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Graph-theoretical approach to algorithmic construction of complex reaction networks

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Review of the kinetics and simulations of the linseed oil autoxidation

This review summarizes computational modeling literature concerning linseed oil autoxidation in the context of oil paint. After discussing chemical structure and composition of linseed oil, an overview is given of polymer properties of the material and the experimental techniques used to infer these properties. The review proceeds with the survey of existing computational modeling techniques, used to investigate the drying process of linseed oil.

Based on: Review of the kinetics and simulations of the linseed oil autoxidation. Y. Orlova[†], R. E. Harmon[†], L.J. Broadbelt, P.D. Ledema. *In preparation* († = equal contribution)

3.1. Introduction

This literature review is motivated by the need for a resource that gathers relevant chemical kinetics for the autoxidation of linseed oil and the opportunities that computer simulation can offer this century-old field. Linseed oil is a prominent drying oil, particularly known for its use as a varnish and oil paint binder since the 15th century¹. At the advent of the paint tube, oil paint production expanded beyond the mortar and pestle where chemists were working to perfect the revolutionizing products. Dried (polymerized) linseed oil is an insoluble binder with stability and structure to last hundreds of years. Its properties depend on composition and crosslinks, each affected by environmental conditions² and additives such as driers³ and elevated temperatures⁴.

Up to this point, several key reviews consolidated literature and resources related to the autoxidation pathways that cure linseed oil and inevitable degradation pathways that wear it down. However, this review is written from the perspective of collaborative research that leverages a century of experiments to understand linseed oil on the molecular level using computer modeling tools as technological advances in the 21st century. It is also centered around the drying oil's application and long-time behavior in art and art conservation science efforts⁵ in contrast to prominent efforts in food science research⁶ with related oils.

Linseed oil and its model systems have been investigated as a binding medium of oil paint in numerous experimental research works⁷⁻⁹ preceding computational modeling. Thorough studies were done regarding the influence of drier on the autoxidation of ethyl linoleate and linseed oil reporting the behaviour of key functional groups and of small volatile compounds¹⁰⁻¹⁸. Reviews by Honzíček¹⁹, Soucek *et al.*²⁰, Juita *et al.*²¹ and van Gorkum *et al.*¹² provide detailed descriptions of the autoxidation reaction mechanism. These research works provide valuable information about the chemistry of linseed oil and serve as a reference for computational modeling.

The term "model" is used in two contexts in this review: 1) a model compound that represents a simplified chemical species and 2) a computational model for simulating a complex, physical system. A chemical model compound shares some essential chemical properties with the real compound, but it can be tested under better defined conditions. For example, ethyl linoleate (EL) is commonly used as a model system for linseed oil, as EL represents the linoleic ester of linseed oil. Also, EL is available as a purified substance, whereas linseed oil is only available as a natural mix of triglycerides with different ratios of fatty esters. Yet, the EL model offers the advantage of a detailed quantitative and theoretical interrogation of the physical system.

This review yields access to key research related to the drying and degradation of

linseed oil of relevant kinetic detail, pathways, and methods and thus forms a starting point for work in this interdisciplinary field. Section 1 characterizes the structure and variations in composition of the linseed oil. Proceeding with the polymerizing nature of linseed oil, Section 2 explains the formation of the linseed oil films in terms of a free radical polymerization process. Section 3 provides an overview of the reaction pathways characterizing linseed oil during its autoxidation including recent findings in β -scission and epoxidation mechanisms. In Section 4, we proceed with the description of several experimental techniques that are relevant for validation of various models. Computational methods elaborated on in Section 5 of this review are quantum chemical calculations and kinetic modeling. Kinetic modeling is most comparable to physical experiments, as concentrations of some initial, intermediate and final compounds can be quantified in a relatively straightforward manner. The sensitivity of systems can also be readily investigated using kinetic modeling. Following the findings in computational modeling, the review finally discusses future directions in modeling for linseed oil research.

3.2. Drying oils

Drying oils are natural, bio-based oils that harden or "dry" into a solid film when being exposed to daylight and to ambient oxygen. The oil is a mixture of triglycerides, where each molecule consists of three fatty acids attached to glycerol by ester bonds. Fatty acids are carboxylic acids with a hydrocarbon chain that is saturated fully with hydrogen atoms or unsaturated with one to four double bonds along the chain. Double bonds may be arranged to form either conjugated or non-conjugated double bonds, the latter causing stronger drier activity.

Properties of drying oils strongly depend on the relative amount of different types of fatty esters. Unsaturated fatty esters undergo a complex autoxidation mechanism eventually forming crosslinks, which lead to the formation of a polymer network. Meanwhile, saturated fatty esters remain virtually unchanged. Depending on the content of various fatty esters, oils are classified as drying, semi-drying and non-drying oils. The ability of an oil to undergo autoxidative drying depends directly on the amount of doubly allylic methylene units (or bis-allylic C-H bonds), which are found in linoleic and linolenic acids. Bis-allylic groups are responsible for the formation of crosslinks, as the bis-allylic H-atom is easily abstracted to form a radical, which forms the onset of reaction pathways ultimately ending up in crosslinks. One bis-allylic group (as in linoleic) may result in up to three crosslinks. This observation leads to the empirical relationship quantifying the oil's ability to dry: $\text{Drying index} = (\% \text{ linoleic acid}) + 2(\% \text{ linolenic acid})$ ²⁰. Oils with a drying index above 70 are classified as drying oils.

The fatty ester content in several oils is summarized in Table 3.1. Although the table provides the most common fatty ester composition, oils have different degree of unsaturation depending on agricultural temperature zone^{17,22} and oil processing methods²³. Saturated fats and oleic acid do not contribute to the drying process, implying that olive and coconut oils never dry, while linseed, soybean, walnut and poppy seed oils are prone to drying via crosslinking. Linolenic acid is a major fatty ester in linseed oil, while linoleic acid is a major fatty ester in soybean, poppy seed and walnut oil¹². Due to their properties, these four oils became widely used as binding media by artists, who were empirically finding the balance in the amounts of linoleic and linolenic acids for their paints²⁴. Work by Stenberg *et al.*²⁵ compares the drying process of linseed oils with a high content of linoleic fatty esters versus a high content of linolenic fatty esters. The authors conclude that a high content of linoleic fatty esters ensures homogeneous drying of the oil film, while linseed oil with a high linolenic fatty ester content dries fast on the surface, leaving unreacted fatty esters below. Drying of linseed oil occurs by chemical crosslinking between monomers, thus increasing viscosity and leading to an insoluble polymer fraction. The viscosity increase is just slow enough to permit artistic changes while creating a painting. Some of the autoxidative drying processes leading to the desired solid polymer network continue afterwards and lead to degradation of the binding medium in the longer term. Therefore, understanding drying and degradation processes of drying oils and their impact on the structure of the binding medium polymer is an important issue in the field of restoration and conservation of art.

Because of the variability of fatty esters in linseed oil mixtures, model systems are often used to isolate certain properties or reactivities to study in a controlled fashion. For example, common model species are unsaturated methyl and ethyl esters of oleic, linoleic, linolenic, and ricinoleic acid^{11,13,16,16,26}, as well as dienes: 4,7-heptadiene²⁷, 3,6-nonadiene²⁸, and 2,5-undecadiene²⁹. While exploring various aspects of the drying process such as speed of drying and emission of volatile compounds, researchers developed a better understanding of elementary reaction steps leading to the final product.

3.3. Polymerization

The extensive usage of linseed oil in works of art is explained by the oil's suitable optical and mechanical properties as a polymer. While drying, linseed oil actively reacts with oxygen and forms a thin continuous film via a polymerization process. Favorable drying properties of linseed oil are achieved due to a high concentrations of linoleic and linolenic acid tails, which are the main polymerizing agents in linseed oil responsible for drying.

Oil	Saturated	Oleic	Linoleic	Linolenic
Linseed oil ²⁰	10	22	16	52
Soybean oil ²⁰	15	25	51	9
Poppy seed oil ³⁰	15	20	65	
Walnut oil ³¹	9	20-26	50-55	14-15
Olive oil ³²	13-20	62-80	5-15	5-8
Coconut oil ²⁰	91	7	2	

Table 3.1: Various ratio of fatty esters in oils (in %)

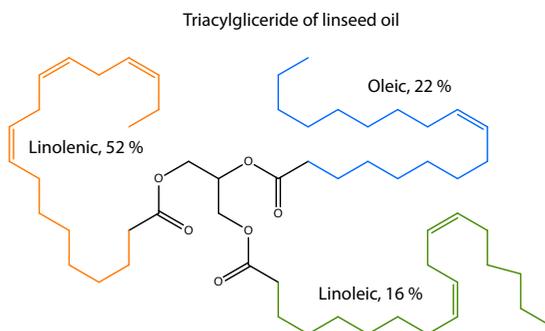


Figure 3.1: An example of triglyceride that would be a molecule found in linseed oil.

Drying and hardening of linseed oil is considered as a polymerization of triglycerides via autoxidation, a process involving free radicals. Individual molecules of liquid linseed oil act as initially disconnected monomers. In the presence of oxygen, the triglyceride monomers form covalent crosslinks, which leads to the formation of oligomers and eventually to infinite-size polymers. Free-radical polymerization reactions consist of three main categories: initiation, propagation and termination³³. Polymerization competes with degradation processes such as scission reactions, decomposition of unstable crosslinks and hydrolysis.

Due to the presence of natural antioxidants in linseed oil^{20,34}, initiation occurs after an induction time and leads to the formation of a reactive bis-allylic radical. Due to the presence of these radicals, linseed oil can react with oxygen forming highly reactive hydroperoxide radicals. This oxygen uptake leads to significant mass increase. During the formation of hydroperoxide groups, the non-conjugated double bonds in the fatty esters become conjugated double bonds. Only unsaturated acids can undergo initiation and are subject to polymerization reactions, while saturated fatty esters remain unreacted along the hydrocarbon chain and act as plasticizers³⁵. Initiation is followed by propagation reactions, by which radicals are propagating from one molecule to another. Termination occurs when two radicals meet and form either a covalent crosslink via recombination or two terminal groups, one saturated and one unsaturated, via disproportionation. Crosslinks may also be formed by addition reactions occurring between hydroperoxide radicals and conjugated double bonds. Termination and addition reactions first lead to the formation of oligomers. As polymerization proceeds, few oligomers become very large and eventually form a polymer network of infinite size. The polymer network molecule forms a gel, which is an insoluble species. The weight fraction of gel continues growing at the expense of the smaller molecules³⁵. While the insoluble fraction is forming, low molecular weight molecules are also formed via oxidative scission of alkyl chains (β scission), decomposition of unstable crosslinks or hydrolysis of ester bonds. Some of these low-molecular compounds are volatile and are released, causing the typical smell of drying paint. The linseed oil polymer does not fully converge into a gel regime, as non-volatile low molecular weight soluble fractions remain in the system even after long drying time¹⁶. Decomposition reactions are characteristic for the late stage of drying of linseed oil, and they are responsible for the degradation of the binding medium. Degradation of the polymer network is enhanced by ambient conditions. Both thermal and photo degradation occur, but the latter is found to be more harmful to the polymer network¹².

The drying process of linseed oil, as a binding medium of paint, may be influenced

by introducing additives, such as driers, extenders and pigments^{9,12,13}. The addition of driers influences the amount of crosslinks formed in the linseed oil film. There are different types of driers: primary driers (surface driers), secondary driers (through-driers) and auxiliary driers. Primary driers influence the hydroperoxide decomposition reaction, while through-driers enhance the amount of crosslinks. Auxiliary driers may influence the action of a primary drier and are added mainly to improve the aesthetics of the paint layer¹². Primary driers are usually combined with secondary driers, as an excess of primary drier may result in wrinkling of the paint film³⁶. In contrast, an excess of secondary drier may result in increased brittleness of the dried oil³⁷. The behavior of soluble fractions in the presence of cobalt drier was studied by Muizebelt *et al.*³⁸. Oligomeric species up to pentamers were detected after one day of drying, while only dimers and compounds with low molecular weights remained in the system after 60 days of drying.

To quantify the extent of drying, the elasticity modulus of the film can be measured. Mecklenburg and Tumosa³⁹ performed a long-term aging study with titanium white pigment in cold-pressed linseed oil and compared these to other commercial white paints. Using tensile testing, they measured the stress-strain behavior of the samples, which led them to conclude that paint continues to become more brittle, even after 10 years. Various factors are known that may further influence the tensile properties of a film. These include degradation processes and cleaning treatments that leach out low molecular weight molecules that had previously plasticized or maintained the flexibility of the film, thus embrittling the film^{40–42}.

Van den Berg *et al.*⁴³ also found that the presence of polyvalent metal ions has an impact on the stability of a polymer film. In a pure linseed oil film without pigments, hydrolysis of the ester bonds between glycerol and fatty esters causes the network to degrade. Polyvalent metal ions stabilize the network by forming ionomers. Hence, when studying polymer models with respect to reactivity and mechanical properties, one has to include the effect of pigments as well.

Numerous research works mentioned above intended to improve paint properties regarding durability. Meanwhile, ongoing work in conservation science is performed to better understand the drying and degradation of existing art objects, based on oil paint. Detailed understanding of the oil autoxidation mechanism is necessary to improve conservation and restoration treatments of precious works of art by enhancing efficiency and reducing the need for invasive analysis. It should be realized that specific detrimental chemical phenomena are closely linked to linseed oil chemistry. For instance, formation of metal soaps is strongly related to the presence of carboxylic acid groups resulting

from autoxidation in the oil film⁴⁴. Therefore, it is desirable to investigate the reaction pathways involving carboxylic acid groups in relation to cleaning, restoration, storage and transport of the art objects.

A remarkable feature of the polymer network formed by linseed oil lies in the diversity of its monomer constituents. The monomers are not identical repeating units as in many industrial polymers (e.g. polyethylene or polystyrene). Linseed oil monomers can undergo many chemical transformations until they reach stable states and become incorporated in the polymer network. Therefore, one may identify two main challenges in understanding the polymerization chemistry of linseed oil: 1) numerous competitive radical reactions involving fatty esters of triglycerides lead to a variety of intermediate molecular species; 2) liquid linseed oil polymerizes to a solid, so reaction conditions change dramatically causing radical reactions to proceed more slowly as their mobility decreases - these reactions will become diffusion-controlled.

In this literature review we report on various aspects of the detailed reaction mechanism of linseed oil polymerization.

3.4. Chemistry and kinetics

The reaction mechanism of triglycerides is an autoxidation process that proceeds under the influence of oxygen and light. It predominantly consists of the following reactions: oxidation, crosslinking and scission⁴⁵. The autoxidation process consists of a very complex scheme of radical reactions occurring repeatedly to the functional groups of the organic linseed oil molecule. Multiple reactions may occur rapidly and essentially simultaneously, leading to products that are not easily isolated in experiments⁴⁶. The autoxidation of linseed oil is characterized by two competing mechanisms: formation of the polymer network and breakdown of the molecules due to β -scission, unstable crosslink decomposition and hydrolysis. The schematic representation of the autoxidation process is shown in Figure 3.2.

Consistent with 3.2 the four main stages of free-radical polymerization will now be discussed: 1) initiation; 2) propagation; 3) termination; 4) degradation. In the case of drying oils, these reaction steps lead to a variety of intermediate and end products. We provide many reported reactions for each fatty ester at various stages of drying. Moreover, where possible, the reactions will be reported together with kinetic rate parameters, which influence the speed of reactions as a function of temperature. It must be noted that kinetic parameters cited in the review possess uncertainty, as there is both experimental and computational error in the values.

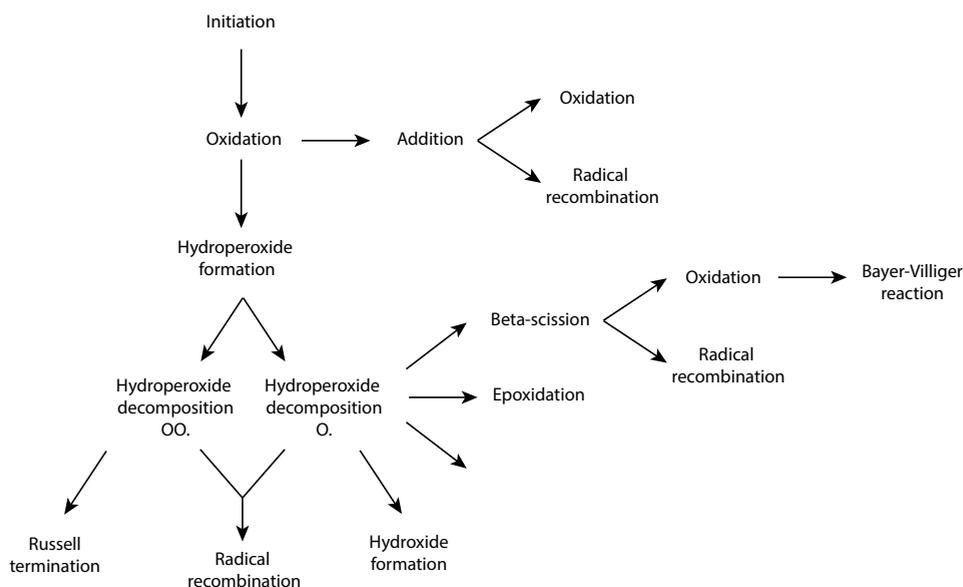


Figure 3.2: A general schematic representation of the reactions occurring during autoxidation of linseed oil.

3.4.1. Initiation

Autoxidation begins with an initiation step involving a tiny amount of radicals that may be created in several ways. During the subsequent propagation step a comparatively higher concentration level of radicals prevails in the system. In linseed oil, the initiation of a radical can be delayed by the presence of natural antioxidants^{20,34}, causing an induction period before propagation starts. Differences in induction period are observed in the temperature ranges above 130 °C, 84-130 °C and below 84 °C. The induction period is short above 130 °C, while in the range of 84-130 °C the length of induction increases slowly as the temperature is lowered; below 84 °C the induction period is long and independent of temperature⁴⁶. Initiation happens in two steps: primary initiation and secondary initiation. Primary initiation creates a tiny amount of peroxy radicals that subsequently take part in the secondary initiation.

During secondary initiation the radical created by primary initiation abstracts a hydrogen atom from a bis-allylic carbon of a linoleic or linolenic fatty ester tail, forming a delocalized pentadienyl or heptadienyl radical, respectively. The alkyl radical rapidly reacts with molecular oxygen and forms a peroxy radical. Allylic hydrogen abstraction happens predominantly at elevated temperatures⁴⁷. For the resonant structures after

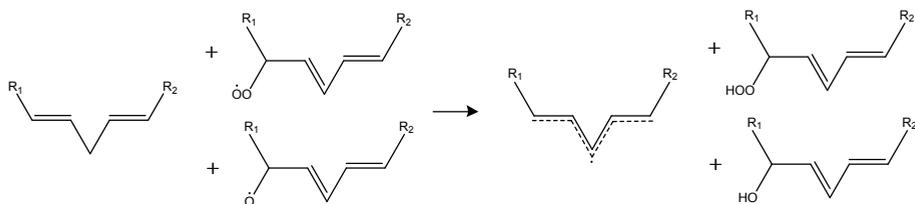
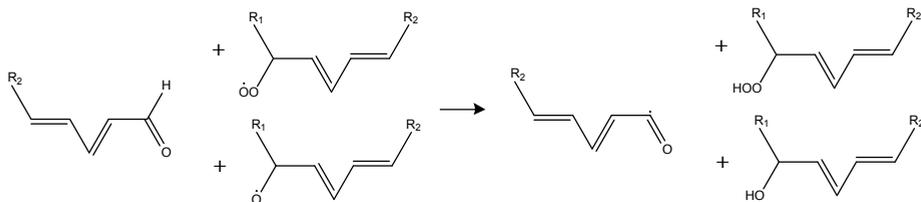
Hydrogen abstraction from bis-allylic carbon:**Hydrogen abstraction from aldehyde:**

Figure 3.3: Propagation of radicals via hydrogen abstraction from bis-allylic carbon (top) and from an aldehyde (bottom) by alkoxy and peroxy radicals.

allylic and bis-allylic hydrogen abstraction, see Figure 3.3. Initiation can occur spontaneously⁴⁸, or with the aid of UV light⁴⁹, singlet oxygen²⁸ or active metal catalysts¹⁵. Spontaneous initiation is rationalized by the fact that linseed oil will cure in air without using a catalyst, although slowly⁴⁸. It has been shown that UV irradiation lowers the activation energy of curing of alkyd resins⁴⁹. Singlet oxygen is much more reactive than triplet oxygen and is capable of attaching to the bis-allylic as well as to allylic carbon and forming a hydroperoxide via a concerted cyclic addition mechanism²⁸. Singlet oxygen is formed from molecular oxygen in the presence of photosensitizers causing the excited state of oxygen by an uptake of at least 22.4 kcal/mol²⁸.

Metal driers are added to oils to speed up decomposition of hydroperoxides and initiate autoxidation. A common transition metal catalyst is cobalt di-ethylhexanoate that undergoes primary initiation by reacting with molecular oxygen forming a peroxy radical with a rate coefficient in the order of 10^{-1} L/mol*s^{13,50}, while Co^{II} becomes Co^{III}. The peroxy radicals follow secondary initiation and abstract hydrogen to form bis-allylic or allylic radicals. Cobalt hydroperoxide then changes back to Co^{II} and splits off a hydroperoxyl group and then may continue its catalytic activity.

Hydrogen abstraction The abstraction of bis-allylic hydrogen occurs at a rate coefficient on the order of 10^{-1} L/mol*s, while allylic hydrogen is 10^5 times less reactive⁵¹.

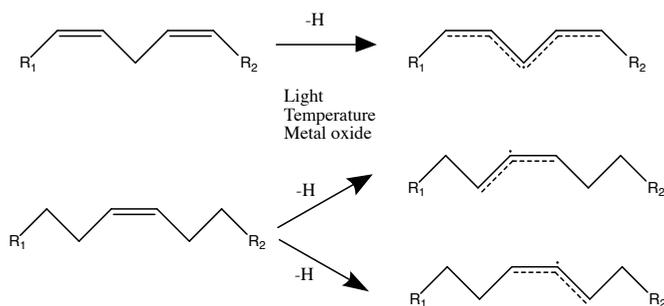


Figure 3.4: Possible initiation of allylic and bis-allylic carbons.

The energy barrier for hydrogen abstraction in the case of oleate is even higher, 80 kcal/mol⁴⁶. During the autoxidation mechanism, alkoxy, peroxy and alkyl radicals are produced, which also take part in hydrogen abstraction. Peroxy radicals play a major role in hydrogen abstraction as they exhibit a rather long half-life (up to 7 s) in comparison with alkoxy (10^{-6} s) and hydroxyl (10^{-9} s) radicals²¹. The rate coefficient of hydrogen abstraction by peroxy radical is estimated to be 6,6 L/mol*s⁵¹. The speed of initiation can be measured experimentally by tracking the decrease of bis-allylic carbon concentration as, after oxygen addition, they disappear while the non-conjugated configuration of the double bonds changes into a conjugated configuration³⁵.

3.4.2. Propagation

The repeated hydrogen abstraction by peroxy radicals and subsequent reaction with oxygen is responsible for a continuous production of radicals, which in polymer reaction engineering is therefore called the propagation step.

Oxidation Alkyl radicals formed via hydrogen abstraction add oxygen, forming peroxy radicals. The oxidation mechanism is shown in Figure 3.5. The reaction of oxygen and alkyl radicals happens very rapidly, with a rate constant on the order of 10^8 L/mol*s and an activation energy of 0 kcal/mol. The rate of oxidation varies depending on conditions, such as temperature, the presence of pro-oxidants (oxidizing agents), antioxidants and dissolved oxygen⁵², and the rate also depends on the degree of unsaturation. As mentioned in the work by Wexler⁴⁶, the oxidation rates of triolein, trilinolein and trilinolenin are increasing in order of degree of unsaturation: 1:20:330. When adding to the resonant structure of the backbone, as in linoleic esters, oxygen prefers the position on the 9th or 13th carbon atom, and the resulting functional group is called an outer

peroxide. Inner peroxides (C-10 and C-12) appear in minor amounts, possibly resulting from the formation of cyclic peroxides (endoperoxides)^{21,53,54}. In the case of linolenic acid, hydroperoxides are found at the external as well as at internal positions³⁵.

Hydroperoxide, hydroxide formation Hydroperoxides are formed from peroxy radicals after they perform hydrogen abstraction. Being stable intermediates, hydroperoxides mark the initial stage of the autoxidation process. Decomposition of hydroperoxides is a slow unimolecular reaction with a rate constant on the order of 10^{-13} s^{-1} and an activation energy of 24.6 kcal/mol⁵⁵. Hydroperoxide decomposes into alkoxy and hydroxyl radicals, and the reaction is accelerated under the influence of light and drying agents containing transition metals like cobalt. The chemistry of hydroperoxide decomposition with cobalt is described in detail in Spier *et al.*¹⁵.

After hydroperoxide decomposition, the alkoxy radicals may proceed along several reaction pathways including secondary scission of alkyl chains, recombination with another radical or hydrogen abstraction. In the case of the latter, an alkoxy radical becomes a hydroxide, which is one of the stable end products of the autoxidation process. The concentration of hydroxides in a linseed oil film reaches a constant value between 200-300 hours of drying time³⁵.

Addition Unsaturated fatty esters participate extensively in hydrogen abstraction, and the addition of oxygen to the alkyl radical is facile, while the previously unsaturated double bonds are rearranged into a conjugated state. The conjugated double bonds are also reactive and are consumed via addition of a peroxy radical forming a dimer. Thereby, the radical is transferred from the peroxide on one fatty ester to the carbon on the other fatty ester (see Figure 3.6). The previously conjugated structure turns into a resonating double bond between two carbon atoms until the radical reacts with oxygen or undergoes termination. The activation energy of peroxy radical addition to a conjugated double bond is 6.7 kcal/mol, where the rate parameter is on the order of $10 \text{ L/mol}\cdot\text{s}$.

General behavior of double bonds As described above, a significant rearrangement of the double bonds occurs during the initial autoxidation steps. In the case of oleic fatty esters, there is a *trans*-C=C (double bond), while the polyunsaturated lipids start with *cis*-C=C, which is further consumed via initiation and is turned into a conjugated double bond. Following the addition reaction, one of the conjugated double bonds is broken and the remaining double bond adopts a *trans* configuration. Thus, the *cis*-C=C

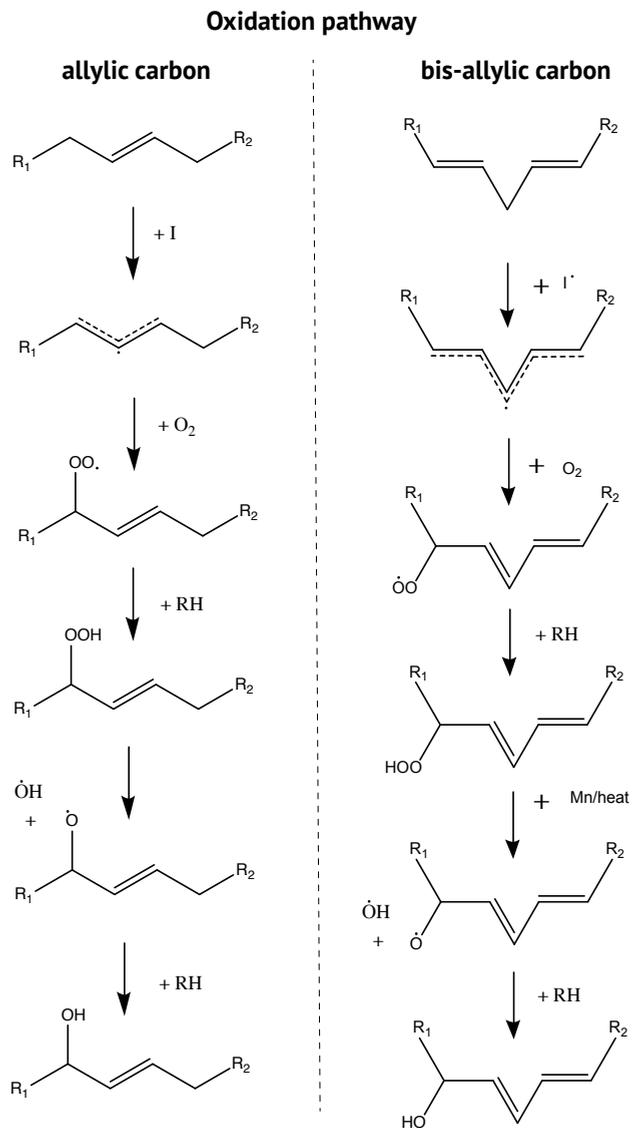


Figure 3.5: Oxidation pathways of fatty esters containing allylic (left) and bis-allylic (right) carbons that are found in fatty esters of linseed oil.

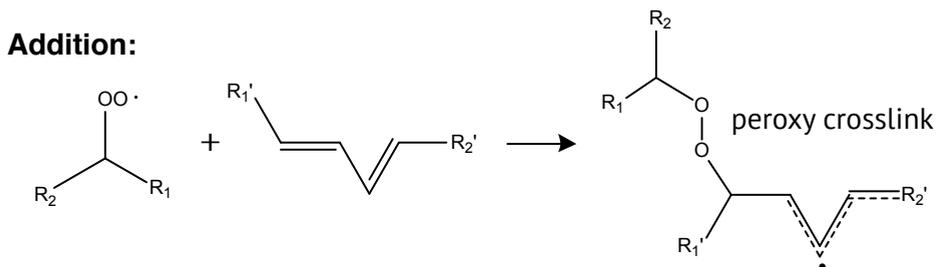


Figure 3.6: Addition of a peroxy radical to a conjugated double bond resulting in a peroxy crosslink and a resonant double bond.

initially present is consumed fast and completely⁴⁶. Thereafter, the concentration of the remaining *trans*-C=C reaches a constant level³⁵.

Epoxidation Epoxides are the simplest cyclic species possible with one oxygen and two carbon atoms. The formation and slow decomposition of epoxides during drying of ethyl linoleate was observed by Muizebelt *et al.*^{16,26}. Using quantum chemical calculations, Oakley *et al.* elucidated the epoxidation of lipid radical species¹⁸ and found that allylic radicals on beta positions to peroxides undergo epoxidation at ambient conditions. The epoxidation proceeds by two pathways representative for the autoxidation of unsaturated fatty esters (shown in Figure 3.8 a) having energies of activation of 17.7 kcal/mol and 19.3 kcal/mol, respectively¹⁸. Both reactions are unimolecular with rate parameters on the order of $10^{-1} - 10^2 \text{ s}^{-1}$. At elevated temperatures epoxides readily decompose due to the ring-strain⁵⁴, while at ambient conditions Muizebelt captured the subsequent epoxide-ring consumption with the decreased concentration of epoxide groups over 500 days¹⁶. There is little consensus of the ring-opening mechanism; thus, the review does not provide a detailed account of this reaction.

3.4.3. Termination

The final step of the free-radical polymerization process is radical termination. In this step, two radicals react and either form a single, non-radical product (recombination) or two distinct non-radical products (disproportionation).

Recombination In the linseed oil system, the three main radical types are alkyl, alkoxy, and peroxy. When they recombine, they form crosslinks. This is one of two ways crosslinks are formed in the linseed oil polymer network, the other being radical

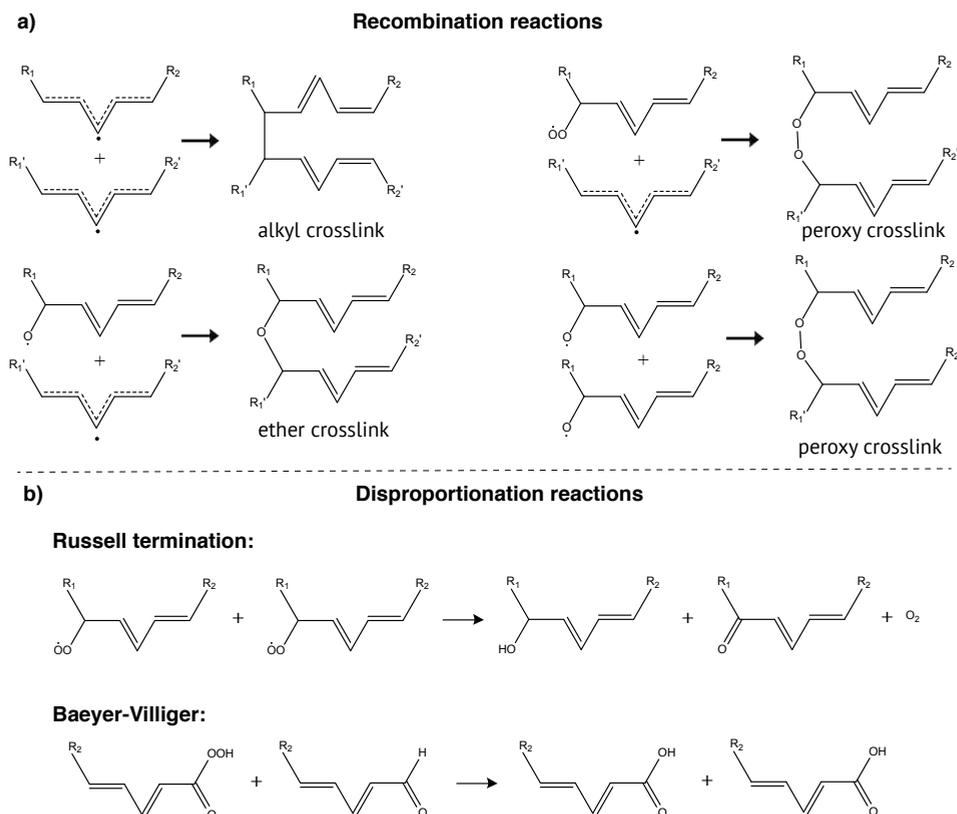


Figure 3.7: (a) Radical recombination reactions lead to three different types of crosslinks: alkyl, ether and peroxy. (b) Disproportionation reactions lead to two distinct stable products.

addition as described above. All radical recombination permutations are shown in Figure 3.7 a. The distribution of crosslinks in the resulting polymer system depends on oxygen concentration. Under conditions of facile oxygen transport, peroxy and ether crosslinks are formed in equivalent amounts, whereas alkyl crosslinks are formed in a minor amount³⁵. Radical recombination is mostly diffusion-controlled; as the polymer becomes more crosslinked, the increased viscosity restricts further radical collisions and thus recombination events^{56,57}. In exothermic reactions, the phenomenon of decreasing rates of termination due to viscosity increase is known as autoacceleration or the Trommsdorff-Norrish effect and can lead to dangerous runaway reactions during polymerization of certain synthetic polymers.^{58,59} The rate of radical recombination varies based on the polymer system. For example, the rate coefficient for radical termination in an acrylate system is on the order of 10^9 L/mol*s, whereas rate coefficients for re-

combination in the linseed oil system ranges from 10^7 to 10^8 L/mol*s (51,55,60,61). The existence of dimers that cannot be split by hydrogen iodide is a marker for the presence of carbon-carbon, or alkyl crosslinks, the amount of which is shown to be minor^{35,46}. Ether links are formed via recombination of alkyl and alkoxy radicals, the latter being formed after hydroperoxide or polyperoxide (polymer with peroxy crosslinks) decomposition. Muizebelt *et al.* used the POMMIE NMR (Phase Oscillations to Maximize Editing in Nuclear Magnetic Resonance Spectroscopy) for an EL system and determined from spectra the relative concentrations of ether and peroxy crosslinks²⁶. They found that peroxy crosslinks remain constant for over a year, but a net generation of ether crosslinks is detected, mainly originating from the slow decrease of double bonds. Muizebelt *et al.* also quantified the concentration of alkyl (C-C) crosslinked species from dimers, finding 1% of alkyl crosslinks in pure unreacted EL, and 5% of alkyl crosslinks in EL in the presence of cobalt after five days of drying²⁶. Dimers with all three types of crosslinks are shown in Figure 3.7 a.

Disproportionation Disproportionation is a second termination reaction, a redox reaction in which the oxidation state of the reactants changes into two different oxidation states of the products. For radical disproportionation, this is commonly in the form of a terminal alkane and a terminal alkene group. In the case of oxygen-rich species, oxygen-centered radicals may collide and form oxidation products such as alcohols and ketones via Russell termination. However, Russell termination is not undisputed for linseed oil polymerization^{19,62} as it has a too high energy barrier for the recombination of secondary alkylperoxy radicals. Further kinetic studies are required to elucidate and validate the mechanism that leads to oxidation products. Another type of disproportionation is the Baeyer-Villiger reaction, where a peroxy acid reacts with an aldehyde, producing two carboxylic acids. Baeyer-Villiger and Russell termination reactions are shown in Figure 3.7 b. The rate coefficient of disproportionation is in the order of 10^6 L/mol*s^{51,55}.

3.4.4. Degradation processes

Hydrolysis In the longer term, after the actual drying process, hydrolysis of ester bonds may disconnect fatty esters from the triglyceride glycerol backbone. Figure 3.8b schematically illustrates hydrolysis, which may occur at each fatty ester leading to glycerol with two remaining fatty esters (diglyceride - DAG), glycerol with one fatty ester (monoglyceride - MAG) or a fully hydrolyzed triglyceride with all fatty esters detached. Hydrolysis is one of the main degradation routes of fatty ester polymer systems. In the presence of water, an ester bond in a triglyceride is broken via hydrolysis and a

carboxylic acid is formed on the side of the free fatty ester and alcohol on the side of glycerol. Baij *et al.*⁶³ studied the origins of carboxylic acids in oil paints with zinc oxide at various relative humidities (RHs). Erdhart and Mecklenberg^{7,64} also studied hydrolysis of oils in detail. They measured the rate of hydrolysis over a decade under varying conditions concerning metal pigments, RH, and temperature and examined the resulting mechanical properties.

β -scission Breaking the beta-bond to an alkoxy radical, β -scission propagates the free radical and forms an olefinic species. β -scission is common in thermal cracking, but at ambient conditions it is of limited importance. Products from scission reactions in drying oil systems vary significantly in carbon chain length, as the location of beta-bonds next to alkoxy radicals may vary in oleic, linoleic and linolenic acids. Products of β -scission in linseed oil degradation include volatile n-aldehydes such as ethanal, propanal, butanal, pentanal, hexanal, heptanal and octanal⁶⁵. Oakley *et al.*⁶⁶ validated the mechanism concerning pentanal and proposed a new mechanism to hexanal in the polymerization of EL, as ones previously proposed in literature were too energetically unfavourable or did not yield the observed product distribution when implemented in a kinetic model. Through quantum chemical calculations, Oakley *et al.* found that β -scission was more likely to happen according to the scheme shown in Figure 3.8c.

Peroxy crosslink decomposition Studies by Muizebelt *et al.*^{16,26} reveal a gradual decrease in peroxy crosslink concentration over one year. This is attributed to slow peroxy crosslink decomposition. In contrast to hydroperoxide decomposition this peroxy crosslink decomposition is apparently not catalyzed by transition metal driers and occurs with an activation energy of 40 kcal/mol⁶¹.

Photodegradation The continuous exposure of a painting to photons, especially in the proper frequencies of light, will degrade a paint film. This is mainly due to light interactions with the binding medium and pigment particles. Azelaic acid was found to be a marker of photodegradation for linseed oil as a binding medium⁶⁷. Regarding linseed oil in the presence of pigment, titanium white paint, containing anatase titanium dioxide, is photocatalytically active in UV-light.⁶⁸ This results in mass loss from the surface of the film and a chalking phenomenon on the surface.

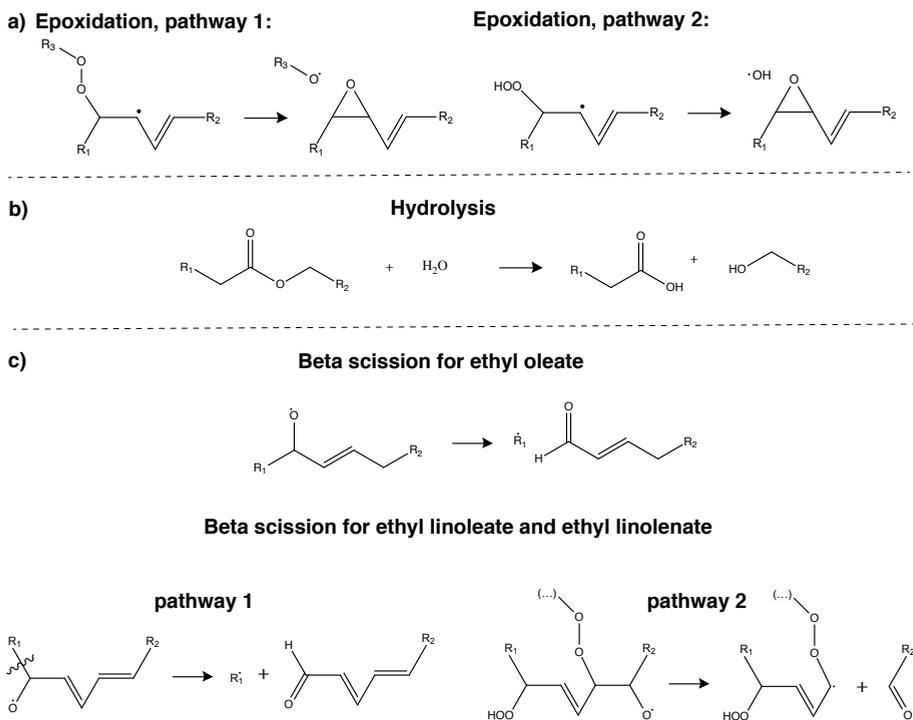


Figure 3.8: (a) Epoxidation from a species with peroxy crosslink (1) and from a species with hydroperoxide (2). (b) Hydrolysis of an ester bond between glycerol and fatty acid. (c) β -scission pathways for oleic fatty ester (top) and for linoleic and linolenic fatty esters (bottom).

3.5. Experiments

Limitations to experimental investigation of linseed oil polymerization mainly arise due to the large sizes of the polymer molecule accompanied by rapid formation of an insoluble fraction, as well as the great variety of the molecular species. Experimental information is only available for a few aspects of an oil's chemistry. Paragraphs below describe several experimental techniques which generate data relevant for the validation of the outcomes of computational models. While experimental data are used to validate models, vice versa, modelling can also greatly help the interpretation of complex experimental results.

Size exclusion chromatography Separating molecules by their sizes, size exclusion chromatography (SEC) provides the molecular weight distribution of the soluble components of a polymer. Oyman *et al.*¹¹ used SEC to explore oligomerization of ethyl linoleate in the presence of driers. The authors show that the difference in measured samples predominately becomes apparent in the peak corresponding to hydroperoxides. This peak gradually appears in the presence of cobalt(II) 2-ethylhexanoate, becoming detectable after 8 hours and remaining visible even after 48 hours in the presence of tris(acetylacetonato) manganese(III). The hydroxide peak intensity is always seen to be lower in the presence of tris(acetylacetonato) manganese(III) with 2,2'-bipyridine. In the work by Lazzari *et al.*³⁵, soluble fractions of linseed oil are analyzed with SEC during drying at the temperature of 80 °C. After 16 hours of drying, the chromatogram shows the original molecules of linseed oil and their dimers, while for an aged sample the chromatogram mainly shows low molecular weight compounds as well as higher order oligomers. SEC data on molecular size distribution may be compared to the computed distributions of connected components in the sol as has been obtained by the application of random graph theory^{69,70}.

Mass spectrometry Exact masses of molecules are measured using mass spectrometry (MS). The intensity of peaks corresponds to relative amount of molecules with these masses in a measured sample. By attributing the peaks to molecular structures, one may track the variations in peaks' intensities by measuring the samples at different stages of the reaction process. The main drawback of such an analytical technique is unwanted fragmentation that occurs to the molecules in the instrument. Moreover, the interpretation of peaks becomes challenging for such systems as linseed oil and its model systems due to a wide variety of peaks indicative of numerous reactions occurring simultaneously. In the pioneering work by Muizebelt *et al.*²⁶, formation of dimers and higher order oligomers during the polymerization of ethyl linoleate was studied using

several MS techniques: secondary ion mass spectrometry (SIMS), fast atom bombardment mass spectrometry (FAB-MS) and direct chemical ionization with ammonia mass spectrometry (DCI-MS). SIMS revealed the size of oligomers in terms of monomer units; however the resolution of the method was not sufficient to track the formation of the species in more detail. Hence, using FAB-MS the range of monomer and dimer masses was recovered, while with the use of DCI-MS masses of higher order oligomers were revealed in great detail.

Electrospray ionization mass spectrometry (ESI-MS) was used to detect various degradation products, such as free fatty acids, products of hydrolysis and diacids in linseed oil samples^{68,71}. This analytical technique provides detailed information about the masses and does not lead to considerable fragmentation of soluble fractions^{72,73}.

In relation to modeling, MS data have a resolution that is comparable to the outcome of automated reaction network generation algorithms^{74–77}, which reconstruct exact molecular structures from pre-defined reaction rules. Connection between the ESI-MS technique and such an algorithm has been shown for triolein⁷⁸, and it results in computer-aided interpretation of numerous peaks measured by MS.

Fourier-transform infrared spectroscopy While previously described methods are applicable to characterize soluble fractions of oil samples, Fourier-transform infrared spectroscopy (FTIR) allows characterization of the whole sample (sol and gel). This analytical technique performs the identification of functional groups in materials by measuring the absorption of IR radiation in a sample. FTIR analysis is reported in numerous research works on drying oils^{9–11,14,35,71}. Table 2 in the work by Lazzari *et al.*³⁵ summarizes important IR vibrational assignments of linseed oil. The results of FTIR measurements are used to reconstruct the time evolution of relative amounts of functional groups or molecular substructures, such as, for example, *cis* or *trans* double bonds, evolution of hydroxides and carbonyl groups. The limitations appear due to overlap of vibrational bands corresponding to more than one functional group, as shown in the work by Bajj *et al.*⁶³, where the contribution of carboxylic acid is hindered by aldehydes and esters. Profiles from IR spectra can be integrated to obtain relative concentrations of functional groups, which may be used for validation of kinetic models, predicting such concentrations over time. Examples of such modeling for ethyl linoleate are found in works by Oakley *et al.*^{50,51}.

Oxygen uptake Significant amounts of oxygen are incorporated in the polymer network during autoxidative drying of oils. This quantity can be measured and further used for kinetic model validation. Works by Oyman *et al.* demonstrate oxygen uptake by

ethyl linoleate (EL) for 100 hours¹¹, and oxygen uptake by linseed and tung oil in the presence of Co(II)-2-ethylhexanoate for 85 hours⁷⁹. The measured oxygen uptake forms an absolute measure of concentrations predicted from kinetic modeling, as in the work by Oakley *et al.*⁵¹.

Peroxide value While exploring driers' activity in oils, one needs to monitor the formation and decomposition of peroxides, as these functional groups are targeted by primary driers. Peroxide content in EL, and linseed and tung oils is reported in several works^{9,11,14,79} using a standard method of reacting peroxides with iodine⁸⁰. Peroxide value is measured as a concentration profile and may be directly compared with the concentration profiles obtained from the solution of a kinetic model^{50,51}.

Other important analytical techniques Many other analytical techniques have been applied in the context of this review about linseed oil polymerization, like thermogravimetric analysis^{35,81}, ¹H NMR, quantitative ¹³C NMR and ¹³C NMR with POMMIE. Focusing on the modeling aspect, we will not describe these methods in great detail, as there is no direct relation between the results of these methods and the results from computational modeling at present^{16,26}.

3.6. Computational modeling

Although performing experiments of the real system are critical in studying the properties of linseed oil-based systems, computational modeling adds in the learning about the kinetics and dynamics of the complex system. One can interrogate a representative model system at different length and time scales ranging from the atomic scale (10^{-15} s and 10^{-10} m) with quantum mechanics to the continuum scale (10^1 s and 10^1 m) with equations describing macroscopic objects. Although explicitly modeling triglycerides like linseed oil is relatively new, there is a wealth of fundamental knowledge about related chemistry that can supplement and offer tools in understanding how linseed oil dries and ages.

One way that computational modeling can improve understanding is calculating or approximating kinetic rate constants, especially for short-lived or low-concentration intermediates that are difficult to study and measure experimentally. These rate coefficients inform kinetic models that, when solved, describe the time evolution of chemical species to simulate real world processes. A computational model provides both qualitative and quantitative information about a chemical system and how it responds to changes in environment and time.

Even though computational modeling might fill some gaps that are not accessible via experiments, it has its own limitations for the systems with such complexity as the drying process of linseed oil. Because linseed oil triglycerides have more diverse functionality and reactivity than monomers in classical polymers, it is difficult to directly apply polymer reaction engineering tools to model their polymerization process. The diversity of chemical species and their size even pose a challenge to the storage of chemical species in the memory of a computer. Moreover, the diverse chemistry that happens on and between triglycerides and fatty esters explodes the number of possibilities for intermediate and product species, not allowing manual reconstruction of a detailed reaction scheme.

This section features existing modeling techniques ranging from calculations of the rate parameters on the quantum scale to modeling macroscopic properties of the material.

3.6.1. Calculating rate parameters

If a kinetic rate constant is known experimentally for a specific reaction, it is typically used directly as a first priority over estimation methods. However, it is not uncommon, especially for radical chemistry and complex systems, that experimental rate coefficients are not available for every reaction. One option is then to use computational approaches to approximate a kinetic rate constant: quantum chemical calculations, transition state theory and kinetic correlations.

Quantum chemical calculations Quantum chemical calculations (QCC) consider the energy contributions from different modes to determine the energy required to overcome the reaction barrier and transform a reactant into the product. For a 7-carbon chain with two saturations, Szori *et al.* evaluated the energy requirements for hydrogen abstraction to initiate autoxidation from the methylene position⁸². The work also compared the energy requirements of allylic to the bi-allylic hydrogen abstraction. Applied to ethyl linoleate as a model molecule, Oakley *et al.* used quantum chemical calculations to determine the mechanism for epoxide formation and aldehyde evolution from β -scission reactions^{18,66}. These calculations helped refute mechanisms proposed in literature and support novel pathways to the formation of hexanal. QCC was successfully applied in the field of catalysis to uncover the reaction between hydroperoxides and Co-EH¹⁵, as well as in the works of Pfaendtner *et al.*^{55,83} to estimate rate parameters for other hydrocarbon reactions relevant to oil chemistry.

Kinetic correlations For short-lived intermediates it can be difficult to measure concentrations over time or get precise data for understudied reactions. Kinetic correlations rely on the thermodynamic similarity between reactions with similar chemistry, such as two hydrogen abstraction reactions, to correlate the enthalpy of reaction to activation energy. Evans-Polanyi correlations, also attributed to Bell and Semenov⁸⁴ are linear free-energy relationships. Correlations are developed by including both experimental and theoretical measures for values characterizing the kinetics and thermodynamics of members of specific reaction families. For each reaction family, the transfer coefficient, or a measure of the relative position of the intermediate along the reaction coordinate, is assumed to be identical, and the pre-exponential factor A is also assumed to be the same. Using kinetic correlations has advantages in an automated scheme where a reaction type can be identified, and just the rate coefficient of reaction k has to be calculated and correlated to the activation energy E_a to be used in the Arrhenius equation: $k = A \exp(-E_a/RT)$.

Relevant to linseed oil chemistry is condensed-phase oxidation of hydrocarbons, and there is a collection of kinetic correlations for families and sub-families^{55,83}. Oakley *et al.* studied the radical epoxidation reaction using theoretical calculations and identified sub-families. They cautioned broad application of reaction families and kinetic correlations, as finer nuances in the local chemistry become significant in the resulting kinetic rate constant as determined from the correlation¹⁸. For reactions with unknown enthalpies of reaction, group-contribution methods can be used to estimate standard enthalpies of formation, and other thermodynamic properties, from local molecular structures. Common methods include the Joback method⁸⁵ and Benson group additivity⁸⁶, the latter used by Oakley *et al.*⁵⁰, drawing group values from empirical data tables and selected quantum chemical calculations.

3.6.2. Existing models

Having calculated rate parameters, computational models of multiple reactions can be constructed to capture the behavior of the concentrations of chemical species as a function of reaction conditions. Nowadays, there exist several microkinetic models describing the drying process of linseed oil and its model systems using different levels of detail, as well as finite element models describing the propagation of cracks caused by the formation of metal soaps. These models are discussed in the section below.

Kinetic model on functional groups The very first deterministic model of the drying process of linseed oil was developed by Iedema *et al.*⁸⁷. A deterministic model is typically

a system of ordinary differential equations, one for each chemical species or functional group describing a homogeneous system as a function of time. Containing no stochastic aspect in its solution, the model is solved numerically, and the solution describes the change in the concentration of species over time. The first model of linseed oil was constructed in terms of functional groups, includes 70 reactions and is sensitive to the presence of drier. The model describes the main steps of an autoxidation mechanism, and its outcome is validated with the experimental results on the total peroxide content and oxygen uptake.

3

Modeling polymer formation The classical understanding of polymers is based on Flory's extensive work, further developed by Stockmayer, giving the Flory-Stockmayer theory on highly functional molecules, which describes the gel point based on functional group conversion^{88,89}. However, this theory assumes that all functional groups are equally as reactive and the monomers do not change, which is not the case for oils. In the work by Kryven *et al.*⁶⁹, the authors model the formation of a linseed oil polymer network as a random graph that accounts for the Euclidean distance between monomers while connecting them. This implies that two monomers that are far apart have lower probability to be connected. Moreover, the authors connect the notion of steric hindrance of the monomer incorporated in the polymer to the centrality of a node in a network, making monomers with more crosslinks less accessible for further reactions. The formation of crosslinks is modeled as a stochastic process using Markov Chain accelerated Gillespie Monte Carlo⁹⁰, which uses a randomly generated number to select the next reaction event to occur within a scaled time-step of weighted reaction probabilities. Because of the stochastic nature of the model results, these are averaged over several runs and provide the information about gel point transition, molecular size distributions and length of linear fragments. Assuming simple chemistry dictated by functionality of fatty esters in linseed oil as an example, the authors demonstrate a novel stochastic approach for modeling molecular networks, which allows applying network theory tools for the analysis of resulting polymers.

Rate-cased automated reaction network generation Several microkinetic models for curing of ethyl linoleate were developed by Oakley *et al.*^{50,51}. In studying a chemical system at a range of length and time scales, microkinetic modeling is a multiscale method to span this range by describing chemistry through elementary reactions with no assumption made about the rate-determining step⁹¹. In the earliest work related to oils by Oakley *et al.*⁵¹, the model includes 160 explicit species of EL taking part in 400 autoxidation reactions. The reaction mechanism is transformed into the system of

differential equations, which is solved with the kinetic Monte Carlo method. Then, in the following work⁹², a model up to tetramers with 68,197 species and over a million reactions is constructed using automated reaction network generation approach. This approach algorithmically transforms reactants into products and is used to uncover explicit reaction steps of complex chemistry^{93,94}. As the resulting system is intractable due to the number of species and size of the ODEs, a reduced model up to hexamers pruning insignificant species determined by rates of formation yields a system of 1384 species and 2898 reactions⁵⁰.

Monomer approach Orlova *et al.*⁹⁵ (see Chapter 5) followed the work of Oakley *et al.*⁵⁰ and developed a similar kinetic model based on the same reaction families including the latest findings on β -scission and epoxidation^{18,66}. The automated reaction network generation methodology transforms initial monomers into further oxidation products and crosslinked species. The advancement in this model is the application of the monomer approach, according to which a polymer network is modeled as a random graph in terms of its unique constituents of the size of monomers. The methodology reconstructs explicit structures of monomers with their adjacent crosslinks (alkyl, ether, peroxy) without explicitly connecting them to their neighbors. The number of these monomer constituents of a polymer is finite; thus, such a representation of a polymer allows modeling time evolution of functional groups in infinitely large polymers without imposing any cutoff on their sizes. Concentrations of each monomer are solved for over time, and lumped functional groups can be compared to experimental values showing good agreement. Polymer species are reassembled using findings in random graph theory from the work by Kryven *et al.*⁶⁹ to obtain the molecular weight distribution of soluble fractions of the polymer and predict temporal formation of the insoluble fraction.

Chemo-mechanical modeling The chemo-mechanical model has been developed by Eumelen *et al.*⁹⁶ predicting crack formation in the paint surface due to growth of metal soap crystals. Modeling of the chemical process of metal soap formation is coupled with a finite element model, which describes paint around the metal soap as a homogeneous continuum. The growth of the metal soap starts from a nucleus of pre-defined size, which interacts with saturated fatty esters and metal ions on its interface with paint. This process is described by the reaction diffusion equation, and its solution provides the change of saturated fatty ester concentration and the change in volume fraction of the crystalline metal soap. The growth of the metal soap causes the mechanical strain in the paint layer and may result in crack formation, which is modeled using the finite element method. Varying the parameters in the simulation shows that crack

formation is sensitive to the mismatch of stiffness between the metal soap and paint, strain due to the formation of the metal soap crystal and the reaction rates between metal ions and saturated fatty esters forming ionomers and their subsequent crystallization. Interestingly, the initial size of the nucleus affects only the moment of appearance of the crack but does not influence the amount of cracks.

3

3.7. Future directions

Most of the models described above do not simulate polymers moving in physical space, which is necessary to obtain certain physical properties like elasticity and glass transition temperature. Molecular dynamics and reactive molecular dynamics simulations do offer such possibilities to the field of modeling of oil polymerization. However, these modeling techniques are not yet feasible due to the computational limitations. The limitations arise due to the size and complexity of linseed oil molecules or even its model systems. Modeling polymerization of linseed oil with molecular dynamics would also allow tracking the reactions in space as well as exploring more realistic calculations of such properties as packing density, radius of gyration, gel point, Young's modulus, etc. This has already been demonstrated on the polymer network generation by a diacrylate⁹⁷.

Modeling chemical reactions often requires knowledge of the detailed reaction mechanism of elementary reaction steps. Thus, exploring the studies that have been performed reveals the existence of a number of uncertain chemical reactions that have not been investigated in detail. Bis-allylic hydrogen abstraction has been explored in the presence of metal drier¹⁵; however, evidence exists that initiation also happen without drier^{9,35}. Hypotheses ascribe this initiation to impurities in oil or to a reaction with singlet oxygen, but none of these have been scientifically confirmed as of writing this review. Russell termination is disputed to be a feasible disproportionation mechanism that occurs in linseed oil-types of systems^{19,62} due to high barrier for the recombination of secondary alkylperoxyl radicals producing ketones. Hence, more thorough investigation is needed to uncover the formation of ketones, which are known to be stable products of autoxidation process³⁸. Epoxide ring opening is underexplored, as there is evidence of this reaction taking place from the observed slow decrease in the epoxide signal in NMR measurements carried out by Muizebelt *et al.*¹⁶.

There is ample room for growth in computational modeling activities of the autoxidation and degradation of linseed oil and related drying molecules. The complexity of the kinetic models is an obvious challenge to improvement. Exploring beyond ethyl linoleate and other single fatty esters to trilinolein or mixtures of fatty acids is necessary to arrive at simulating linseed oil. Also, incorporating light, diffusion effects, other catalysts and

pigments is necessary for real-world applications and implications^{98,99}.

There is still a great need to link/correlate/connect chemical changes on the molecular level to macroscopic, physical changes observed in linseed oil films. This requires work in understanding physical interactions between chemical moieties and potentially more coarse-grained approaches like that of finite element analysis⁹⁶. Additionally, developing models that can realistically predict phenomena on long time scales such as degradation is pertinent to the understanding of aging mechanisms and the impact of different factors like diffusion, light and heat.

3.8. Concluding remarks

With the improvement of computing power, modeling the polymerization of oils becomes an attractive research topic. In this review, we provide a detailed description of chemical processes occurring in oils together with their chemical kinetics. This review is focused on the polymerization and degradation of linseed oil and its model systems in the context of drying and degradation of oil paint. The work provides an overview of chemical processes happening during the drying process of linseed oil including recent findings in β -scission and epoxidation mechanisms. The description of the reaction mechanism includes chemical kinetics data, which have been estimated computationally or experimentally in past works and are relevant to computational modeling.

Common analytical techniques exploring the drying and degradation of oils provide a vast amount of data, which can be used to validate computational models. Meanwhile, models overcome some of the experimental limitations and are able to assist the interpretation of experimental results. The review provides an overview of existing computational models related to oils and their chemistry. Models vary in their complexity and level of detail ranging from studying individual reactions with QCC and extending up to chemo-mechanical models simulating cracks in a paint layer.

Numerous reaction pathways in autoxidative drying of oils are explored in great detail, while other reactions still need thorough explanation. In this review, we highlighted reaction pathways, which lack detailed exploration of elementary reaction steps and their kinetic parameters, suggesting these as an interesting subject for further experimental or computational investigation. This review summarizes the key information needed to carry out computational modeling on linseed oil and its model systems, making the exploration of the degradation of the binding medium of oil paint less invasive for our cultural heritage.

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