability on the other hand, e.g. to account for different packaging scenarios and to be able to combine the model with current models for gas transport.

Overall, this thesis aims at providing basic knowledge on the oxygen absorption kinetics of GA in order to enable the software-based design of packaging materials incorporating GA as an oxygen scavenger.

3. RESULTS

3.1 Gallic acid as an oxygen scavenger in bio-based multilayer films[1]

Gallic acid (GA), a natural phenol, is a potential oxygen scavenger for food packaging applications due to its high capacity for binding oxygen.

In this work, the application of GA in multilayer packaging films was studied. A 2:1 (w/w) mixture of GA and sodium carbonate was used as an oxygen scavenger (OSc). In a three-step process including compounding, cast film extrusion and lamination, multilayer films with the following structure were produced:

PLA 200 µm / adhesive 12 µm / PE+OSc 220 µm / PE 60 µm.

Here, the active layer PE+OSc contained 15% (w/w) of OSc. The films were shown to be thermoformable so that packaging trays could be produced. Initially, the film color was brownish-red but changed to a greenish-black during the reaction with oxygen under humid conditions.

The oxygen absorption of the films was determined at different relative humidities (RH) and temperatures. For comparison, the oxygen absorption of OSc powder and the active layer containing GA was also assessed.

A maximum absorption capacity of 447 mg O_2/g GA at 21 °C and 100% RH was observed for OSc powder. For the packaging films it was shown that the manufacture, which involved temperatures up to 220 °C, did not significantly decrease the absorption capacity of the films.

Reaction kinetics was described using the initial rate constant k_{init}. This approach is based on fitting a zero-order kinetic model to the initial linear part of the absorption curve. The incorporation of GA into a polymer matrix reduced k_{init} compared to OSc powder because the polymer acted as a barrier to oxygen and water vapor diffusion. As expected, temperature had a significant effect on k_{init} of the multilayer films; the corresponding activation energy was $75.4\,\text{kJ}\,\text{mol}^{-1}$. It was also shown that k_{init} increased in line with the RH whereas there was no oxygen absorption if the RH was below 31%.

These results demonstrate for the first time the production and the properties of a bio-based multilayer packaging film with GA as the oxygen scavenger. Potential applications include the packaging of food products with high water activity.

Contributions: The doctoral candidate conceived and designed the study, performed the experiments, analyzed the data and wrote the manuscript.

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Gallic Acid as an Oxygen Scavenger in Bio-Based Multilayer Packaging Films

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Abstract: Oxygen scavengers are used in food packaging to protect oxygen-sensitive food products. A mixture of gallic acid (GA) and sodium carbonate was used as an oxygen scavenger (OSc) in bio-based multilayer packaging films produced in a three-step process: compounding, flat film extrusion, and lamination. We investigated the film surface color as well as oxygen absorption at different relative humidities (RHs) and temperatures, and compared the oxygen absorption of OSc powder, monolayer films, and multilayer films. The films were initially brownish-red in color but changed to greenish-black during oxygen absorption under humid conditions. We observed a maximum absorption capacity of 447 mg O_2/g GA at 21 °C and 100% RH. The incorporation of GA into a polymer matrix reduced the rate of oxygen absorption compared to the GA powder because the polymer acted as a barrier to oxygen and water vapor diffusion. As expected, the temperature had a significant effect on the initial absorption rate of the multilayer films; the corresponding activation energy was 75.4 kJ/mol. Higher RH significantly increased the oxygen absorption rate. These results demonstrate for the first time the production and the properties of a bio-based multilayer packaging film with GA as the oxygen scavenger. Potential applications include the packaging of food products with high water activity ($a_w > 0.86$).

Keywords: food packaging; absorber; active packaging; polyphenol

1. Introduction

In active packaging technology, oxygen (O_2) scavengers are used to protect O_2-sensitive food products [1–3]. Current examples include scavenger sachets, which are not common in Europe, and active packaging materials containing O_2-scavenging substances in the polymer matrix [1,3]. Scavengers can also be classified according to their active substances, i.e., the substance that reacts with O_2. Many commercially available scavengers are based on iron, oxidizable polymers, or sulfite [3–7].

Materials based on renewable resources support the development of sustainable packaging. Research has therefore focused on the development and improvement of bio-based packaging materials [8–10]. Some natural substances can be used as bio-based O_2 scavengers including plant extracts, tocopherol, ascorbic acid, and especially polyphenols, which are known for their ability to react with O_2 [11–14].

One polyphenol that is potentially suitable as an O_2 scavenger for packaging applications is gallic acid (3,4,5-trihydroxybenzoic acid, GA) because it absorbs large amounts of O_2 under alkaline conditions [13,15,16]. To provide alkaline conditions in the packaging material, GA must be combined with a base. Furthermore, the presence of water is required [13,16]. During the reaction between GA and O_2, a change of color from white (pure GA) to dark brown, dark green, or black may be observed, depending on which base is used [13]. Therefore, GA was also proposed as an O_2 indicator [13,16,17].

The incorporation of GA into packaging films has not been investigated in great detail. Langowski and Wanner first mentioned gallic acid as an O_2 scavenger for packaging applications [16]. Goldhan et al. and Wanner described application trials, in which combinations of GA and different bases were integrated either in the adhesive layer or the coating of packaging films [13,17]. Recently, Ahn et al. reported the production of monolayer films containing GA and potassium carbonate [18]. However, the use of GA as a scavenger in packaging films requires multilayer structures comprising an outer O_2 barrier layer to limit O_2 ingress from the environment, and an inner food contact layer to prevent direct contact between GA and the packed food.

In this study, we describe the O_2 absorption properties of bio-based packaging films containing GA as a natural O_2 scavenger. Multilayer packaging films entirely based on renewable resources were produced in a three-step process involving compounding, cast film extrusion, and lamination. We investigated the effects of the polymer matrix, the relative humidity, and the temperature on oxygen absorption and determined the change in surface color caused by the reaction. The results provide insight into the O_2 scavenging properties of GA and its potential applications in food packaging.

2. Results

2.1. Film Properties

A multilayer packaging film was produced in a pilot-scale three-step process involving compounding, cast film extrusion, and lamination. The film comprised a food contact layer (BioPE), an active layer containing the scavenger (BioPE + 15% (w/w) OSc), a bio-based adhesive, and an outer barrier layer (PLA) that reduces O_2 ingress from the environment. The thicknesses of the individual layers of the produced film were determined in a microscopic analysis of the cross section and are given in Figure 1.

The film had a brownish red color after production with some small darker particles. These particles were most probably OSc powder agglomerates formed during processing. Powder agglomerates may affect the mechanical properties and barrier properties of the film. Thus, the process must be optimized in order to avoid agglomerates.

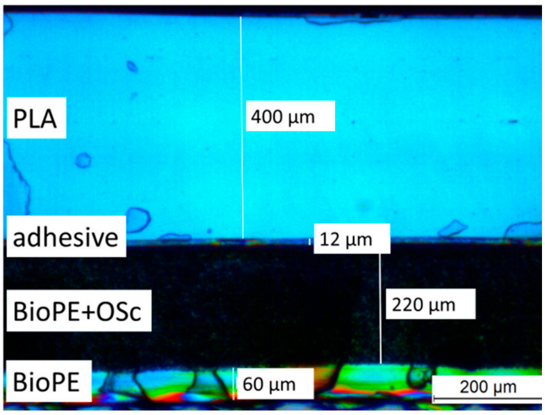

Figure 1. The multilayer structure of the bio-based packaging film containing the gallic acid scavenger (OSc).

One potential application of the bio-based multilayer film is the production of O_2-scavenging food packaging trays. In such a packaging setup, the main function of GA would be to scavenge residual O_2 from the package headspace. Preliminary tests showed that the films can be thermoformed into trays (Figure 2). Future studies will therefore include storage tests with oxygen-sensitive food products to evaluate the GA-based scavenger under real packaging conditions.

Figure 2. Thermoformed trays (144 mm × 144 mm × 40 mm) containing gallic acid as the O_2 scavenger.

2.2. Film Color

The dry OSc mixture was white in color, but the first step of film production (compounding) resulted in light-purple compound pellets. This color change indicated that GA had reacted with O_2 during the process. The multilayer film showed a darker brownish-red color, probably reflecting an additional reaction with O_2. When stored under humid conditions, the film rapidly turned into a dark greenish-black (Figure 3), which is reflected by a decrease in L*, a*, and b* values.

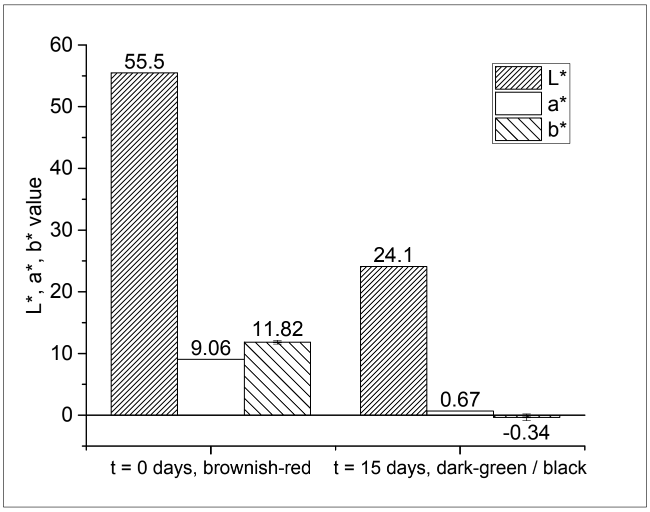

Figure 3. Multilayer film color after production (t = 0) and after storage at 21 °C and 100% RH (t = 15 days), expressed as CIE L*a*b* values.

Alkaline conditions promote a rapid reaction between GA and O_2 and can be provided combining a basic substance and water [16]. This is reflected by the observed color changes during processing, which are slow under dry conditions but accelerate during storage at higher humidities. The color of polyphenols is determined by the presence of chromophoric groups that interact with light [14]. Dark reaction products of polyphenol oxidation, e.g., brown or black polycondensates, can be found in wine or humic substances [19,20]. The color change of the multilayer films indicated that GA formed larger molecules during the reaction with O_2. Although these reaction products have not yet been characterized, they may represent dimers, as previously reported by Tulyathan et al. [15].

Remarkably, the observed color change was not proportional to the O_2 absorption of GA. During the O_2 absorption experiments (see Section 2.3), we noticed that the films continued absorbing O_2 when the color had already turned into black, i.e., in the later stages of the reaction, the film color could not be related to the amount of O_2 that was absorbed. This limits the O_2-indicating function of GA to the first stages of the reaction. However, assessing the potential of GA as an O_2 indicator requires further investigation of the correlation between color and O_2 absorption.

2.3. Oxygen Absorption of Gallic Acid

O_2 absorption was measured in closed cells with a defined initial O_2 concentration of 20% (v/v) by monitoring the decrease in headspace O_2 partial pressure over time. Varying storage conditions were used to determine the effect of temperature, relative humidity, and the polymer matrix on O_2 absorption by GA. For better comparison, the results of the O_2 absorption measurements are expressed as mg O_2/g GA.

2.3.1. Effect of Temperature

The application temperature (i.e., the storage temperature of the packed product) is an important factor for the performance of O_2 scavengers in terms of their absorption rate [7,21–24]. As described above, the O_2 scavenging effect of GA relies on the chemical reaction of GA with oxygen. Therefore, a positive influence of temperature on the O_2 absorption rate could be expected. We examined the O_2 absorption by the produced multilayer films at 4, 21, and 38 °C during 16 days of storage. The results are presented in Figure 4. Higher storage temperatures led to increased O_2 absorption; temperature had a significant effect on the initial reaction rate ($p < 0.05$).

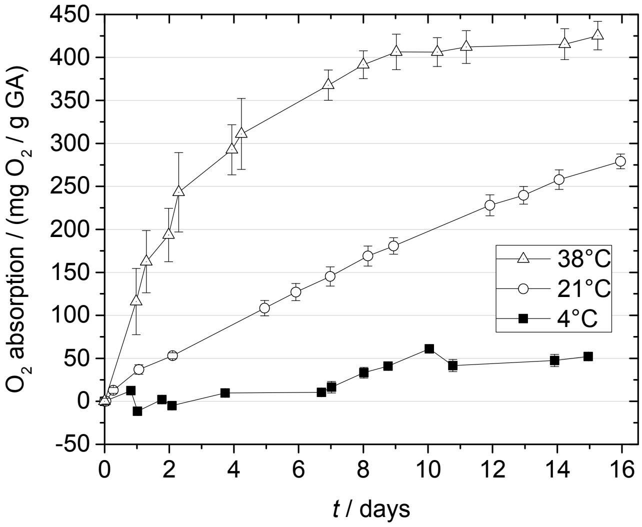

Figure 4. O_2 absorption by gallic acid (GA) in multilayer films at 100% RH and varying temperatures.

The initial reaction rate constants k_{init}, obtained from the initial linear increase in O_2 absorption, were 4.2 ± 0.6, 20.0 ± 0.5, and 124.0 ± 5.8 mg O_2/(g GA d) for 4, 21, and 38 °C, respectively. This implies that O_2 absorption in the beginning of the measurement was twice as high at 21 °C and 5 times higher at 38 °C compared to 4 °C.

In the linear fit of $\ln k_{init}$ vs. $1/T$, Arrhenius-like behavior was observed ($R^2 > 0.99$). The temperature-dependence of the initial rate constant k_{init} can therefore be described with the following equation:

$$k_{init}\ (T) = 6.90 \cdot 10^{13} \mathrm{mg\ O_2/(g\ GA \cdot d)}\ \exp(-75.4 \frac{\mathrm{kJ}}{\mathrm{mol}} / (R \cdot T)).$$

The activation energy (E_a) of O_2 absorption by the multilayer films was 75.4 kJ/mol. Lower E_a values in the range of 44.1 to 49.0 kJ/mol have been reported for commercially available iron-based scavengers [25,26]. Hence, for the analyzed films, the temperature has a greater effect on the GA-based scavenger than on the iron-based scavengers. The positive effect of temperature on the activity of the scavenger film can be explained as follows: The two main processes that determine O_2 absorption of the scavenger film, O_2 transport through the polymer matrix and the chemical reaction between O_2 and GA, are both temperature-dependent and can be described by the Arrhenius law [27,28]. Therefore, the O_2 absorption of the film is accelerated at higher temperatures.

These results reveal the influence of temperature on the performance of GA-based O_2 scavengers and should therefore be taken into account for future applications.

2.3.2. Effect of Relative Humidity

Humidity, i.e., the availability of water, has been described as an important trigger of the scavenging reaction by GA [13,16,18]. The scavenging reaction is initiated by the deprotonation of GA in alkaline solution [29]. To enable this acid–base reaction in the produced multilayer films, humidity from the environment is needed. In our experiments, we determined the effect of RH on the O_2 absorption by GA by storing multilayer films at 21 °C under different RH conditions (Figure 5). The RH conditions were chosen to simulate typical storage conditions for different types of food, characterized by different water activities (a_w), i.e., dry powder products or cookies (31% RH), jam (75% RH), gammon or salami (86% RH), and beverages (100%) [22,30,31].

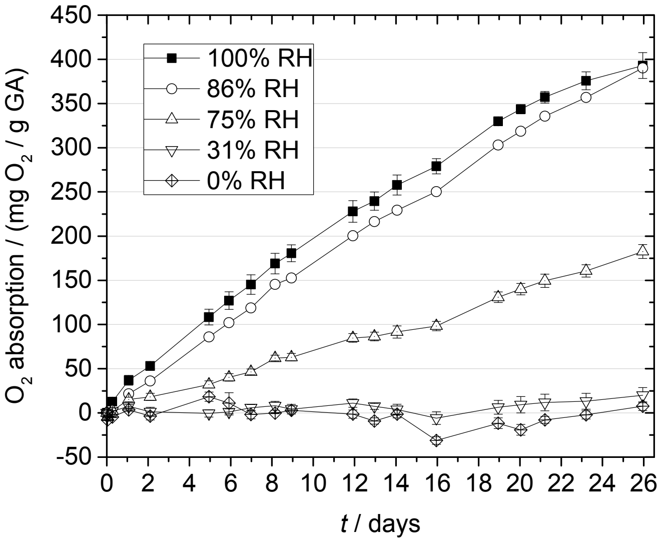

Figure 5. O_2 absorption by gallic acid (GA) incorporated in multilayer films at 21 °C and different relative humidities (RHs).

The amount of water present in the environment of the film significantly influenced O_2 absorption by GA ($p < 0.05$). After 26 days, the samples stored at 100% or 86% RH achieved the highest absorption of ca. 390 mg O_2/g GA, followed by those stored at 75% RH, which absorbed 185 mg O_2/g GA. In comparison, storage at 31% or 0% RH resulted in negligibly low O_2 absorption.

Remarkably, we found that the differences in O_2 absorption were not proportional to the differences in RH. Higher RH led to a disproportionate increase in O_2 absorption rate, whereas O_2 absorption after 26 days was not significantly different at RH of 86% and 100% ($p < 0.05$). More research is therefore needed to characterize the influence of water on O_2 scavenging by GA in more detail, and for quantitative analysis, a parameter other than RH may be required.

Overall, our results show that humid conditions are necessary for GA to scavenge O_2 rapidly, and we therefore recommend GA for the packaging of moist products with water activities >0.86.

2.3.3. The Effect of Film Structure

The incorporation of GA into a polymer matrix led to a reduced O_2 absorption, especially during the first few days of the reaction (Figure 6).

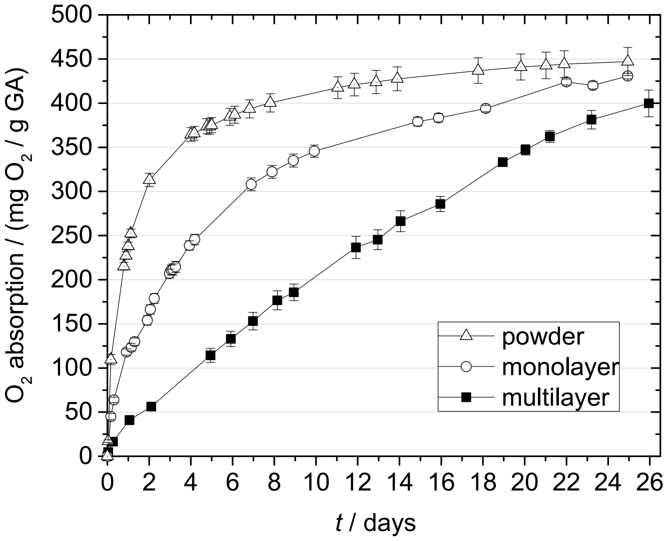

Figure 6. O_2 absorption by gallic acid (GA) in mono- and multilayer films and in powder form at 21 °C and 100% RH.

After 2 days, the OSc powder absorbed twice as much O_2 as the monolayer films. As expected, this effect was even more pronounced in multilayer films. In the powder experiment, the maximum O_2 absorption capacity of the GA scavenger was determined to be 447 ± 16 mg O_2/g GA, and this was achieved after 25 days storage at 21 °C and 100% RH, after which the O_2 absorption remained constant. The measured O_2 absorption capacity is in line with the results of Wanner who reported an absorption capacity of 340 ± 7 cm^3 O_2/g GA for a GA-based scavenger at 25 °C, 100% RH, and 1013 hPa (equal to 445 mg O_2/g GA) [13]. Ahn et al. observed a much lower maximum absorption capacity of app. 64 cm^3 O_2/g GA for GA combined with potassium carbonate in monolayer films stored at 23 °C and 95% RH [18]. However, this difference might be attributed to different processing conditions and film structures.

Compared to commercially available O_2 scavengers, such as iron-based or polymer-based systems, GA shows a remarkably high absorption capacity. Table 1 gives an overview of the absorption capacities of different O_2 scavengers. For a better comparison, O_2 absorption is related to the amount of scavenger additive used, e.g., the amount of the OSc mixture in this study.

Table 1. O_2 absorption capacities of different O_2 scavengers.

Scavenger Type	**Absorption Capacity mg O_2/g Scavenger**	**References**
OSc powder (gallic acid + sodium carbonate, 2:1)	298	this study
polymer additive with iron powder (SHELFPLUS® O_2 2710)	39–48	[5]
polymer additive: copolyester-based polymer (Amosorb DFC 4020, Colormatrix Europe, Liverpool, UK)	43–47	[32]
polymer: ethylene methylacrylate cyclohexenylmethyl acrylate 'OSP™'	60–100	[23,33]
polymer: metal-catalysed poly(1,4-butadiene)	140	[34]
coating: cyclo-olefin bonded to a silicate backbone 'ORMOCER®'	90	[6]

The monolayer and multilayer films absorbed 430 or 380 mg O_2/g GA during the 25-day storage period but did not achieve their maximum absorption capacity due to their lower absorption rate (Figure 6). However, it seems like the film production process, which involved temperatures up to 220 °C, did not considerably reduce the O_2 absorption capacity of GA compared to the untreated OSc powder.

The slower reaction of monolayer and multilayer films may reflect the gas barrier properties of the polymer matrix. Before the reaction with GA, the O_2 must dissolve in the polymer and diffuse to the immobilized scavenger. The same applies for water vapor, which is also necessary for the reaction. Thus, the films can be regarded as complex reaction-diffusion systems. The reaction rate of such systems is determined by both the diffusivity of the reactants (O_2 and water vapor) in the matrix and the rate constant for the actual scavenging reaction. The current research of our group focuses on developing a mathematical model that describes O_2 scavenging films as a reaction–diffusion system, accounting for both O_2 and water permeation. The aim is to get a deeper understanding of the underlying reaction mechanism, thereby providing further guidance for the design of tailor-made GA-based scavengers.

3. Materials and Methods

3.1. Materials

The scavenger (OSc) was obtained by blending gallic acid (GA) monohydrate powder (99%) and water-free sodium carbonate (Na_2CO_3), both from ABCR (Karlsruhe, Germany) at a ratio of 2:1. GA is a weak acid with the formula $C_6H_2(OH)_3COOH$. At room temperature, it is a yellowish-white crystalline powder. At 253 °C, GA decomposes to form CO_2 and pyrogallol [35].

A bio-based linear low-density polyethylene (BioPE, SLL218, Braskem, Brazil) served both as the polymer matrix for the OSc powder and as the food contact layer. BioPE was chosen due to its high O_2 permeability (see Table 2) in order to allow for rapid oxygen transport from the packaging headspace to the embedded OSc particles.

A 400 µm polylactide (PLA) film produced at Fraunhofer IVV (Freising, Germany) from PLA IngeoTM2003 D (Natureworks LLC, Minnetonka, MN, USA), served as an outer barrier layer for the packaging film.

For lamination, the bio-based adhesive EpotalR P100 ECO was mixed with 3% (w/w) hardener Basonat LR9056 (BASF SE, Ludwigshafen, Germany).

The thermal properties and the gas permeability of BioPE and PLA are given in Table 2.

Table 2. Properties of the used polymers.

	Thermal Properties			**Gas Permeability**	
Polymer	**Glass Transition Temperature °C**	**Melting Temperature °C**	**Crystallinity Degree %**	**O_2 cm^3 (STP) 100 µm/(m^2 d bar)**	**H_2O g 100 µm/(m^2 d)**
BioPE	n.d.	125.6	24.6	1898	1
PLA	60.1	152.3	39.1	153	58

The thermal properties were determined by differential scanning calorimetry (DSC) using a DSC 821^e (Mettler-Toledo, Columbus, OH, USA) under a nitrogen atmosphere. Two heating runs (23 °C to 300 °C) were made with a heating rate of 10 K/min. The degree of crystallinity X_c was calculated by relating the determined melting enthalpy ΔH_m to the theoretical melting enthalpy of 100% crystalline samples, which was taken to be 93.7 J/g (PLA) or 277.1 J/g (LDPE), respectively [36,37].

All gas permeation measurements were carried out on two replicate samples of 50 µm films.

O_2 permeability was determined at 23 °C and 50% RH according to the DIN 53 380 standard method using an Oxtran device (Mocon, Brooklyn Park, MN, USA).

The water vapor transmission rates were determined according to DIN EN ISO 15106-3 with a Brugger device (WDDG, Brugger, Germany) at 23 °C and an 85–0% gradient of RH.

3.2. Film Production

3.2.1. Compounding

The OSc powder (15% (w/w)) was melt-blended with BioPE in a co-rotating twin screw extruder (Collin Teach-Line Bench Top Compounder ZK 25 T × 24 D; Dr. Collin GmbH, Ebersberg, Germany). The melt strain was then cooled on dry ice and pelletized (Pelletizer CSG 171 T; Dr. Collin GmbH). The temperature profile of the process comprised five zones at 20/100/125/115/120 °C. The rotational screw speed was 80 rpm, the melt pressure was 125 bar, and the melt temperature at the rod die was 160 °C. The BioPE-OSc compound was stored in hermetically sealed aluminum bags under a nitrogen atmosphere at 23 °C. The final concentrations of GA, Na_2CO_3, and BioPE in the compound were 10%, 5%, and 85% (w/w), respectively.

3.2.2. Cast Film Extrusion

Monolayer and multilayer cast films were produced on a flat film co-extrusion line (Dr. Collin GmbH) with a nozzle width of 300 mm.

Monolayer film: The BioPE-OSc compound was extruded by applying temperatures of 60/120/140/160/180/180 °C (zones 1–6) in an extruder with an L/D ratio of 30.

Multilayer film: An additional BioPE layer was co-extruded onto the monolayer film. The temperature profile in the extruder (L/D = 24) was 60/160/180/200/220 °C (Zones 1–5). The feedblock and nozzle temperatures were 200 °C and 220 °C, respectively.

3.2.3. Lamination

The co-extruded film was laminated to a 400 µm PLA film (lacquering and lamination pilot plant, Fraunhofer IVV, Freising, Germany). To improve surface properties, both films were Corona-discharge-treated beforehand. The adhesive was applied using a gravure roll.

The resulting laminate was packed in an aluminum bag under a nitrogen atmosphere. It was stored for 24 h at 50 °C to ensure complete hardening of the adhesive and thereafter stored at 23 °C.

3.2.4. Thermoforming

Samples of the bio-based multilayer films (ca. 650 cm^2) were thermoformed into packaging trays using a semi-automatic thermoforming device (LDFG23B, Illig, Germany) in order to assess the potential of the film for thermoforming applications. The heating time was 12 s with a heating plate temperature of 520 °C. The moulding time was 6 s. The tray dimensions were 144 mm × 144 mm × 40 mm. In the present study, there was no further analysis of the trays.

3.3. Film Characterization

3.3.1. Layer Thickness

Microtome cut cross sections (20 µm) were obtained using a Jung Autocut 2055 (Leica, Wetzlar, Germany). Micrographs of these cross sections were made with a transmitted light microscope (Leitz GmbH, Wetzlar, Germany) and the thicknesses of the individual layers were determined using the corresponding microscope software (LAS V 4.0, Leica, Wetzlar, Germany).

3.3.2. Color Measurement

The surface color of the monolayer and multilayer films was analyzed before (t = 0) and after oxygen absorption (15 days at 21 °C and 100% RH) using the non-digital color imaging system DigiEye (DigiEye v2.62, VeriVide, UK). The system settings and calibration have been described by

Böhner et al. [38]. Average surface color was determined from measurements of 10 points evenly distributed over the film surface and expressed as CIE L*a*b* values. In the CIE L*a*b color space, the L* axis gives the lightness. The a* axis represents the red/green opponent colors, and the b* axis represents the yellow/blue colors.

3.3.3. Oxygen Absorption

Film samples were stored in stainless steel cells equipped with two valves for gas flushing. For a detailed description, see Rieblinger et al. [39]. The cells were hermetically closed with a glass lid and had a free headspace volume of 86 cm^3 or 106 cm^3.

Relative humidity in the cells was adjusted with silica gel, calcium chloride, sodium chloride, potassium chloride, or water (0, 31, 75, 86, and 100% RH at 21 °C, respectively) [40–42].

The initial headspace gas atmosphere of 20% O_2 and 80% N_2 (v/v) was established by flushing the cell with synthetic air (Linde Gas, Munich, Germany). The decrease in the headspace O_2 partial pressure (p_{O2}) was then measured non-destructively during storage using Fibox 4 Trace, a luminescence-based oxygen detection system (PreSens Precision Sensing GmbH, Regensburg, Germany). For this, an optical sensor spot (PSt3) was placed inside the cell at the glass top.

The following samples were analyzed:

OSc powder: 0.06 g;
Monolayer: 0.25 g film: ~2.5 × 5 cm;
Multilayer: 0.96 g film ~2.5 × 5 cm.

All O_2 absorption measurements were carried out on at least three replicate samples of films or powder, except for the measurement at 86% RH, for which only one replicate is available.

The results (decrease in p_{O2}) were converted into the mass of absorbed O_2 (m_{O2}) using the ideal gas law: $m_{O2} = (p_{O2}\ V_{HS}\ M_{O2})/(R\ T)$, where V_{HS} denotes the headspace volume of the cell, M_{O2} the molar mass of O_2, R = 8.13446 J/(mol K) the ideal gas constant, and T is the temperature in Kelvin. For better comparison, m_{O2} was normalized to the mass of the GA contained in the film or in the scavenging powder, so all O_2 absorption values are given in mg O_2/g GA.

The initial rate constants of O_2 absorption k_{init}/(mg O_2/(g GA day)) were determined from the initial absorption values (up to 130 mg O_2/g GA) by linear regression. In the initial phase of O_2 absorption, the influence of the reactant concentrations on the reaction rate can be neglected so that this simplified approach of estimating k_{init} can be used.

The temperature dependence of k_{init} was analyzed by fitting the linearized form of the Arrhenius equation $\ln(k) = (-Ea/R)(1/T) + \ln(A)$.

3.4. Data Treatment

OriginPro 2016G (OriginLab Corp., Northampton, MA, USA) was used for the analysis of the absorption data. The effect of treatments was examined in a one-way analysis of variance (ANOVA); the null hypothesis was rejected with a significance level of 0.05.

The presented results denote the arithmetic means of at least three replicate samples; error bars represent the standard deviation.

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Author Contributions: A.P. and S.S. conceived and designed the experiments, A.P. performed the experiments, A.P. and K.M. analyzed the data, S.S. and K.M. contributed analysis tools and expertise, and A.P. wrote the manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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3.2 Kinetic modeling of scavenger reactions: Parameter estimation for an oxygen scavenger based on gallic acid[2]

The software-based design of active packaging requires mathematical models of oxygen scavenger reactions. This study presents an approach for describing such reactions with a second-order kinetic model. The reaction of the scavenger (SC) with oxygen (O_2) was reduced to the following net reaction:

$$\mathrm{SC} + \mathrm{n}\,\mathrm{O_2} \xrightarrow{k} \mathrm{SC_{ox}}$$

where n can be interpreted as the absorption capacity and k is the reaction rate coefficient. This approach focuses on the major feature of a scavenger, i.e. the uptake of oxygen related to the amount of scavenger used, while neglecting reaction products and intermediates.

The model was fitted to experimental data obtained for an oxygen scavenger based on gallic acid (GA) in order to determine k and n. Here, the parameter estimation by a downhill-simplex-based algorithm for numerical optimization was evaluated.

All experiments could be sufficiently described with the chosen model and the simulation error was adequate in relation to the experimental error. For an in-deep analysis of the fit, the k-n parameter space was mapped in terms of the objective function (sum of squared residuals). This allowed for tracking the optimization steps and for the identification of potential multiple local minima.

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. For the scavenger reactions at 75% RH and 100% RH unambiguous minima could be found. However, at 0% RH, there was no detectable scavenger reaction and fitting the noisy experimental data led to ambiguous solutions without physical meaning.

This study provides the evaluation of an application-oriented modeling approach for scavenger reactions. This is the basis for using kinetic data from oxygen scavenger experiments for software-based active packaging design.

Contributions: The doctoral candidate conceived and designed the study, performed the model fit and parameter estimation, analyzed the data and wrote the manuscript.

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

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KEYWORDS

Scavenger Kinetics, Food Packaging, Numerical Optimization

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 $1.347 \cdot 10^{-7} \mathrm{m}^3/(\mathrm{mol} \cdot \mathrm{s})$ and $1.496 \cdot 10^{-6} \mathrm{m}^3/(\mathrm{mol} \cdot \mathrm{s})$ 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:

$$\mathrm{SC} + \mathrm{n}\, \mathrm{O}_2 \rightleftarrows \mathrm{SC}_{\mathrm{ox}} \tag{1}$$

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

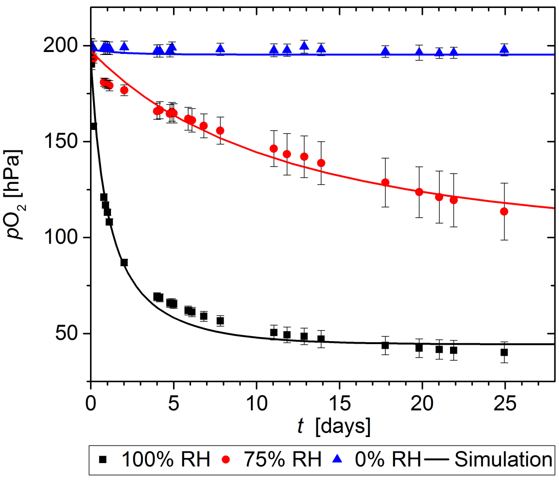

Figure 1: Oxygen Absorption of a Gallic Acid-based Scavenger at various Relative Humidities (RH)

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. O_2 or SC. This is a reasonable approximation when there is large excess of either O_2 or SC (pseudo first-order reaction). In most packaging applications, however, this assumption is not valid (i.e. there are low concentrations of O_2 and SC) so that first-order kinetic parameters cannot be transferred to other packaging systems.

For the software-based design of active packaging including O_2 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 O_2 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 O_2 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 O_2 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 (Na_2CO_3) 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:

$$\mathrm{GA} + \mathrm{n\,O_2} \longrightarrow \mathrm{GA_{ox}} \tag{2}$$

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:

$$r = k \cdot [\mathrm{GA}] \cdot [\mathrm{O_2}] \tag{3}$$

Here, r depends on the concentrations of both reactants, [GA] and $[O_2]$, and k is the reaction rate coefficient. Based on this kinetic law, the net rates of consumption of GA and O_2 were described with a system of ordinary differential equations (ODE):

$$\frac{d[\mathrm{GA}]}{dt} = -k \cdot [\mathrm{GA}] \cdot [\mathrm{O_2}] \tag{4}$$

$$\frac{d[\mathrm{O_2}]}{dt} = -n \cdot k \cdot [\mathrm{GA}] \cdot [\mathrm{O_2}] \tag{5}$$

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 O_2 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 cm^3 or 108 cm^3 and the O_2 absorption (i.e. the decrease of the O_2 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 (O_2 partial pressure in hPa) was transferred to O_2 concentrations $[O_2]$ in mol/m^3 using the ideal gas law. The mean square deviation for each experimental condition was then calculated as follows:

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

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 AbsTol $= 10^{-6}$ and 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:

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

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:

$$\text{RMSE} = \sqrt{\frac{\text{SSQ}}{N - p}} \tag{8}$$

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 RMSE threshold $= \text{RMSE}_{\text{min}} + \text{MSE}_{\text{exp}}$ 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 GA-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 100% RH than at 75% RH. This may be explained by the mechanism of the scavenger reaction which includes the deprotonation of the GA and a subsequent multistep 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)

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

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 $\mathrm{mol/m^3}$, 0.633 $\mathrm{mol/m^3}$ or 0.373 $\mathrm{mol/m^3}$ 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 $k = 1.496 \cdot 10^{-6} \mathrm{m^3/(mol \cdot s)}$, 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 $k = 1.347 \cdot 10^{-6} \mathrm{m^3/(mol \cdot s)}$.

For 0% RH, already from the experimental data it could be seen that $k = 0\,\mathrm{m^3/(mol \cdot s)}$ and $n = 0$ since there was no detectable O_2 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 O_2 absorption data of a gallic acid-based O_2 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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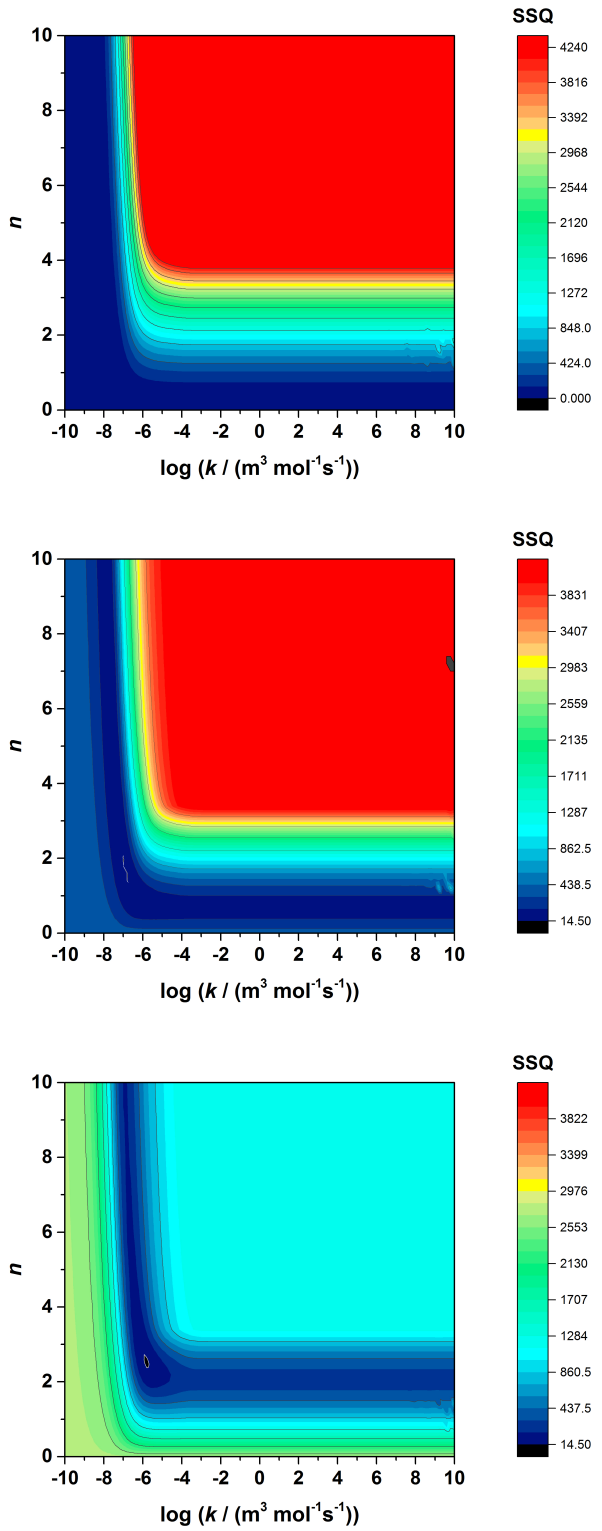

Figure 2: Contour Plots of the Parameter Spaces at various Relative Humidities (RH)

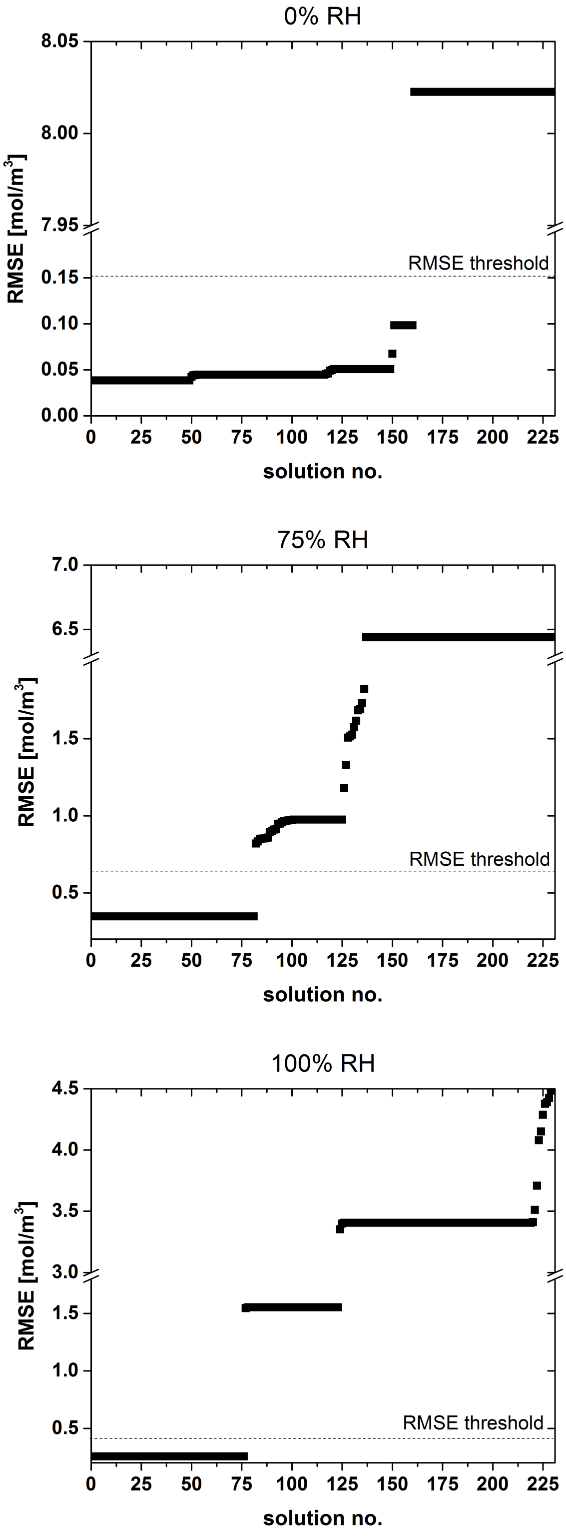

Figure 3: RMSE Values of the Optimization Results for various Relative Humidities (RH)

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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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3.3 Effect of temperature and relative humidity on the reaction kinetics of an oxygen scavenger based on gallic acid[3]

Temperature and relative humidity are two major factors for the performance of oxygen scavengers. In packaging applications, these parameters are determined by the storage environment and/or the packed food product.

In this study we investigated the effect of temperature and relative humidity (RH) on the reaction kinetics of an oxygen scavenger consisting of a 2:1 (w/w) mixture of gallic acid (GA) and sodium carbonate.

The reaction was described by a second-order kinetic model (see also Section 3.2) and the reaction rate coefficient k as well as the scavenger capacity n were determined from experimental from oxygen absorption experiments reflecting various storage conditions. All experimental data set could be well described with the used model, resulting in good agreement between experimental data and simulation results.

Both k and n increased in line with temperature. However, the temperature-dependence of the k did not follow the Arrhenius law. This might be due to the choice of the second-order kinetic model; non-Arrhenius behaviour has been observed in many cases where complex reactions chains are described by a simplifying net reaction.

At 21°C it was shown that both the rate coefficient and the scavenger capacity increased significantly with higher RH. However, below 54% RH, there was no detectable reaction.

For optimum scavenger performance we therefore recommend GA-based scavengers for packaging of food products with a high water activity stored at room temperature. Prior to application, the packaging materials with GA-based scavengers can be stored at 21°C and 54% RH without losing their scavenger activity.

In this work, a mechanistic model for oxygen absorption is combined with an empirical study of the effect of external packaging-relevant factors such as temperature and relative humidity. The obtained results, i.e. the relationship between the external factors and the kinetic parameters, can be used for simulating active packaging scenarios involving GA-based oxygen scavengers.

Contributions: The doctoral candidate conceived and designed the experiments, did the simulations and parameter estimation and wrote the paper.

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[3] Pant, A. F., Dorn, J. and Reinelt, M. (2018). Effect of Temperature and Relative Humidity on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid. Frontiers in Chemistry, 6:587.

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ORIGINAL RESEARCH
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Effect of Temperature and Relative Humidity on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid

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Gallic acid (GA) is a potential oxygen scavenger for food packaging applications. In this study we investigated the effect of temperature and relative humidity (RH) on the reaction kinetics of an oxygen scavenger consisting of GA and sodium carbonate. The reaction was described by a second-order kinetic law and the reaction rate coefficient k as well as the scavenger capacity n were determined from experimental data using a multiple-run downhill simplex method. Both the rate coefficient and the scavenger capacity increased significantly with higher temperatures. At 21°C it was shown that both the rate coefficient and the scavenger capacity increased significantly with higher RH. However, below 54% RH, there was no detectable reaction. For optimum scavenger performance we therefore recommend GA-based scavengers for packaging of food products with a high water activity stored at room temperature. Prior to application, the packaging materials with GA-based scavengers can be stored at 21°C and 54% RH without losing their scavenger activity. The results of this study provide the basis for the functional design of active packaging systems with GA-based oxygen scavengers.

Keywords: active packaging, food packaging, oxygen absorber, kinetic model, polyphenol, 3,4,5-trihydroxybenzoic acid

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1. INTRODUCTION

In food packaging technology, oxygen (O_2) scavengers are used to protect O_2 sensitive food products (Vermeiren et al., 2003). O_2 scavengers are substances that bind O_2 in a chemical reaction, thereby preventing the oxidation of food components. Depending on the packaging system, O_2 scavengers can either remove O_2 from the headspace of the package or improve the O_2 barrier function of the packaging material. Common applications include sachets containing the scavenger in powder form that are added to a package and also packaging films (monolayer or multilayer) incorporating the scavenger (Singh et al., 2011; Realini and Marcos, 2014). Many commercial O_2 scavengers are based on iron, sulfite, or oxidizable polymers and they have been in use since the 1990s (Rooney, 2005; Saengerlaub and Mueller, 2017). Besides these established systems, the application of polyphenols as O_2 scavengers has gained attention due to their availability from renewable resources and their high O_2 absorption capacity (Wanner, 2010). The O_2 scavenging effect of polyphenols relies on their autoxidation in alkaline media (Tulyathan et al., 1989; Scoccia et al., 2016).

Gallic acid (3,4,5-trihydroxybenzoic acid, GA) is a simple polyphenol that has been tested as an O_2 scavenger for packaging applications. Langowski and Wanner (2005) first mentioned GA-based O_2 scavengers consisting of GA and a base. Application tests with GA-based scavengers integrated either into the adhesive layer or into the coating of packaging films were reported by Goldhan et al. (2007) and Wanner (2010). Concerning the extrusion of packaging films containing GA, Ahn et al. (2016) reported the manufacture of monolayer films based on low density polyethylene. Multilayer films combining layers of biobased linear low density polyethylene and polylactide were produced and characterized by Pant et al. (2017). Using these biobased multilayer films it was shown that the O_2 absorption by GA-based O_2 scavengers depends significantly on the relative humidity (RH) and temperature, therefore targeting food products with high water activity. However, to date there is no quantitative description of the reaction kinetics of GA-based O_2 scavengers and how the kinetics can be influenced by the storage conditions.

In the literature, different approaches for characterizing O_2 scavengers are mentioned. The intuitive concept of O_2 absorption capacity is usually applied to indicate the amount of O_2 that can be absorbed by a defined amount of scavenger. To describe the time-dependent absorption of O_2, first-order kinetic models have been applied in many cases. This approach often resulted in a good fit of the experimental data (Charles et al., 2003; Galotto et al., 2009). However, it is based on the assumption that one of the reactants, i.e. O_2 or the scavenging substance, is not limiting for the reaction. This can be the case if there is large excess of either O_2 or the O_2 scavenger. In most packaging applications, however, this assumption is not valid, meaning that the kinetic parameters cannot be transferred to packaging systems having different initial O_2 or scavenger contents. Therefore, first-order kinetic coefficients can merely be used to compare different O_2 scavengers, but they are meaningless for actual packaging design. To overcome this, some research groups have recently successfully applied second-order kinetic models to scavenger reactions: Dombre et al. (2015) and Di Maio et al. (2017) described the O_2 absorption of polymer-based scavengers, resulting in reaction coefficients independent of the initial reactant concentrations.

In this study we investigated the influence of temperature and relative humidity on the O_2 scavenging properties of a GA-based O_2 scavenger. A second-order kinetic model was developed and the model parameters were obtained by fitting the experimental data. The effects of temperature and relative humidity on the parameters were analyzed. The results provide insight into the properties of GA-based O_2 scavengers in relation to the main storage parameters for typical packaging applications.

2. MATERIALS AND METHODS

2.1. Preparation of the Oxygen Scavenger

Gallic acid (GA) monohydrate powder (99%) was obtained from ABCR, Karlsruhe, Germany. At room temperature GA is yellowish-white crystalline powder (Beyer and Walter, 1991). Water-free sodium carbonate (99.8%, Na_2CO_3) was obtained from Th.Geyer, Germany.

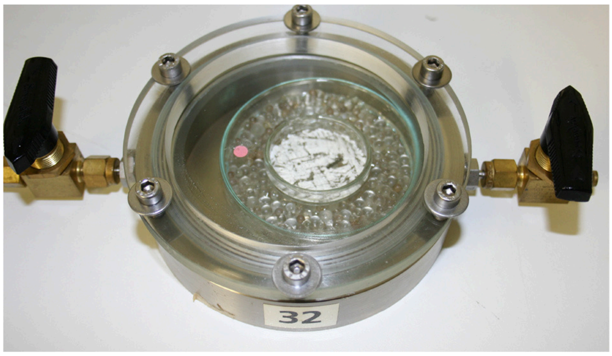

FIGURE 1 | Experimental setup for the oxygen absorption measurements.

The GA-based O_2 scavenger (GA-Sc) was prepared by blending gallic acid monohydrate and sodium carbonate in a mass ratio of 2:1. This ratio of GA and carbonate has successfully been used as an O_2 scavenger in packaging films in previous studies (Pant et al., 2017).

2.2. Oxygen Absorption Measurement

For the O_2 absorption measurements, a thin layer of GA-Sc powder (0.060 g) was spread in a glass bowl and stored in stainless steel cells equipped with two valves for gas flushing (**Figure 1**). The cells were hermetically closed with a glass lid, sealed with a viton O-ring and had a free headspace volume of 88 cm^3 or 108 cm^3.

The relative humidity (RH) in the cells was adjusted with silica gel, calcium chloride, sodium chloride, potassium chloride, or water (0% RH, 38% RH, 75% RH, 86% RH, and 100% RH at 21°C, respectively). The storage temperature (5°C, 10°C, 21°C, and 38°C) was adjusted by storing the cells in climatic chambers. The initial headspace gas atmosphere was air. During storage, the decrease in the headspace O_2 partial pressure (p_{O_2}) due to the scavenger reaction was monitored non-destructively using Fibox 4 Trace, a luminescence-based oxygen detection system (PreSens Precision Sensing GmbH, Regensburg, Germany). For this, an optical sensor spot (PSt3) was placed inside the cell at the glass top (**Figure 1**). Absorption data p_{O_2} in hPa were transferred to concentrations using the ideal gas law

$$m_{O_2} = (p_{O_2} \cdot V_{HS} \cdot M_{O_2})/(R \cdot T) \tag{1}$$

where V_{HS} denotes the headspace volume of the cell, M_{O_2} is the molar mass of O_2, $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ the ideal gas constant, and T is the temperature in Kelvin.

Water vapor partial pressure values p_{H2O} were calculated using the following equations:

$$p_{H2O} = \frac{RH}{100} \cdot e_{sw} \tag{2}$$

$$e_{sw} = c_1 \cdot e^{\left(\frac{c_2 \cdot T}{c_3 + T}\right)} \tag{3}$$

where RH is the relative humidity in %, e_{sw} is the saturation vapor pressure over liquid water in hPa, T is the temperature in °C and $c_1 = 6.112\,13$ hPa, $c_2 = 17.5043$ and $c_3 = 241.2°C$ are the given model parameters of the Magnus equation (Wernecke, 2003).

For experiments at different temperatures and 100% RH, threefold determinations were made, except for 5°C where only data from two measurements were available. The effect of RH was determined in four parallel experiments for each condition. All results are given as the arithmetic mean together with the standard deviation.

The mean square deviation of the observed O_2 concentrations was then calculated for each experiment as follows:

$$\mathrm{MSE_{exp}} = \sqrt{\frac{1}{N}\sum_{i=1}^{m}\sum_{l=1}^{q}([O_2]_{exp} - [O_2]_{mean})^2} \tag{4}$$

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

2.3. Mathematical Model

The autoxidation of GA under alkaline conditions has been described as a complex multi-step chain reaction leading to different oxidation products (Tulyathan et al., 1989). However, for the application of GA as an O_2 scavenger in packaging applications, the main focus lies on describing the rates of reactant consumption, i.e., the time-dependent depletion of O_2 in relation to the used amount of GA. The following overall reaction was assumed:

$$\mathrm{GA} + \mathrm{n\,O_2} \rightarrow \mathrm{GA_{ox}} \tag{5}$$

where n is a stoichiometric factor and GA_{ox} accounts for the various reaction products. The reaction is assumed to be irreversible.

We approximated the kinetic law of this reaction by the kinetic law of a second-order elementary reaction with the reaction rate r being expressed as follows:

$$r = k \cdot [GA] \cdot [O_2] \tag{6}$$

where [GA] and $[O_2]$ denote the concentrations of non-reacted GA and O_2 in mol m^{-3}, respectively, and k is the reaction rate coefficient in $m^3\,mol^{-1}\,s^{-1}$. Based on this kinetic law, the net rates of consumption of GA and O_2 were described using the following system of ordinary differential equations (ODE):

$$\frac{d[GA]}{dt} = -k \cdot [\mathrm{GA}] \cdot [O_2] \tag{7}$$

$$\frac{d[O_2]}{dt} = -n \cdot k \cdot [\mathrm{GA}] \cdot [O_2] \tag{8}$$

The ODE system gives an initial value problem and was solved in MATLAB R2014a (The MathWorks, Inc., Natick, MA, USA) using the multistep solver ode15s. The model was fitted to the experimental data to obtain the model parameters k and n. The fit was optimized based on the minimization of the sum of squared residuals (SSQ):

$$\mathrm{SSQ} = \sum_{i=1}^{m}\sum_{l=1}^{q}([O_2]_{sim} - [O_2]_{exp})^2 \tag{9}$$

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

For the minimization of SSQ, the MATLAB function fminsearch was used. This function is based on a Nelder-Mead downhill-simplex algorithm as described by Lagarias et al. (1998), a simple and widely-used algorithm for local optimization. The termination tolerance of the function value was 10^{-4} and the lower bound on the size of a step was 10^{-4} (MATLAB default settings). The optimization terminates when both stopping criteria are fulfilled. Depending on the start values, the downhill simplex algorithm can be stuck in a local minimum and therefore fail to find the optimum combination of k and n. Therefore the start values were varied systematically in the range of $n = 0..10$ and $k = 10^{-10}..10^{10}$ so that in total 231 different combinations of k and n were used. The results were analyzed for an unambiguous total minimum, which was then considered to represent the optimum values for k and n. As a measure of the goodness of fit, the root mean square error (RMSE) was calculated according to equation 10:

$$\mathrm{RMSE} = \sqrt{\frac{\mathrm{SSQ}}{N-p}} \tag{10}$$

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

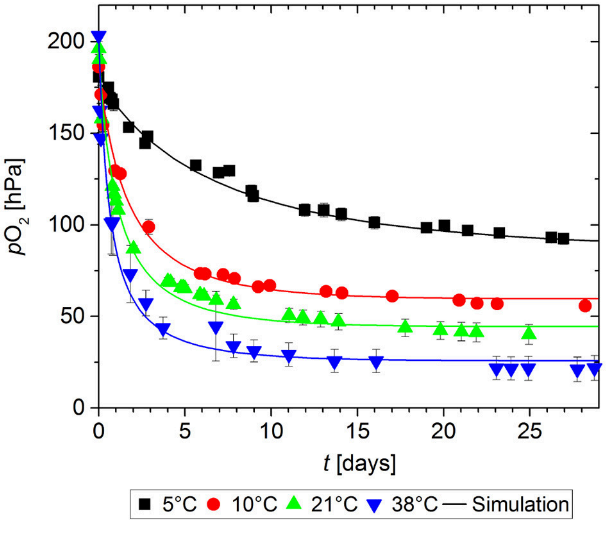

FIGURE 2 | Oxygen absorption by a gallic acid-based oxygen scavenger stored at different temperatures. Symbols show the experimental data and lines show the simulation results.

3. RESULTS AND DISCUSSION

Temperature and relative humidity have been described as the most important factors for the performance of oxygen scavengers (Braga et al., 2010; Polyakov and Miltz, 2010, 2016). In packaging applications, these parameters are determined by the storage environment and/or the packed food product. In the present study, the effect of temperature and relative humidity on the O_2 absorption kinetics of a novel GA-based scavenger was studied in order to identify possible applications and to provide necessary kinetic information for packaging design.

3.1. Effect of Temperature on Oxygen Absorption

In order to determine the effect of storage temperature on the O_2 absorption of GA-Sc, samples of the scavenger were stored at 100% RH at temperatures in the range of 5 to 38°C for 28 days. The chosen temperatures represent typical storage conditions for food products ranging from chilled conditions to tropical conditions. The results of the O_2 absorption measurements are shown in **Figure 2**. Higher storage temperatures lead to a faster decrease of the O_2 partial pressure in the measurement cell. All experimental data sets could be sufficiently described with the chosen kinetic model: The results of the simulation are in good agreement with the experimental values as shown by RMSE values in the order of magnitude of the experimental error (**Table 1**).

The kinetic parameters k and n were determined by fitting a second-order kinetic model to the available experimental data sets. **Table 1** gives an overview of the model parameters. All parameters could be determined using the multiple-step downhill simplex optimization. **Figure 3** shows the values for k and n as a function of temperature.

As could be expected for an oxidation reaction, the rate of O_2 consumption increased with increasing temperature. However, the effect of temperature cannot be described by the Arrhenius law; only in the 10°C to 38°C range is the Arrhenius plot a straight line. (**Figure 3**, right). Non-Arrhenius behavior has been observed in many cases where complex reaction chains are described with a simple overall reaction and has also been described for iron-based scavengers (Polyakov and Miltz, 2016).

TABLE 1 | Model parameters.

Temperature °C	Relative humidity%	RMSE $\mathrm{mol\,m^{-3}}$	$\mathrm{MSE_{exp}}$ $\mathrm{mol\,m^{-3}}$	k $\mathrm{m^3\,mol^{-1}\,s^{-1}}$	n
5	100	0.135	0.079	$2.478 \cdot 10^{-7}$	2.03
10	100	0.198	0.090	$9.803 \cdot 10^{-7}$	2.23
21	100	0.256	0.117	$1.496 \cdot 10^{-6}$	2.53
38	100	0.469	0.303	$2.533 \cdot 10^{-6}$	3.49

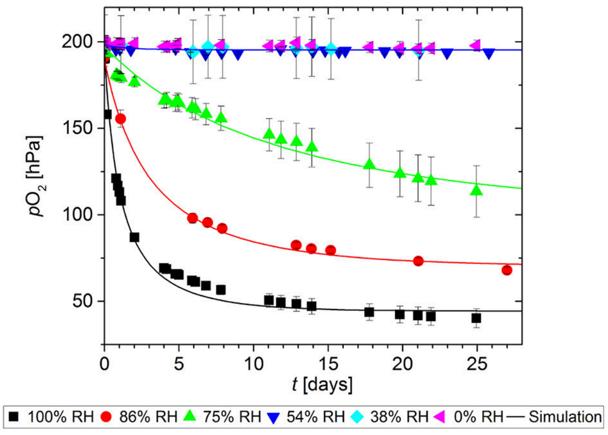

FIGURE 4 | Oxygen absorption by a gallic acid-based scavenger stored at different relative humidities (RH). Symbols show the experimental data and lines show the simulation results.

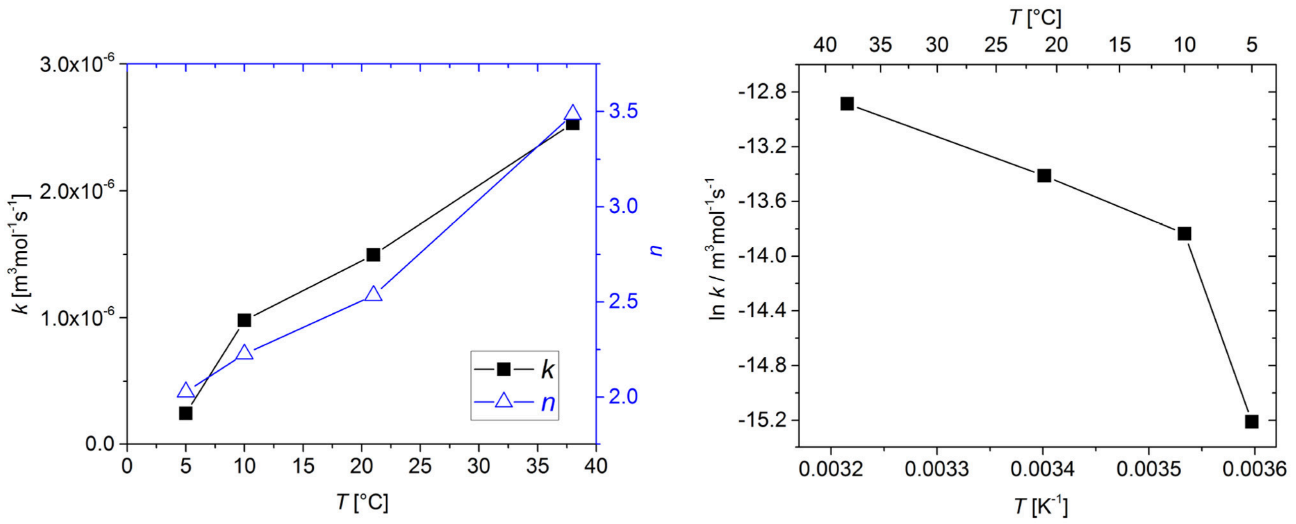

FIGURE 3 | Effect of temperature on the reaction rate coefficient k and the stoichiometric coefficient n (left) and the associated Arrhenius plot (right). Connecting lines are shown to guide the eye.

The stoichiometric coefficient n also showed significant temperature dependence. n can be interpreted as the scavenger capacity, i.e., the number of O_2 molecules that are consumed per molecule of GA. The oxidation of GA involves multiple equilibria and parallel or subsequent oxidation reactions and is not yet fully understood (Tulyathan et al., 1989). Both the pathway and the extent of these chain reactions determine the total amount of O_2 that is consumed and therefore the scavenger capacity. Additionally, the presence of transition metal ions may influence the reaction (Mochizuki et al., 2002). Our results indicate that the reaction pathway and/or the extent of the reaction changes with temperature. However, for a deeper understanding of this temperature dependence more knowledge about the oxidation mechanism is necessary.

3.2. Effect of Relative Humidity on Oxygen Absorption

As with many other oxygen scavengers, the scavenging function of GA-Sc is triggered by humidity (Pant et al., 2017). To quantify the effect of RH on the O_2 absorption kinetics, samples of GA-Sc were stored at different RH for 27 days. The results are shown in **Figure 4**. At 0% RH, 38% RH and also 54% RH there was no significant decrease in the O_2 partial pressure, i.e., no scavenger reaction occurred. In the range from 75% RH to 100% RH there was a faster decrease in the O_2 partial pressure with higher levels of RH.

TABLE 2 | Model parameters.

Temperature °C	Relative humidity %	RMSE mol m^{-3}	MSE$_{exp}$ mol m^{-3}	k m^3 mol^{-1} s^{-1}	n
21	0	0.038	0.116	0*	0*
21	38	0.147	0.179	0*	0*
21	54	0.051	0.041	0*	0*
21	75	0.347	0.286	$1.348 \cdot 10^{-7}$	1.64
21	86	0.136	0.109	$5.354 \cdot 10^{-7}$	2.01
21	100	0.256	0.117	$1.496 \cdot 10^{-6}$	2.53

** no detectable reaction.*

The model parameters k and n were determined by fitting the second-order kinetic model. The results are presented in **Table 2**. A detailed description of the downhill simplex-based optimization and potential pitfalls are given elsewhere (Pant and Reinelt, 2018).

The effect of RH on the model parameters is shown in **Figure 5**. The values of both the reaction rate constant k and the stoichiometric factor n show an increase at higher relative humidity, with the threshold being between 54% RH and 75% RH.

These results confirm the triggering effect of humidity on the scavenger reaction of GA. Prior to the reaction with O_2, the scavenger reaction involves the deprotonation of the GA (Tulyathan et al., 1989; Eslami et al., 2010). Each GA molecule can donate up to four protons. The extent of the deprotonation is determined by the acid-base equilibrium established by the scavenger mixture of GA and sodium carbonate in the presence of water. Here, water serves as the medium for the proton transfer. Therefore, the amount of available water determines if there is a reaction and, in combination with the base, also determines the extend of the deprotonation, which in turn may influence the subsequent oxidation pathway.

4. CONCLUSION

This study investigated the effect of temperature and relative humidity on the scavenger kinetics of a GA-based scavenger. It was shown that both the reaction rate coefficient and the scavenger capacity of the GA-based O_2 scavenger increased with higher temperature. Therefore, GA-based scavengers are best suited for products stored at temperatures higher than 10°C. At chilling temperatures, there is an disproportionate decrease in the scavenger activity in terms of the rate of O_2 uptake. Relative humidity was shown to be the trigger for the scavenger reaction.

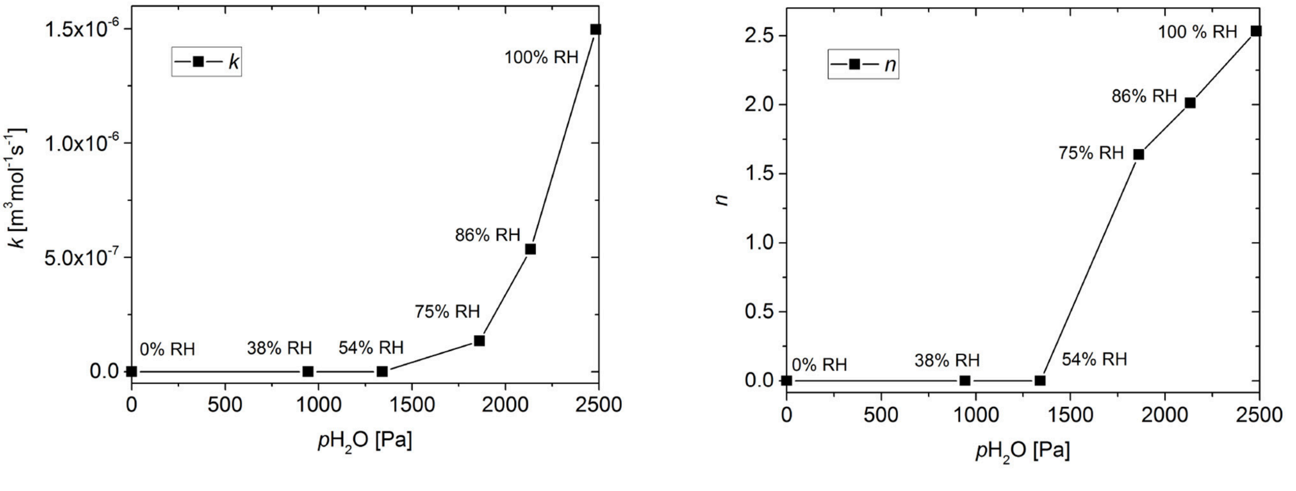

FIGURE 5 | Effect of relative humidity (RH) on the reaction rate coefficient k and the stoichiometric coefficient n. Connecting lines are shown to guide the eye.

While there was no detectable reaction below 54% RH, both the reaction rate coefficient and the scavenger capacity increased significantly at higher relative humidity in the range from 75% to 100% RH. This effect can be utilized for the application of GA-based scavengers in packaging: Packaging films containing the scavenger can be stored under typical room conditions (21°C and 54% RH) without losing their capacity. The scavenger function is only activated at higher levels of RH, i.e., when in contact with moist food products. We therefore recommend their use for products with very high water activity ($a_w > 0.9$) in order to ensure a fast reaction and high scavenger capacity.

AUTHOR CONTRIBUTIONS

AP conceived and designed the experiments, did the simulations and parameter estimations and wrote the paper. JD contributed in experimental design, carried out the oxygen absorption measurement and revised the paper. MR contributed in modeling and simulation techniques and revised the paper.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

3.4 Effect of deprotonation on the reaction kinetics of an oxygen scavenger based on gallic acid[4]

The oxygen-scavenging function of scavengers based on gallic acid (GA) relies on the autoxidation of GA in alkaline solution. Hence, for the application as an oxygen scavenger GA has to be combined with a base.

The aim of this study was to determine the effect of adding a base, either sodium carbonate or sodium hydroxide, on the reactions kinetics of GA-based scavengers. In aqueous solution, the inherent property of GA that is influenced by adding a base is the degree of deprotonation (DoD), i.e the average deprotonation of the GA molecules. Thus, the degree of deprotonation was chosen as the key property to be optimized in scavenger design.

The acid-base system was described using a set of nonlinear equations including the acid-base equilibria of gallic acid, the respective base and water. From this model, the pH-dependent GA species distribution was obtained and the DoD was calculated.

In oxygen absorption experiments, the time-dependent oxygen uptake by aqueous GA solutions in the pH range 2.9-13.8 was determined. The oxygen absorption was described with the second-order kinetic model presented in previous publications (see Sections 3.2 and 3.3) and the effect of the DoD on the model parameters was analysed. This revealed that both the reaction rate coefficient k and the scavenger capacity n were significantly influenced by the DoD. Below a DoD of 0.25 there was no considerable reaction.

k increased exponentially with increasing DoD, i.e. the scavenging rate increased with the amount of base added. However, in solution, the amount of base that can be added is restricted by the respective solubility.

n had a maximum at a DoD of ∼0.6-0.7. This shows that GA oxidation is maximized if the majority of GA molecules is present as trianions. In principle a target DoD can be adjusted by using any base, but a strong base is more efficient in terms of the needed quantity: To reach the maximum absorption capacity, more than twice as much sodium carbonate is necessary compared to sodium hydroxide. The results show, for the first time, how scavenger performance is affected by the quantity and type of base added, thereby providing the basis for the functional design of scavenger mixtures based on GA.

Contributions: The doctoral candidate conceived and designed the study, performed part of the oxygen absorption measurements, analyzed the data, conducted the simulations and parameter estimations, and wrote the paper.

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[4] Pant, A. F., Özkasikci, D., Fürtauer, S. and Reinelt, M. (2019). The Effect of Deprotonation on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid. Frontiers in Chemistry, 7:680.

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The Effect of Deprotonation on the Reaction Kinetics of an Oxygen Scavenger Based on Gallic Acid

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Oxygen scavengers based on gallic acid (GA) usually contain a base that establishes the alkaline conditions necessary for the humidity-induced scavenger reaction. Here we measured the effect of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) on the reaction kinetics of such scavengers. The time-dependent oxygen absorption of aqueous GA solutions (pH 2.9–13.8) was determined and the results were described using a second-order kinetic model. We calculated the degree of deprotonation (DoD) of GA in the solutions from the species distribution curves, and assessed the effect of the DoD on the reaction kinetics. This revealed that both the reaction rate coefficient k and the scavenger capacity n were significantly affected by the DoD. If the DoD fell below 0.25, there was no significant reaction. Although k increased with the DoD, n reached a maximum at DoD = 0.6–0.7. In principle, target DoD values can be achieved using any base, but a strong base is more efficient because lower quantities are required. In our experiments, the amount of Na_2CO_3 required to reach the maximum DoD was more than twice that of NaOH. Our results provide the basis for the functional design of active packaging systems incorporating optimized GA-based oxygen scavengers.

Keywords: active packaging, food packaging, oxygen absorber, polyphenol, 3,4,5-trihydroxybenzoic acid

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1. INTRODUCTION

Gallic acid (GA), also known as 3,4,5-trihydroxybenzoic acid, is a natural polyphenol found in many plants either as a free acid or as a component of tannins (Shahidi and Naczk, 2003; Belitz and Grosch, 2013). When combined with a base, GA can be used as an oxygen (O_2) scavenger for packaging applications, preventing the oxidation of sensitive food products (Langowski and Wanner, 2005). O_2 scavengers based on GA (e.g., a mixture of GA and sodium carbonate) have a high O_2 absorption capacity and can be integrated into packaging films (Ahn et al., 2016; Pant et al., 2017). Depending on the film structure, the scavenger can either improve the barrier function of the packaging material or absorb residual O_2 from the headspace. The scavenger function is activated by humidity derived from the product or in the environment (Wanner, 2010).

Chemically, the O_2 scavenging function of GA-based O_2 scavengers relies on the autoxidation of GA in alkaline solution. GA is a weak polyprotic acid (**Figure 1**) with four acidic protons that can be transferred to an acceptor base.

The solution pH determines the species distribution of GA, i.e., the proportions of GA and the different gallate anions present in the solution, and therefore also the type of GA radicals formed

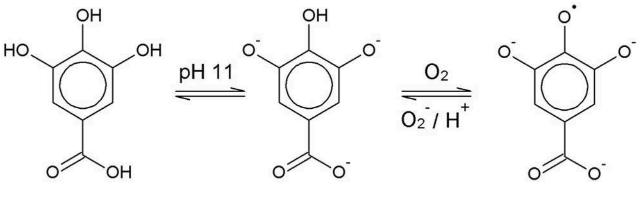

FIGURE 1 | Formation of a gallate radical by single electron transfer at pH 11.

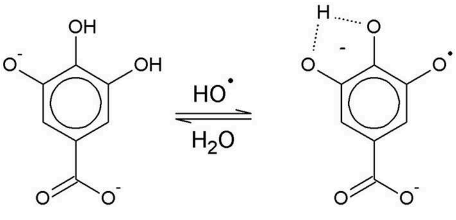

FIGURE 2 | Hydrogen atom transfer from the gallate dianion to the hydroxyl radical at pH 9.

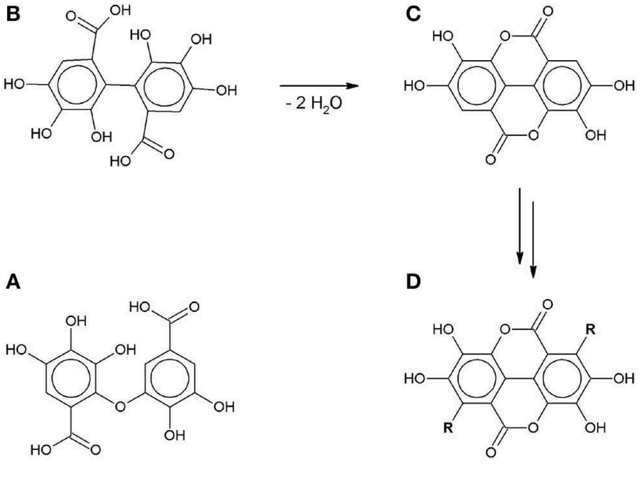

FIGURE 3 | Gallic acid autoxidation intermediates: **(A)** C-O dimer (Oniki and Takahama, 2004). **(B)** C-C dimer (Caregnato et al., 2008). **(C)** Ellagic acid (Nikolic et al., 2011). **(D)** gallate-based polymer (R: gallate-derived group).

during autoxidation. For autoxidation at high pH Yoshioka et al. (2003) described radical formation by single electron transfer (SET) from the gallate anion to a dissolved O_2 molecule (**Figure 1**). The by-product hydrogen peroxide (H_2O_2) undergoes homolysis to form two hydroxyl radicals when exposed to UV radiation from ambient sunlight (Holleman, 2007). Alternatively, metal ions such as Fe^{2+}, which could be present as impurities, can be oxidized by H_2O_2 to form a hydroxyl radical and a hydroxyl anion (Walling, 1975). The hydroxyl radicals may in turn directly withdraw a hydrogen atom from GA in aqueous solution by hydrogen atom transfer (HAT) (Milenkovic et al., 2018). A HAT reaction at pH 9 is shown as an example in **Figure 2**.

Both SET and HAT can lead to the formation of gallate radicals, which has been confirmed by electron spin resonance spectroscopy and shown in theoretical models (Yoshioka et al., 2003; Severino et al., 2009; Eslami et al., 2010). These gallate radicals can take part in further reactions. Tulyathan et al. (1989) proposed a multi-step oxidation mechanism including a ring-opening step, but did not report any qualitative or quantitative analysis of the reaction products. Hotta et al. (2001) proposed an oxidative polymerization mechanism in an alkaline environment in order to explain the unusually high number of transferred electrons compared to the number of hydroxyl groups. More recently some of the intermediates in this radical-induced polymerization pathway have been identified: C-O dimers (Oniki and Takahama, 2004), C-C dimers (Caregnato et al., 2008) and ellagic acid (Nikolic et al., 2011) (**Figure 3**).

An autoxidation that generates dark-colored reaction products has been described for several phenolic compounds (Cilliers and Singleton, 1989; Friedman and Juergens, 2000). Although the complete reaction pathway and the oxidation products have not yet been identified, the type and quantity of oxidation products changes with pH (Cilliers and Singleton, 1989; Friedman and Juergens, 2000). Wanner (2010) reported that a pH higher than 8 is necessary to enable the GA scavenger reaction and that the type of base used determined the reaction kinetics. Tulyathan et al. (1989) investigated the O_2 absorption capacity of GA in the pH range 10–14 and observed a maximum first-order reaction rate constant at pH 12. For the polyphenol caffeic acid Cilliers and Singleton (1989) studied O_2 absorption in the pH range 4–8 and reported increasing reaction rate constants at higher pH values.

Considering these results, the pH-dependent deprotonation of GA is likely to play a key role in selecting the autoxidation reaction and therefore the scavenger performance.

We previously used a 2:1 mass ratio GA:sodium carbonate as an O_2 scavenger for packaging applications and investigated the effect of temperature and relative humidity on the second-order reaction rate constant and absorption capacity (Pant et al., 2018). However, it remains unclear which type of base and which mixing ratio achieves optimal oxygen scavenger activity.

Therefore, the aim of this work was to study the effect of the type of base on the oxygen scavenger kinetics of GA. The autoxidation of GA was studied in aqueous solutions adjusted to different pH values by adding either NaOH or Na_2CO_3. The second-order reaction rate coefficent and the absorption capacity were determined as well as their dependence on the deprotonation of GA.

2. MATERIALS AND METHODS

2.1. Materials

Gallic acid monohydrate (GA, 99%) was obtained from ABCR (Karlsruhe, Germany). Water-free sodium carbonate (Na_2CO_3, 99.8%) and sodium hydroxide (NaOH, 98.8%) were obtained from Th.Geyer (Renningen, Germany).

To prepare aqueous GA solutions at different pH values, samples of 0.040 g GA powder and the appropriate amount of base were mixed with 5 mL destilled water in a Petri dish at 23 °C. Solutions were prepared with NaOH at pH 5.7, 7.9, 9.1, 11.1, 13.0, 13.8. Solutions were prepared with Na_2CO_3 at pH 5.1, 7.7, 8.3, 9.3, 10.4. The pH meter was calibrated with standard solutions at pH 7.0, 9.0, and 11.0. A GA solution without added base (pH = 2.9) was used as a reference.

2.2. Modeling the Acid-Base System

An aqueous solution of GA includes several acid-base equilibria, each characterized by its corresponding equilibrium constant K, as shown in Equations (1)–(5).

$$H_4A + H_2O \rightleftarrows H_3A^- + H_3O^+ \qquad K_{a1} = \frac{[H_3A^-][H_3O^+]}{[H_4A]} \tag{1}$$

$$H_3A^- + H_2O \rightleftarrows H_2A^{2-} + H_3O^+ \qquad K_{a2} = \frac{[H_2A^{2-}][H_3O^+]}{[H_3A^-]} \tag{2}$$

$$H_2A^{2-} + H_2O \rightleftarrows HA^{3-} + H_3O^+ \qquad K_{a3} = \frac{[HA^{3-}][H_3O^+]}{[H_2A^{2-}]} \tag{3}$$

$$HA^{3-} + H_2O \rightleftarrows A^{4-} + H_3O^+ \qquad K_{a4} = \frac{[A^{4-}][H_3O^+]}{[HA^{3-}]} \tag{4}$$

$$2\,H_2O \rightleftarrows H_3O^+ + OH^- \qquad K_w = [H_3O^+][OH^-] \tag{5}$$

where H_4A, H_3A^-, H_2A^{2-}, HA^{3-}, and A^{4-} denote the GA species with 4, 3, 2, 1, and 0 acidic protons, respectively. Equations (1)–(4) describe the GA deprotonation equilibria characterized by the equilibrium constants $pK_{a_1} = 4.39$ which is related to the carboxylic proton and $pK_{a_2} = 8.50$, $pK_{a_3} = 10.38$, $pK_{a_4} = 13$ (Eslami et al., 2010; Jabbari, 2015), which are related to the phenolic hydroxy groups. Equation (5) shows the ion product of water, $K_w = 10^{-14}$.

The acid-base system is further characterized by the mass balance of the GA species (Equation 6) and the charge balance (Equation 7):

$$\begin{aligned} c_A &= [A^{4-}] + [HA^{3-}] \\ &\quad + [H_2A^{2-}] + [H_3A^-] + [H_4A] \qquad (6) \\ [H_3O^+] + [Na^+] &= [OH^-] + [H_3A^-] + 2\,[H_2A^{2-}] \\ &\quad + 3\,[HA^{3-}] + 4\,[A^{4-}] \qquad (7) \end{aligned}$$

where c_A is the initial GA concentration and $[A^{4-}]$, $[HA^{3-}]$, $[H_2A^{2-}]$, $[H_3A^-]$, $[H_4A]$, $[H_3O^+]$, $[OH^-]$, $[Na^+]$ are the equilibrium concentrations of the different GA species and the hydronium, hydroxide and sodium ions, respectively.

The system of Equations (1)–(7) was solved in MATLAB R2014a (The MathWorks, Inc., Natick, MA, USA) using the *fsolve* function. The pH (i.e., the concentration of H_3O^+), was varied systematically to obtain the pH-dependent distribution of the GA species. From this species distribution, the degree of deprotonation (DoD) was calculated according to Equation (8):

FIGURE 4 | Experimental setup for oxygen absorption measurements.

$$\text{DoD} = \frac{\text{donated acidic } H^+}{\text{total acidic } H^+} \tag{8}$$

where total acidic H^+ refers to the total amount of acidic H^+ available from the GA molecules in the solution, and donated H^+ refers to the total amount of acidic H^+ transferred to the solution at a certain pH.

If Na_2CO_3, a biprotic base, is added to the solution, additional equilibria have to be considered as shown in Equations (9) and (10).

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \qquad K_{b1} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \tag{9}$$

$$H_2CO_3^* + H_2O \rightleftarrows HCO_3^- + H_3O^+ \qquad K_{b2} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3^*]} \tag{10}$$

where HCO_3^- and CO_3^{2-} denote the bicarbonate and carbonate ions, respectively. $H_2CO_3^*$ accounts for both carbonic acid and dissolved CO_2. The equilibrium constants we used were $pK_{b_1} = 10.3$ and $pK_{b_2} = 6.3$ (Lower, 1999).

2.3. Measurement of Oxygen Absorption

The absorption of O_2 by the aqueous GA solutions was measured in hermetically closed stainless-steel cells with a free headspace volume of 88 cm^3 (**Figure 4**). The Petri dishes containing the GA solutions were placed in the cells and their O_2 uptake from the headspace (initial gas atmosphere: air) was monitored for 30 days at 23°C using Fibox 4 Trace, a luminescence-based O_2 detection system (PreSens Precision Sensing GmbH, Regensburg, Germany). To minimize the effect of O_2 transport limits in the solution, the Petri dishes were only partially filled.

The p_{O_2} absorption data in hPa were converted to concentrations c_{O_2} using the ideal gas law (Equation 11).

$$c_{O_2} = n_{O_2}/V_{HS} = p_{O_2}/(R \cdot T) \tag{11}$$

where n_{O_2} is the amount of substance of O_2, V_{HS} is the headspace volume of the cell, $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is the ideal gas constant, and T is the temperature in Kelvin.

Each experiment was carried out at least three times and the results are presented as the arithmetic mean with standard deviations.

The mean square error ($\mathrm{MSE_{exp}}$) of the observed O_2 concentrations was calculated as shown in Equation (12):

$$\mathrm{MSE_{exp}} = \sqrt{\frac{1}{N}\sum_{i=1}^{m}\sum_{j=1}^{q}([O_2]_{exp} - [O_2]_{mean})^2} \quad (12)$$

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

2.4. Modeling the Oxidation Kinetics

The autoxidation of gallic acid can be described by the simplified net reaction shown in Equation (13) (Pant et al., 2018):

$$\mathrm{GA} + \mathrm{n}\,O_2 \longrightarrow \mathrm{GA_{ox}} \quad (13)$$

where GA represents all non-oxidized GA species, n is a stoichiometric factor and $\mathrm{GA_{ox}}$ accounts for the various reaction products. This simplified, application-oriented approach is based on the following assumptions: (i) we do not differentiate between the different GA species; (ii) the oxygen uptake is irreversible; and (iii) all oxidation products are summarized as $\mathrm{GA_{ox}}$.

The kinetic law of this reaction was approximated as a second-order elementary reaction and the reaction rate r was expressed as shown in Equation (14):

$$r = k \cdot [\mathrm{GA}] \cdot [O_2] \quad (14)$$

where [GA] and $[O_2]$ denote the concentrations of GA and O_2, respectively $[\mathrm{mol\,m^{-3}}]$ and k is the reaction rate coefficient $[\mathrm{m^3\,mol^{-1}\,s^{-1}}]$. Based on this kinetic law, the net consumption rates of GA and O_2 were described with the system of ordinary differential equations (ODEs) shown as Equations (15) and (16)

$$\frac{d[GA]}{dt} = -\,k \cdot [\mathrm{GA}] \cdot [O_2] \quad (15)$$

$$\frac{d[O_2]}{dt} = -\,n \cdot k \cdot [\mathrm{GA}] \cdot [O_2] \quad (16)$$

The ODE system was solved in MATLAB R2014a using the multistep solver *ode15s*. The model was fitted to the experimental data to determine the kinetic parameters k and n. The fit was optimized using a downhill simplex method as described by Pant and Reinelt (2018).

3. RESULTS AND DISCUSSION

3.1. Deprotonation of Gallic Acid in Aqueous Solution

The acid-base system studied in the oxidation experiments (i.e., an aqueous solution of GA) was described using Equations (1)–(10). GA is present as a range of deprotonated GA species that depend on the pH of the solution. The equilibrium concentrations of the different GA species at a given pH are determined by the acidity constants of the acidic protons. **Figure 5** shows the simulated pH-dependent species distribution for aqueous GA solutions. When the pH is low, H_4A is the dominant species, representing a GA molecule with four protons. As the pH increases, the relative proportions of the species change until almost all protons are donated at pH 14. The species distribution was used to calculate the DoD as a measure of the average deprotonation of GA (**Figure 5**). The DoD increases in line with higher pH values and almost complete deprotonation is achieved at pH∼14. At pH 9.5 the DoD is 0.5, indicating that the GA molecules have donated an average of two acidic protons.

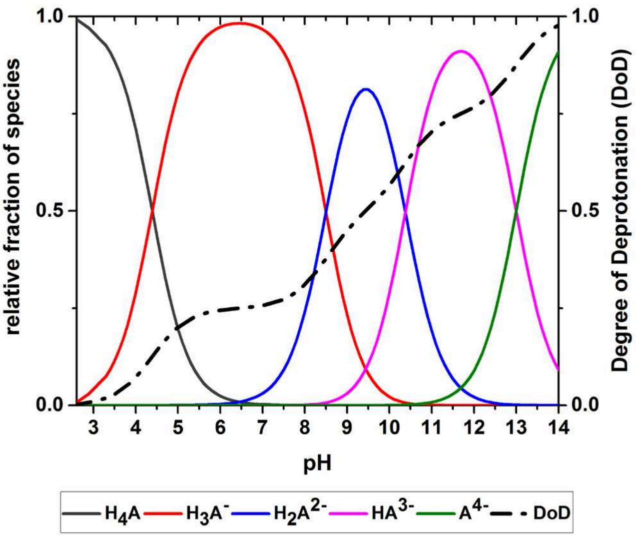

FIGURE 5 | Species distribution of an aqueous gallic acid solution allowing the calculation of the degree of deprotonation (DoD).

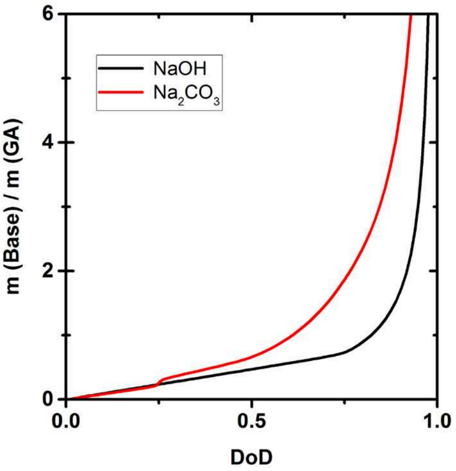

FIGURE 6 | Effect of the base:gallic acid (GA) mass ratio on the degree of deprotonation (DoD).

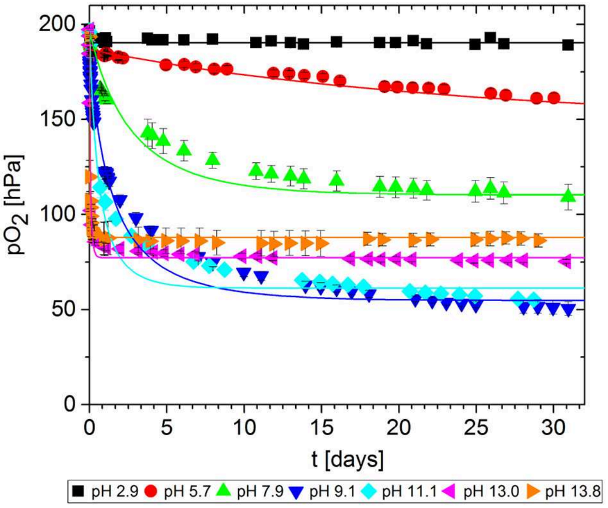

FIGURE 7 | Oxygen absorption by aqueous solutions of gallic acid and NaOH (5 mL) at 23°C. Symbols shows the experimental data and lines show the simulation results.

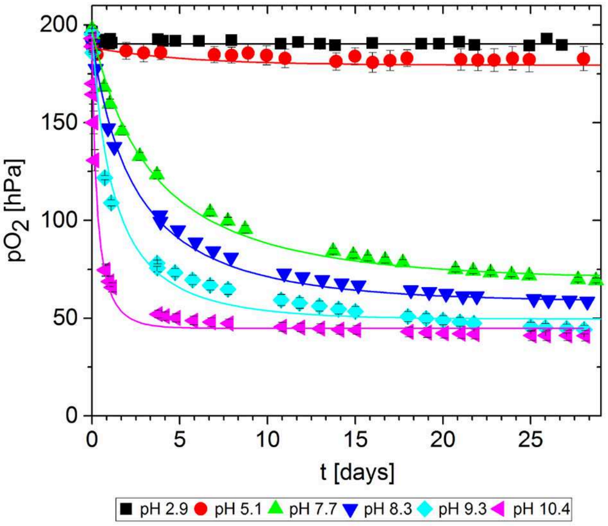

FIGURE 8 | Oxygen absorption by aqueous solutions of gallic acid and Na_2CO_3 (5 mL) at 23°C. Symbols show the experimental data and lines show the simulation results.

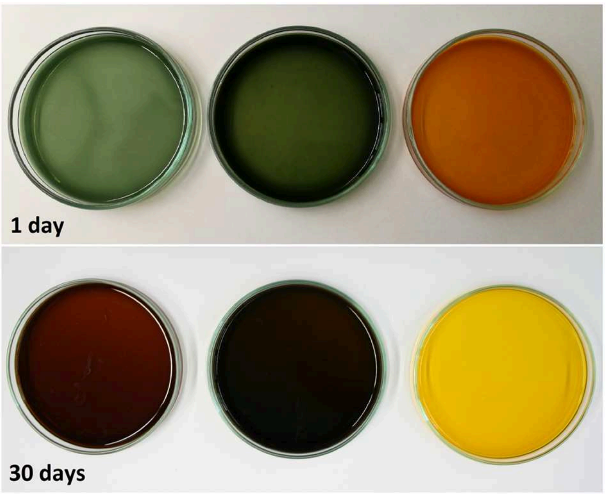

FIGURE 9 | Color evolution of gallic acid solutions with pH 7.2, pH 11.1, and pH 13.0 (left to right).

Figure 6 shows how much NaOH or Na_2CO_3 is necessary to achieve a certain DoD according to the simulation. Due to the different strength of the two bases, the amounts differ significantly and the difference in the quantity of each base required becomes larger as the DoD increases. For example, to achieve a DoD of 0.75 using Na_2CO_3, base:GA weight ratio is 2, but this falls to only 0.8 when using NaOH.

3.2. Effect of pH on Oxygen Absorption

In packaging materials, GA-based O_2 scavengers can absorb O_2 if water is present, i.e., in aqueous solutions comprising GA and a base. We assessed the effect of the base on the ability of GA to absorb O_2 in solutions at different pH values, prepared by adding either NaOH (**Figure 7**) or Na_2CO_3 (**Figure 8**). Progress was monitored over 30 days of storage at 23°C.

The reference solution with no base added (pH = 2.9) did not absorb any O_2. Regardless of which base was added, the more alkaline solutions generally absorbed greater quantities of O_2 by promoting faster O_2 uptake and thus more O_2 absorption in total after 30 days. However, for NaOH solutions, the O_2 absorption capacity peaked at ∼10 and dropped again. Accordingly, the absorption capacity of GA at pH 11.1. was almost equal to that at pH 9.1, and the capacity was lower at pH 13.0 and 13.8. Tulyathan et al. (1989) also reported an O_2 absorption peak but at slightly higher pH. In the case of Na_2CO_3, it was not possible to prepare solutions with a pH higher than 10.4 due to the buffer effect of the HCO_3^- - $H_2CO_3^*$ system ($pK_{b_1} = 10.3$): The necessary quantities to achieve higher pH values would not dissolve in the GA solution.

The experiment was stopped after 30 days, but not all samples reached their maximum absorption capacity during this period because the scavenging reaction was too slow. The observed differences in O_2 absorption must reflect a pH-dependent effect on the mechanism of the oxidation reaction, leading to different ways of incorporating O_2 and thereby to different oxidation products. This was confirmed by the color development of the samples. **Figure 9** shows samples from the solutions at pH 7.2, pH 11.1 and pH 13.0 after 1 day and after 30 days of storage. Initially ($t = 0$), the solutions were almost colorless with a slight yellow tint. Between days 1 and 30, the solutions at pH 7.2 and 11.1 changed from green to brown, whereas the solution at pH 13.0 change from organge to yellow. For autoxidation experiments in the pH range 2.6–11, Tóth et al. (2014) reported a similar profile of long-term color development. This qualitative observation supports previous reports that different polymerization products are formed during the autoxidation of GA in alkaline solutions (Cilliers and Singleton, 1989; Tulyathan et al., 1989; Hotta et al., 2001; Tóth et al., 2014). Further studies should be carried out to investigate the oxidation mechanism in more detail, including the effect of traces of metal ions on the reaction.

The O_2 absorption measurements clearly demonstrated that pH has an effect on scavenger kinetics. However, the pH only provides information about conditions external to the reaction and, strictly speaking, the concept of pH can only be used to describe dilute aqueous solutions. For the design of O_2 scavenger mixtures for packaging applications, it therefore seems more reasonable to describe the autoxidation process as a function of an intrinsic property of GA, the DoD.

The kinetic parameters k and n were determined for each experimental dataset by fitting a second-order kinetic model (**Table 1**). For most experiments, the simulation results were in good agreement with the empirical data: the root-mean-square error (RMSE) was in the same order of magnitude as the experimental error MSE_{exp}. The fitted curves are shown in **Figures 7**, **8**. These results show that the simple second-order model can be used to describe the O_2 uptake by GA under diverse conditions.

TABLE 1 | Model parameters.

Base	pH	RMSE mol m^{-3}	MSE$_{exp}$ mol m^{-3}	k m^3 mol^{-1} s^{-1}	n
–	2.9	0.065	0.037	0*	0*
NaOH	5.7	0.139	0.063	$6.292 \cdot 10^{-8}$	0.68
	7.9	0.327	0.175	$5.961 \cdot 10^{-7}$	1.44
	9.1	0.320	0.084	$1.169 \cdot 10^{-6}$	2.16
	11.1	0.311	0.093	$1.923 \cdot 10^{-6}$	2.24
	13.0	0.146	0.058	$2.995 \cdot 10^{-5}$	2.01
	13.8	0.225	0.159	$1.837 \cdot 10^{-4}$	1.77
Na_2CO_3	5.1	0.065	0.056	$2.871 \cdot 10^{-7}$	0.15
	7.7	0.128	0.062	$4.639 \cdot 10^{-7}$	2.14
	8.3	0.113	0.035	$6.625 \cdot 10^{-7}$	2.25
	9.3	0.242	0.073	$1.285 \cdot 10^{-6}$	2.45
	10.4	0.158	0.098	$5.868 \cdot 10^{-6}$	2.50

*No detectable reaction.

Figure 10 shows the effect of the DoD on the reaction rate constant k and the absorption capacity n in the presence of each base. We found that k increased in line with the DoD, but that n reached a maximum at a DoD value of 0.6–0.7 equating to a pH of 10–11 under our experimental conditions. When the DoD fell below 0.2–0.3 there was no significant O_2 absorption. At a DoD value of 0.6–0.7 the predominant species in the solution are HA^{3-} and H_2A^{2-} (**Figure 5**). These species can participate in an autoxidation reaction involving an SET step as described in **Figure 1**. Our results indicate that this pathway may be preferred in terms of achieving a maximum absorption capacity. In contrast, autoxidation based on A^{4-} is likely to involve a different reaction pathway leading to a lower absorption capacity.

Figure 6 shows the amounts of NaOH and Na_2CO_3 required to achieve a certain DoD in the solution and this relationship is the basis for the development of an optimized scavenger composition. For maximum O_2 scavenger capacity, the DoD should be 0.6–0.7. This requires a base:GA mass ration of ∼1.8:1 for Na_2CO_3 and ∼0.8:1 for NaOH. As expected, a much smaller amount of the strong base NaOH is required to reach any given DoD compared to the weaker base Na_2CO_3. In terms of the design and processing of packaging materials incorporating scavengers based on GA, the amount of base required is important in terms of the precessability of the packaging material and the cost efficiency of the process.

4. CONCLUSION

In this study, we found that the amount and type of base added to an aqueous GA solution changes the O_2 absorption properties of the system in terms of the reaction rate constant and also the maximum absorption capacity. The addition of a base changes the acid-base equilibrium of the solution and therefore the type and amount of GA species that are present, which in turn influences the autoxidation reaction and ultimately the absorption of O_2. The key property that must be targeted when designing O_2 scavengers based on GA is therefore the DoD. We found that no reaction occurred at DoD values below 0.25. The

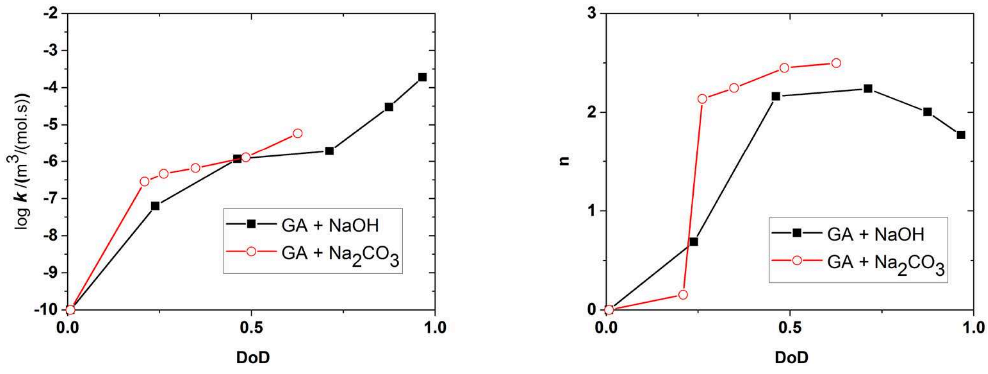

FIGURE 10 | Effect of the degree of deprotonation (DoD) on the reaction rate coefficient k and absorption capacity n. Connecting lines are shown for clarity.

absorption capacity *n* reaches its maximum value when the DoD is 0.6–0.7 whereas the reaction rate constant *k* increases with the DoD. Accordingly, the optimum DoD can be achieved by adding either NaOH or Na_2CO_3, but a strong base is more efficient because a lower quantity is required to reach the desired DoD value. These results, together with the models describing the GA solution and the autoxidation reaction, provide guidance for the development of packaging systems incorporating O_2 scavengers based on GA.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

AP conceived and designed the experiments, performed some of the oxygen absorption measurements, conducted the simulations and parameter estimations, and wrote the paper. DÖ contributed to the experimental design and performed some of the oxygen absorption measurements. SF contributed to the analysis and interpretation of the results and helped to write and revise the paper. MR contributed to the experimental design as well as modeling and simulation techniques and revised the paper.

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4. DISCUSSION AND CONCLUSION

This thesis aimed at studying the reaction kinetics of gallic-acid-based oxygen scavengers in order to provide basic knowledge for the application of such scavengers in packaging.

Thus, the two main objectives were to experimentally study the oxygen absorption reaction of GA and, based on these results, to develop an application-oriented modeling approach to describe the scavenger reaction.

The first part of the work (Section 3.1) dealt with the processing of a GA-based scavenger and the production of packaging films. As a proof of concept, biobased multilayer films incorporating GA were produced. The subsequent experimental characterization of the films showed the influence of high-temperature processing, humidity, temperature and film structure on the oxygen scavenging properties and thereby the need for a further analysis of the reaction kinetics.

The major part of this work was therefore dedicated to elaborating the reaction kinetics of the scavenger reaction, i.e. the kinetics of GA autoxidation. A second-order kinetic model was introduced, together with the in-deep evaluation of the fitting of such a model to experimental data from oxygen absorption experiments using a downhill-simplex based optimization method (Section 3.2).

This model was then used to describe experimental data sets reflecting various conditions of relative humidity, temperature and pH / deprotonation in order to analyse the effect of these factors on the scavenger kinetics in terms of the reaction rate coefficient and the total absorption capacity (Sections 3.3 and 3.4).

The main contributions of this research, that will be discussed in this chapter, are therefore related to modeling and simulation of scavenger reactions on the one hand and to the application of GA in packaging on the other hand.

4.1 Kinetic Modeling of Scavenger Reactions

The focus of this work was to describe the oxygen-scavenging reaction of GA with a model that can be used for simulation-based active packaging design. In this context, the model has to fulfill several requirements:

- The model should describe the time-dependent oxygen uptake in way that allows for simulating different packaging szenarios, e.g. packaging sizes and headspace gas compositions.
- The model should be able to account for external conditions such as temperature and other factors that are relevant for the scavenger reaction, e.g. humidity and deprotonation in the case of gallic acid.
- The model should be usable in current laboratory practice for the evaluation of oxygen absorption experiments.
- The model should be usable in combination with current software-tools simulating gas transport in packaging systems

The approach of this work, that will be discussed in the following sections, was to combine a **mechanistic model** for oxygen absorption with an **empirical description** of external factors, such as temperature and relative humidity.

Modeling time-dependent oxygen absorption

The oxygen absorbing function of oxygen scavengers relies on a chemical reaction, i.e. oxygen is bound by an oxidation reaction. As with GA, these oxidation reactions may follow complex mechanisms involving multiple oxidation steps (Section 1.4). Here, the scavenger reaction of GA was described with the net reaction given in Equation (4.1).

$$\mathrm{SC} + \mathrm{n\,O_2} \xrightarrow{k} \mathrm{SC_{ox}} \tag{4.1}$$

where n is a stoichiometric factor, k is the reaction rate coefficient, SC denotes the scavenger, and $\mathrm{SC_{ox}}$ the oxidized scavenger.

This net reaction summarizes all oxidation steps and correlates the amount of oxygen consumed to the quantity of scavenger that is oxidized. n can be interpreted as the scavenger capacity, i.e. the maximum quantity of O_2 that is absorbed per scavenger molecule.

This is a straightforward approach focusing on oxygen consumption as the most relevant property of scavengers while neglecting information such as reaction intermediates and reaction products. Thus, for using this approach, only oxygen absorption data is necessary, but no information on the chemical properties of the scavenger. This corresponds with current laboratory practice where usually only oxygen absorption is measured to characterize a scavenger reaction (Section 1.3.3). Moreover, due to these characteristics, this modeling approach is not specific to gallic acid but can be used to describe any scavenger reaction.

Second-order kinetic model

The kinetic law of the reaction given in Equation (4.1) was approximated by a second-order elementary reaction as shown in Equation (4.2).

$$r = k \cdot [\mathrm{SC}] \cdot [\mathrm{O_2}] \tag{4.2}$$

where r is the reaction rate and [SC] and $[\mathrm{O_2}]$ are the concentrations of the scavenger and $\mathrm{O_2}$, respectively.

Based on this kinetic law, the net consumption rates of GA and $\mathrm{O_2}$ were described with the system of ordinary differential equations (ODEs) shown as Equations (4.3) and (4.4)

$$\frac{d[\mathrm{SC}]}{dt} = -k \cdot [\mathrm{SC}] \cdot [\mathrm{O_2}] \tag{4.3}$$

$$\frac{d[\mathrm{O_2}]}{dt} = -n \cdot k \cdot [\mathrm{SC}] \cdot [\mathrm{O_2}] \tag{4.4}$$

This approach differs from kinetic models that are currently used in the field of active packaging which describe the reaction as a pseudo-first-order elementary reaction [13, 19, 41]. Although it has been shown in several studies that oxygen absorption experiments can be sufficiently described using pseudo-first-order kinetics, this approach is not useful when simulating actual packaging systems, as it is restricted by the assumption that either oxygen or the scavenger are available in excess so that the total amount can be considered constant.

This assumption is only valid for few packaging scenarios, e.g. for an active package containing a sachet with a high amount of oxygen scavenger compared to the amount of residual oxygen in the headspace to be scavenged. In this scenario only a neglectable amount of the scavenger is used to absorb the residual oxygen, so that the amount of scavenger may be assumed constant. However, during storage of said active package, the amount of available oxygen scavenger may decrease continuously due to the reaction with oxygen permeating into the headspace so that from a certain point of time the amount of scavenger cannot be considered constant anymore, so that the pseudo-first-order assumption fails here. This example illustrates the limitations of the pseudo-first-order kinetic model when it comes to describing actual application scenarios.

The second-order kinetic model, in contrast, describes the reaction rate as a function of both reactants so that real conditions in the package can be simulated, where either the oxygen concentration or the (residual) scavenger concentration may be limiting for the reaction. The second-order model is therefore the simplest usable approach for modeling scavenger reactions. Recently, second-order kinetic models were also used to describe the reaction of polymer-based oxygen scavengers [29, 31].

Current laboratory practice could benefit from this modeling approach in terms of efficient scavenger characterization: Industry standards are based on determining the pseudo-first-order reaction rate coefficient from oxygen absorption experiments [2]. Therefore, in practice, the oxygen absorption is typically determined at an initial oxygen concentration of 21% (v/v) and additionally at one or more different oxygen concentrations, e.g. at 2% (v/v), which is a typical residual oxygen content in modified atmosphere packages. Using the described second-order kinetic model, only one experiment would be necessary to predict the oxygen scavenging function at other initial oxygen concentrations, thereby reducing the experimental effort.

Estimation of the kinetic parameters

The model used in this work includes two parameters: The reaction rate constant k and the scavenger capacity n. For GA-based scavengers, these parameters were determined by fitting the second-order kinetic model to experimental data from oxygen absorption measurements. For the example of a downhill-simplex-based algorithm, it was shown how the best-fit combination of k and n is determined (Section 3.2). Besides downhill-simplex methods, current mathematical software (e.g. the MATLAB optimization toolbox) provides several optimization algorithms that can be used.

Fitting the experimental data resulted in various sets of k and n. Each set is specific to the reaction of a scavenger at given test conditions. Together with the model, k and n contain all information that are necessary to describe the oxygen uptake by the respective scavenger. These datasets can therefore be used to compare the oxygen-scavenging function of different substances, irrespective of their oxygen absorption mechanism.

In contrast to pseudo-first-order kinetics, where a simple analytical solution is available, the ODE system derived from the second-order kinetic model has to be solved numerically. This may have hindered the usage of the model in the packaging industry in the past, but current mathematical software allows for an easy numerical solution, e.g. manual fitting of the model to experimental data in EXCEL or automatical fitting by software tools that can be programmed in MATLAB, Octave etc.

Effect of external conditions

The parameters k and n are independent from inital concentrations, but may include several other dependencies that cannot be resolved by the model. For examples, the parameters may be affected by external factors such as temperature and humidity. To describe the effect of these external factors on the kinetic parameters, an empirical approach was used in this work.

The oxygen absorption experiments showed that the external factors temperature and humidity had a significant influence on the oxygen scavenging effect of GA-based scavengers. Furthermore, as a third factor, the pH (or more specifically the deprotonation of the GA molecules) had to be considered because the autoxidation of GA is highly affected by the types of gallate ion that are present (Section 3.4).

The effect of humidity, temperature and deprotonation on k and n were studied in oxygen absorption experiment and typical results are shown in Figure 4.1. For example, the plot of k vs. humidity suggests an exponential relationship and the arrhenius plot shows, that the arrhenius model could be used to describe the effect of temperature in the range of 10 °C to 38 °C. Fitting such empirical models, the kinetic parameters could be described as a function of an external factor, allowing for predictions within the range of conditions studied in the experiment, e.g. to predict k at 90 % RH.

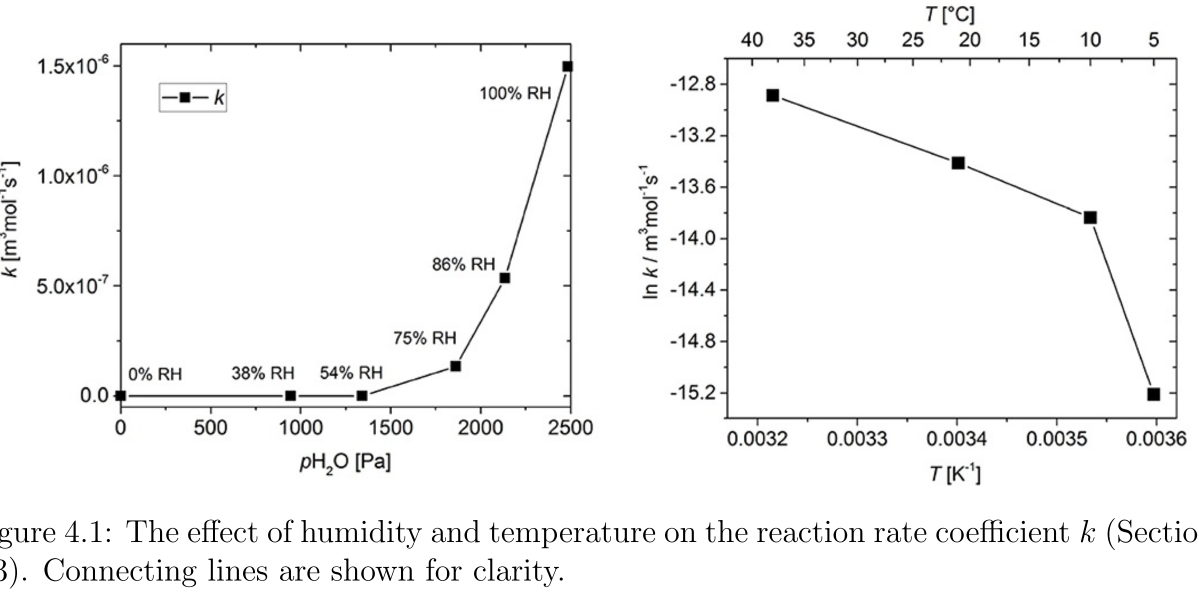

Figure 4.1: The effect of humidity and temperature on the reaction rate coefficient k (Section 3.3). Connecting lines are shown for clarity.

If there are several factors affecting the kinetic parameters it is likely that there are also interactions between these factors which have to be considered. The idea behind the response surface methodology (RSM) is to use designed experiments to describe the influence of several factors (so-called explanatory variables) on one or more response variables in order to find an optimal response [74]. For this, a statistical model, e.g. a second-order polynomial can be used [74].

To apply this method to scavenger experiments, in a first step, all external variables that may influence k and n have to be identified. In a designed experiment, selected combinations of these external variables have to be tested. Braga et al. used such a statistical approach to describe the effect of temperature and relative humidity on the first-order rate coefficient of an iron-based scavenger [13]. This approach can be extended to more than two external factors. With such an empirical model, the values for k or n for different conditions (within the range tested) can be calculated. Furthermore, the model can be used for finding optimum values of k or n [74].

Outlook: Simulation of packaging scenarios

Packaging materials incorporating an oxygen scavenger can be seen as reaction-diffusion-systems. Thus, two main processes have to be considered in a model describing such packaging systems: the gas transport through the polymer and the local reaction of the active component, which creates the oxygen-scavenging effect [40].

An example for coupling the second-order kinetic model presented in this thesis to gas transport is given by Laridon et al.[1]. In this theoretical study, the second-order kinetic model describing the scavenger reaction of GA was used for simulating an active packaging case study. Here, the GA-based scavenger was assumed to be incorporated into a PLA-based packaging material used for packaging of apple sauce. Additionally, as a measure of product decay, the oxidation kinetics of ascorbic acid was included into the model. The storage of 100 mL apple sauce in a PLA-based package was simulated for a period of 15 days.

The results show that a scavenger concentration of 5% (w/w) led to a significantly lower oxidation of the apple sauce compared to storage in a package made from pure PLA: The ascorbic acid content decreased to 20 mg after 15 days while it decreased to 3.5 mg when using PLA films. In the same way, different scavenger concentrations or polymer materials could be compared in a simulation.

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[1] Laridon, Y., Kurek, M., Pant, A., Reinelt, M., Stramm, C. and V. Guillard: Inclusion of O_2 scavenger to enhance barrier properties of PLA: application to packed food systems (to be submitted)

For this work the mechanistic description of oxygen absorption was used together with the kinetic parameters determined for a 2:1 mixture of GA and sodium carbonate stored at 23 °C and 100% RH to simulate the headspace oxygen content during storage.

In a next step, the model could be amended by empirical models describing the effect of external conditions (e.g relative humidity) on the kinetic parameter in order to be able to simulate varying storage conditions.

4.2 Application of gallic acid as an oxygen scavenger

The oxygen-scavenging function of GA relies on a complex autoxidation reaction which includes several oxidation steps [103]. Therefore, tailoring the scavenger function mainly involves optimizing the autoxidation, i.e. to provide optimum reaction conditons in the packaging material.

The kinetic studies of this thesis revealed several features of the GA scavenger reaction that have to be considered in the design and manufacture of active packaging materials:

- **Deprotonation**: The gallate ions are the active substance that is oxidized. Thus, prior to oxidation gallate ions have to be formed in an acid-base reaction (Section 3.4).
- **Humidity**: The acid-base reaction takes place in solution. Thus, humidity is required as a trigger for the reaction. During the acid-base reaction additional water is produced leading to a self-enforcing effect. Both the reaction rate constant and the scavenger capacity are affected by relative humidity (Section 3.3).
- **Temperature**: The reaction rate constant and the scavenger capacity are affected by the reaction temperature (Section 3.3).
- **Color**: The oxidation products are colored, ranging from yellow or orange to dark green, dark brown or black, depending on the scavenger composition and progress of the oxidation (Section 3.4).

In this section, the features of the GA scavenger reaction are discussed in the context of potential packaging applications.

Scavenger composition

It has been known for years that GA-based scavengers should include a base to ensure a fast scavenger reaction and different types of bases have already been tested [3, 60, 108]. In this thesis, it was shown, that in principle any base can be used in the scavenger mixture. The target property for scavenger design is the degree of deprotonation, i.e. the average deprotonation of the GA molecules.

Oxygen absorption experiments in model solutions revealed that the reaction rate coefficient increases with increasing degree of deprotonation. The oxygen absorption capacity was maximized at a degree of deprotonation of 0.6 to 0.7. This means that for an optimized absorption capacity, the majority of the gallic acid molecules should be present as gallate trianions, which should be reached by adding a base. For this, the strength of the base and the quantity have to be considered. In terms of the quantity needed, using a strong base such as NaOH is more efficient. The model developed in this work, which relates the quantity of base to the degree of deprotonation (Section 3.4) can be used for optimizing the composition of GA-based scavengers, depending on design requirements, e.g. the desired scavenger capacity or the maximum amount of additive in the film.

Production of packaging materials

GA-based scavengers can be integrated in polymer films by a process including a compounding step and a subsequent cast film extrusion (Section 3.1).The process temperatures should be lower than the decomposition temperature of GA, ~253 °C, to avoid the decomposition of GA into pyrogallol and carbon dioxide [12].

The produced films had a brownish-purple color, which showed that GA autoxidation occured during processing. Presumably this was due to humidity derived from the environment, combined with the high processing temperatures. However, despite the strong color development, the oxygen absorption capacity of the films was only slightly reduced compared to unprocessed scavenger powder (430 mg compared to 447 $\mathrm{mg\,g^{-1}}$ GA).

Compared to commercially available scavengers, GA-based scavengers have a high absorption capacity (Section 3.1). The 2:1 mixture of GA and sodium carbonate that was tested in this thesis had an absorption capacity of 298 $\mathrm{mg\,g^{-1}}$ scavenger. For the iron-based scavengers Shelfplus O_2 2710 a scavenger capacity of $43-47\,\mathrm{mg\,g^{-1}}$ scavenger has been reported [63]. Polymer-based scavengers show absorption capacities up to and $60-100\,\mathrm{mg\,g^{-1}}$ scavenger for OSP$^{\mathrm{TM}}$ (ethylene methylacrylate cyclohexenylmethyl) and 140 $\mathrm{mg\,g^{-1}}$ scavenger for metal-catalyzed poly(1,4-butadiene) [20, 65, 98].

Since humidity cannot fully be excluded from film production processes, it has to be noted that carbon dioxide will be formed during the initial acid-base reaction if carbonates are used as the basic component of the scavenger. In this case, degassing of the polymer melt is necessary to prevent unintended foaming of the polymer strain or polymer film. If the acid-base reaction is triggered by humidity derived from the environment, more water is produced in the reaction. As a consequence, small quantities of an alkaline solution are present during the process, which may lead to a decomposition of polymers that are prone to alkaline hydrolysis such as polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) [47, 115].

Due to the colored reaction products, GA is not suitable for packaging solutions which require transparency in order to show the product, e.g. lid films, trays and bottles. Regarding intransparent packaging it has to be noted that GA changes its color with ongoing reaction and that the brownish color may not be appealing to the consumer. Therefore multilayer structures with colored outer layers covering the GA-containing active layer are recommended. An inner layer (sealing layer) is also necessary to prevent direct contact between the product and the alkaline GA solution in order to avoid discoloration or changes in taste.

Besides the application in packaging films, GA-based scavengers could also be used in scavenger sachets containg the powder mixture. Here, the sachet material has to ensure that the colored, alkaline solution formed during the scavenger reaction does not migrate to the packed product. At the same time, the sachet has to be permeable for oxygen to enable the scavenger reaction.

Applications in food packaging

For the application in food packaging, an oxygen scavenger has to be suitable for the desired type of packaging, the target product and the desired storage conditions.

Kinetic studies showed that the oxygen scavenging function of GA-based scavengers is highly influenced by relative humidity and that at 23 °C the scavenger can be considered active at a relative humidity higher than 75% (Sections 3.1 and 3.3). On the other hand, packaging films containing GA-based scavengers can be stored at 23 °C and 53 % RH without losing their scavenging function. Thus, GA-based scavengers are recommended for packaging of products with a high water activity.

Due to the strong influence of temperature on the reaction rate constant, GA-based scavengers should be used for products stored at room temperature rather than for chilled storage. Potential applications include therefore bag-in-box solutions for beverages or beverage carton boxes.

Besides these general recommendations, it is as case-by-case decision, if the GA-based scavenger is suitable for a certain packaging application. The full packaging system has to be considered, e.g. the target product and its storage conditions as well as the packaging material and the headspace volume. To facilitate functional packaging design the kinetic model presented in this thesis, together with the experimentally determined kinetic parameters, can be used to simulate different packaging scenarios. Thereby, potential applications of the GA-based scavenger can be identified.

Outlook: Oxygen scavengers based on polyphenols

In the past few years, research has focused on the development of sustainable packaging materials. Oxygen scavengers based on renewable resources such as GA support this trend and are therefore of special interest for packaging development. Besides GA, other (poly-)phenols could also be used as oxygen scavengers. Especially the usage of polyphenol mixtures that are available in high amounts as a by-product from agricultural production (e.g. olive oil) can be seen as a potential sustainable resource for active packaging [25, 66].

As discussed in Section 1.4, GA shows typical properties of polyphenols and the galloyl moiety is part of hydrolyzable tannins. Thus, it is likely that the results of this thesis regarding the oxygen-scavenging properties of GA can be tranferred to other polyphenols.

As a first proof of concept is was shown recently by APICELLA ET AL. that the second-order kinetic model can be used to describe the oxygen absorption by polyphenolic extracts obtained from olive pomace. Furthermore, the oxygen absorption could be described as a function of the total phenol content (expressed as GA equivalents, GAE)[2]. This means, that the oxygen scavenging properties of a polyphenol or mixture of polyphenols can be predicted if the GAE value is known, thus allowing for a fast judgement of the scavenging potential.

To date, GA or other polyphenols are not listed as active substances according to Regulation (EC) No. 450/2009, i.e. prior to commercial use in the EU, a safety assessment by the EFSA is necessary [34]. This requires studies e.g. on the reaction products that are formed during autoxidation including a toxicological assessment and migration testing.

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[2] Apicella, A., Pant, A.F., Staebler, A., Leistl, D., Incarnato, L. (2019): Antioxidant properties of olive pomace extract. 3rd Innovations in Food Packaging, Shelf Life and Food Safety. 8-10 Oct. Munich, Germany

5. SUMMARY

Oxygen scavengers are an active packaging technology aiming at improved protection for oxygen-sensitive food products. Among potential oxygen scavengers, the hydroxyphenol gallic acid (GA) stands out due to its high oxygen absorption capacity and its availability from natural resources.

The design of active packaging is challenging since the scavenger function has to be tailored to the individual packaging system. Mathematical models describing the packaging system can support this design process in order to avoid inefficient "trial and error" testing. However, such a simulation-based design approach requires a suitable model of the oxygen absorption reaction of the respective scavenger.

This thesis aimed at providing basic knowledge on the reaction kinetics of GA in order to identify possible fields of application and to enable the simulation-based design of packaging materials incorporating GA as an oxygen scavenger. This was reached by experimental studies of the oxygen absorption reaction of GA-based oxygen scavengers and the concomitant development of an application-oriented modeling approach for the reaction kinetics.

The scavenger reaction of GA is based on a multistep autoxidation. It was shown that this autoxidation can be well described with a second-order kinetic model including the reaction rate coefficient k and the absorption capacity n. Here, the multiple steps of the autoxidation were summarized in a single overall oxidation step where n O_2 molecules are absorbed per GA molecule. For the example of a downhill-simplex-based optimization algorithm the estimation of the model parameters from oxygen absorption data was validated.

The oxygen absorption experiments revealed that temperature, humidity and the deprotonation of the GA molecules are the main factors that have to be considered in active packaging design. To account for these factors, the mechanistic model of oxygen absorption was amended with an empirical description of the factors influencing k and n.

This modeling approach fulfills all requirements for the application in packaging development: It is independent from initial reactant concentrations and it accounts for external factors, thus allowing for the simulation of different packaging scenarios over time. Moreover, the model can be used with data obtained with current lab equipment for scavenger characterization. Furthermore it has been shown that the model can be combined with models for gas transport, thereby building full active packaging models.

The kinetic studies showed that the scavenger reaction of GA is triggered by humidity. It was found that there is no scavenging effect at a relative humidity below 53 % RH. Apart from that, higher levels of relative humidity lead to a faster reaction and a higher scavenger capacity. Similarly, the reaction rate coefficient and the scavenger capacity increased in line with temperature.

For optimum scavenger performance it is crucial to combine GA with a base. Here, the target property for scavenger optimization was shown to be the degree of deprotonation of GA. The oxygen absorption capacity was maximized at a degree of deprotonation of 0.6-0.7. For practical application, the model presented in this thesis can be used to determine the optimum scavenger mixture for a base with given acidity constants.

The production of active multilayer films incorporating a GA-based scavenger was studied in extrusion trials. It was found that the oxygen absorption capacity of GA was only slightly reduced after extrusion. For the processing of packaging films containing GA it is important to avoid temperatures above the GA decomposition temperature. Degassing of the polymer melt may be necessary due to CO_2 development. It is also considerable that the scavenger reaction of GA results in dark-colored products so that transparent packaging is not possible.

Based on the results of this work, GA-based scavengers are recommended for packaging of products with a high water activity stored at room temperature since the experiments showed poor scavenger performance both at dry and chilled conditions. Packaging films containing GA can be stored at room temperature and up to 53 % RH without losing the scavenging effect. Besides these general recommendations, it is a case by case decision if GA-based scavengers are suitable for a certain packaging system. The model for oxygen absorption presented in this thesis can be used support this decision.

Overall it can be stated that this thesis contributes to the field of active packaging by providing a quantitative description of the properties of GA that are relevant for the application in active packaging on the one hand and on the other hand by presenting a modeling approach that can be used to describe scavenger kinetics in practice.

ZUSAMMENFASSUNG

Der Einsatz von Sauerstoff-Scavengern ist eine aktive Verpackungsstrategie, die auf den Schutz sauerstoffempfindlicher Lebensmittel abzielt. Unter potentiellen Sauerstoff-Scavengern zeichnet sich Gallussäure (engl. gallic acid, GA) dadurch aus, dass sie eine hohe Sauerstoffaufnahmekapazität aufweist und zudem ein nachwachsender Rohstoff ist.

Die Entwicklung aktiver Verpackungen stellt eine Herausforderung dar, da die Scavenger-Funktion an das jeweilige Verpackungssystem angepasst werden muss. Mathematische Modelle des Verpackungssystems können dabei unterstützend eingesetzt werden, um einen ineffizienten ”trial and error”- Entwicklungsprozess zu vermeiden. Für einen simulationsgestützten Entwicklungsansatz ist jedoch ein geeignetes Modell zur Beschreibung der Sauerstoffaufnahme durch den jeweiligen Scavenger erforderlich.

Das Ziel der vorliegenden Arbeit war es, grundlegende Erkenntnisse zur Reaktionskinetik von GA zu gewinnen, um zum einen mögliche Anwendungsgebiete zu identifzieren und zum anderen die simulationsgestützte Entwicklung von aktiven Verpackungen mit GA zu ermöglichen. Dies wurde erreicht durch die experimentelle Untersuchung der Sauerstoffaufnahmereaktion von GA-basierten Scavengern sowie die begleitende Entwicklung eines anwendungsorientierten Ansatzes zur Modellierung der Reaktionskinetik.

Die Scavenger-Reaktion von GA basiert auf einer mehrstufigen Autoxidation. Es wurde gezeigt, dass diese Autoxidation mit einem kinetischen Modell zweiter Ordnung beschrieben werden kann, welches den Ratenkoeffizienten k und die Sauerstoffaufnahmekapazität n enthält. Dabei wurde die mehrstufige Reaktion in einer einzigen Gesamtreaktion zusammengefasst, in welcher n Sauerstoffmoleküle pro GA-Molekül aufgenommen werden. Am Beispiel eines Algorithmus, der auf einer Downhill-Simplex-Optimierung basiert, wurde die Bestimmung der Modellparameter aus experimentellen Daten aus Sauerstoffabsorptionsmessungen validiert.

Die Sauerstoffabsorptionsmessungen zeigten, dass die Temperatur, Feuchte und die Deprotonierung der GA-Moleküle die wichtigsten Einflussfaktoren sind, die für die Entwicklung aktiver Verpackungen relevant sind. Zur Berücksichtigung dieser Faktoren im Modell wurde die mechanistische Beschreibung der Sauerstoffabsorption um eine empirische Beschreibung

des Einflusses der Faktoren auf k and n ergänzt.

Dieser Modellierungsansatz erfüllt alle Kriterien für den Einsatz in der Verpackungsentwicklung: Die Modellparameter sind unabhängig von den Anfangskonzentrationen der Edukte und das Modell berücksichtigt den Einfluss externer Faktoren auf die Modellparameter. Es können daher unterschiedlichste Szenarien simuliert werden. Weiterhin kann das Modell mit Datensätzen aus gängiger Laborpraxis verwendet werden. Darüber hinaus wurde gezeigt, dass das Modell mit Gastransportmodellen gekoppelt werden kann, so dass es möglich ist, aktive Verpackungssysteme zu simulieren.

Die reaktionskinetischen Untersuchungen zeigten, dass die Sauerstoffaufnahmereaktion von GA durch Feuchtigkeit getriggert wird. Bei einer relativen Feuchte von weniger als 53% RH konnte keine Scavengerwirkung festgestellt werden. Ansonsten gilt, dass eine höhere relative Feuchte zu einer schnelleren Reaktion und einer höheren Scavengerkapazität führt. In gleicher Weise erhöhen sich der Ratenkoeffizient und die Scavengerkapazität bei höheren Temperaturen.

Um eine optimale Scavengerwirkung zu erzielen ist es entscheidend, dass der Scavenger aus einem Gemisch aus GA und einer Base besteht. Die Zielgröße zur Optimierung des Scavengers ist hierbei der Deprotonierungsgrad von GA. Die höchste Scavengerkapazität wurde bei einem Deprotonierungsgrad von 0.6-0.7 erreicht. Das im Rahmen dieser Arbeit vorgestellte Modell kann verwendet werden, um das optimale Mischungsverhältnis von GA und einer Base mit bekannter Säurekonstante zu berechnen.

Die Herstellung von aktiven Mehrschichtfolien mit GA-basierten Scavengern wurde in Extrusionsversuchen untersucht. Es wurde gezeigt, dass die Scavengerkapazität von GA durch die Extrusion nur leicht reduziert wird. Für die Herstellung von Packstoffen mit GA ist es entscheidend, dass Temperaturen oberhalb der Zersetzungstemperatur von GA vermieden werden. Zusätzlich kann eine Entgasung der Schmelze aufgrund von CO_2-Bildung während der Extrusion notwendig sein. Für die Gestaltung von Verpackungen ist ebenfalls relevant, dass während der Autoxidation von Gallussäure farbige, dunkle Reaktionsprodukte entstehen, so dass es nicht möglich ist, transparente Packstoffe herzustellen.

Auf Grundlage der Ergebnisse dieser Arbeit wird der Einsatz von GA-basierten Scavengern empfohlen für Produkte mit einer hohen Wasseraktivität, die bei Raumtemperatur gelagert werden, da die Scavenger sowohl bei kühlen als auch bei trockenen Bedingungen nur eine mäßige Scavengerwirkung zeigten. Abgesehen von dieser generellen Empfehlung muss jedoch die Entscheidung, ob ein GA-basierter Scavenger geeignet ist, individuell für das jeweilige Verpackungssystem getroffen werden. Der in dieser Arbeit vorgestellte Modellierungsansatz ermöglicht die Simulation unterschiedlicher Verpackungsszenarien und kann daher als effiziente Entscheidungshilfe verwendet werden.

Insgesamt leistet diese Arbeit einen Beitrag auf dem Gebiet der aktiven Verpackung, indem zum einen eine quantitative Beschreibung der verpackungsrelevanten Eigenschaften von GA bereitgestellt wird und zum anderen ein praxistauglicher Modellierungsansatz für Scavengerreaktionen vorgestellt wird.

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