EFFECT OF ROASTING ON THE FORMATION OF MAILLARD REACTION PRODUCTS IN SESAMES

KAVURMANIN SUSAMLARDA MAİLLARD REAKSİYON ÜRÜNLERİ OLUŞUMUNA ETKİSİ

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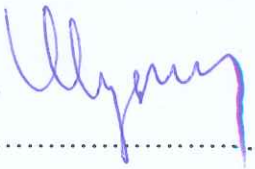
Head ..... 

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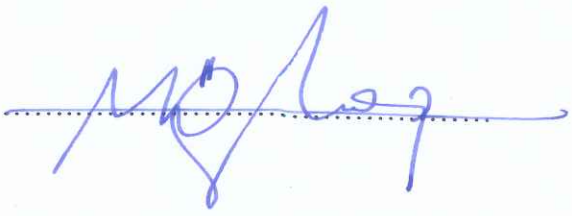
Member ..... 

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ABSTRACT

EFFECT OF ROASTING ON THE FORMATION OF MAILLARD REACTION PRODUCTS IN SESAMES

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Sesame seed is highly susceptible to chemical changes because of consisting especially high lipid content and various amino acids. Among these chemical reactions, Maillard reaction is of great importance during roasting of sesame seeds. The Maillard reaction induces desirable changes in color, flavor and texture properties in the processing of sesame seeds, but also leads to nutritional losses and formation of heat-induced compounds. The new compounds could have both antioxidant activity and potentially toxic properties. The aim of this MSc thesis is the investigation of Maillard reaction products and the changes in their concentrations in sesame seeds under different roasting conditions. For this purpose, 5-hydroxymethylfurfural, acrylamide, furan and dicarbonyl compounds (1-deoxyglucosone, 3-deoxyglucosone, methylglyoxal and diacetyl) together with glycation products namely furosine, N-ε-carboxymethyllysine and N-ε-carboxyethyllysine, were monitored as a result of roasting. After that, two different multiresponse kinetic models were asserted, in this way, major and less significant reaction steps of Maillard reaction and caramelization occurring during roasting of sesame seeds were uncovered.

Firstly, some of Maillard reaction and caramelization products were analyzed mentioned above. According to the results, roasting induced the formation of 5-hydroxymethylfurfural, acrylamide, furan and dicarbonyl compounds significantly. From the dicarbonyl compounds, 3-deoxyglucosone was the highest and the rest was in the following order; methylglyoxal > 1-deoxyglucosone > diacetyl. Expectedly, 5-hydroxymethylfurfural concentration increased with the thermal load applied. Since the amount of asparagine was the limiting precursor for the acrylamide formation, acrylamide concentration was correlated with the changes in asparagine level. Furosine concentration reached to the highest at 5 min of roasting at 150°C, then it decreased with the roasting temperature increased. The reason for the decreasing furosine might be the formation of N-ε-carboxymethyllysine, N-ε-carboxyethyllysine by degradation or oxidation of furosine under those conditions.

Secondly, two different multiresponse kinetic models of Maillard reaction and caramelization occurring during roasting of sesame seeds were asserted. The reaction steps were sucrose degradation into glucose and fructofuranosyl cation, formation of Amadori and Heyns products from sucrose degradation products, formation of α-dicarbonyl compounds pathways, N-ε-carboxymethyllysine and N-ε-carboxyethyllysine formation through Amadori/Heyns product or dicarbonyl compounds were included to the first model and the reaction steps were sucrose degradation into glucose and fructofuranosyl cation, formation of 3-deoxyglucosone from glucose or Heyns product, 5-hydroxymethylfurfural formation through fructofuranosyl cation, acrylamide formation through the reaction of asparagine with 5-hydroxymethylfurfural or glucose, degradation products of these compounds were added to second model. The goodness of fit and estimation of reaction rate constant was evaluated via model discrimination. It was found that methylglyoxal-lysine was the dominant pathway in N-ε-carboxymethyllysine formation in the initial of roasting, while Heyns product became predominant at the end of roasting. 5-hydroxymethylfurfural formation was promoted by the pathway via fructofuranosyl cation, not 3-deoxyglucosone. It was concluded that 5-hydroxymethylfurfural acted as a potent carbonyl source in acrylamide formation during sesame roasting. Hence, it was enabled to understand how Maillard reaction and caramelization progressed in the course of roasting.

Keywords: sesame, roasting, Maillard reaction, caramelization, glycation products, multiresponse kinetic modelling

ÖZET

KAVURMANIN SUSAMLARDA MAİLLARD REAKSİYON ÜRÜNLERİ OLUŞUMUNA ETKİSİ

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Yüksek Lisans, Gıda Mühendisliği Bölümü

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Susam, özellikle yüksek lipit içermesi ve çeşitli amino asitlere sahip olması nedeniyle kimyasal değişimlere karşı oldukça açıktır. Bu değişimlerden, Maillard reaksiyonu susamın kavrulmasıyla oluşan büyük öneme sahip bir reaksiyondur. Maillard reaksiyonu susamın işlenmesi sırasında renk, tat-koku ve yapıda istenen değişimlere neden olurken aynı zamanda besinsel kayıplara ve ısıl işlem kaynaklı bileşiklerin oluşumuna da yol açar. Bu yeni bileşikler hem antioksidan aktiviteye hem de toksik özelliğe sahip olabilir. Bu yüksek lisans tezinin amacı, susamda farklı kavurma koşullarında meydana gelen Maillard reaksiyonu ürünlerinin ve bu ürünlerin konsantrasyonlarındaki değişimin araştırılmasıdır. Bu amaçla, 5-hidroksimetilfurfural, akrilamid, furan ve dikarbonil bileşikleriyle birlikte (1-deoksiglukozon, 3-deoksiglukozon, metilglioksal ve diasetil), furosin, karboksimetillizin ve karboksietillizin gibi glikasyon ürünlerinin oluşumu izlenmiştir. Daha sonra iki farklı kinetik model önerilerek susamda kavurma sırasında oluşan Maillard reaksiyonu ve karamelizasyonun önemli reaksiyon basamakları belirlenmiştir.

Tezin ilk kısmından elde edilen sonuçlara göre, kavurma işlemi susamda, önemli ölçüde 5-hidroksimetilfurfural, akrilamid, furan ve dikarbonil bileşiklerinin oluşumuna neden olmuştur. Dikarbonil bileşikleri arasında 3-deoksiglukozon en yüksek konsantrasyona ulaşmıştır. Diğer dikarbonillerin konsantrasyonu metilglioksal > 1-deoksiglukozon > diasetil şeklindedir. Beklendiği gibi 5-hidroksimetilfurfural konsantrasyonu uygulanan termal yük ile artış göstermiştir. Akrilamid oluşumunda asparajin miktarı sınırlayıcı öncül olduğundan, akrilamid konsantrasyonu ortamdaki asparajinin azalmasıyla korelasyon göstermiştir. Furosin miktarı kavurmanın 5. dakikasında maksimuma ulaşmış, daha sonra kavurma sıcaklığının artmasıyla azalmıştır. Bunun nedeni furosinin degrade ya da okside olarak karboksimetillizin ve karboksietillizin gibi ileri glikasyon ürünlerinin oluşumunu tetiklemesi olabilir.

İkinci kısımda, susamda kavurmayla oluşan Maillard reaksiyonu ve karamelizasyonun çok değişkenli kinetik modelleri ileri sürülmüştür. Sukroz degradasyonu ile fruktofuranozil katyon ve glukoz oluşumu, Amadori ve Heyns ürünlerinin oluşumu, α-dikarbonil bileşiklerinin oluşumu, karboksimetillizin ve karboksietillizin oluşumu ilk modelin reaksiyon basamaklarına eklenmiştir. İkinci model ise, sukroz degradasyonu, 3-deoksiglukozon oluşumu, fruktofuranozil katyondan 5-hidroksimetilfurfural oluşumu, asparajinin 5-hidroksimetilfurfural ya da glukoz ile reaksiyonu sonucu akrilamid oluşumu ve bu bileşiklerin degradasyon ürünleri reaksiyon basamaklarını oluşturmaktadır. Model diskriminasyonu ile modellerin uygunluğu ve hesaplanan reaksiyon hız sabitleri değerlendirilerek son model elde edilmiştir. Kavurma işleminin başında, karboksimetillizin oluşumunda metilglioksal-lizin yolu baskın iken, kavurmanın sonunda Heyns ürünleri baskın hale gelmiştir. 5-hidroksimetilfurfural oluşumunun, 3-deoksiglukozondan değil fruktofuranozil katyon üzerinden ilerlediği sonucuna ulaşılmıştır. Ayrıca susamın kavrulması sırasında akrilamid oluşumunda 5-hidroksimetilfurfural etkili bir karbonil kaynağı görevi görmüştür. Bu bölümde, susamın kavrulması sürecinde Maillard reaksiyonu ve karamelizasyonun nasıl ilerlediğini anlamak mümkün olmuştur.

Anahtar kelimeler: susam, kavurma, Maillard reaksiyonu, karamelizasyon, glikasyon ürünleri, çok değişkenli kinetik modelleme

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SYMBOLS AND ABBREVIATIONS

Symbols

E_a	Activation energy
k	Reaction rate constant
R	Gas constant
T	Temperature
t	time

Abbreviations

AA	Amino acids
ACR	Acrylamide
AGEs	Advanced glycation end products
ALEs	Advanced lipoxidation products
AP	Amadori product
APA	3-aminopropionamide
ASN	Asparagine
CEL	N-ε-carboxyethyllysine
CML	N-ε-carboxymyethyllysine
DA	Diacetyl
DETAPAC	Diethylenetriaminepentaacetic acid
DOLD	3-deoxyglucosone-methyl-dimer
1-DG	1-Deoxyglucosone
3-DG	3-Deoxyglucosone
3,4-DG	3,4-Dideoxyglucosone
EFSA	European Food Safety Authority
FFC	Fructofuranosyl cation
FL	Fructosyllysine
G	Glucosone
GC-MS	Gas chromatography mass spectrometry
GLU	Glucose
GO	Glyoxal

GOLD	Glyoxal-methyl-dimer
HLB	Hydrophilic-lipophilic-balanced
HMF	5-Hydroxymethylfurfural
HP	Heyns product
HPD	Highest posterior density
HPLC	High performance liquid chromatography
IARC	International Agency for Research on Cancer
LC/MS	High performance liquid chromatography mass spectrometry
LOQ	Limit of quantification
Lys	Protein bound lysine
MCX	Mixed mode cation exchange reversed phase
MG	Methylglyoxal
MS	Mass spectrometry
MOLD	Methylglyoxal-methyl-dimer
MRP	Maillard reaction product
P	Product
PUFA	Polyunsaturated fatty acid
RID	Refractive index detector
SUC	Sucrose
USDA	The United States Department and Agriculture

INTRODUCTION

Sesame (*Sesamum indicum* L.) seed is an attractive foodstuff for human because it has been utilized in various ways such as bakery and confectionary products, also cooking oil, tahini and salad dressing for many years in human life [1]. There are many reasons that make sesame attractive to people; the main ones are being a good source of energy (up to 50% oil) and high nutritional value owing to its 20% protein content [1,2]. Additionally, sesame seed shows resistance to oxidative deterioration because of being rich in bioactive components [2]. The composition of sesame seeds is suitable for chemical reactions resulting from roasting. Since it is mostly consumed after roasting at high temperatures, investigation of the chemical changes as a result of roasting is of importance. Roasting process not only provides desirable consequences to foods but also leads to some reactions such as Maillard reaction, sugar degradation, protein denaturation, lipid oxidation and vitamin degradation, as well [3]. As a result of these reactions, formation of new compounds having antioxidant activity, a desirable outcome, however, undesirable changes may also occur, leading to nutritional losses and formation of potentially toxic compounds [3]. However, the information about the chemical changes induced by roasting is lacking in the literature. This study provides the information about the chemical reactions ongoing during processing of an important crop and the levels of some process induced contaminants as well as glycation products formed in sesame seeds which are important for human health. It is also ensured to understand the reaction mechanism by model discrimination of Maillard reaction and caramelization during sesame roasting.

The first chapter of the thesis gives information about the composition of sesame seed, roasting and, chemical reactions, especially Maillard reaction and sugar degradation. The second chapter investigates on the Maillard reaction products in sesame seeds induced by roasting, and the third chapter discusses the important reaction steps by performing multi-response kinetic modelling.

The results of Chapter 2 were published in the following article;
E. Berk, A. Hamzalıoglu, V. Gökmen, Investigations on the Maillard reaction in sesame (Sesamum indicum L.) seeds induced by roasting, Journal of Agricultural and Food Chemistry, 67 (**2019)** 4923-4930.

1. GENERAL INFORMATION

1.1. Sesame

Sesame (*Sesamum indicum* L.) is a significant source of edible seed for people, whose origin dates back to about 6000 years ago [1]. The genus *Sesamum* belongs to Pedaliaceae family, consists of 36 species along with *S. indicum* that is the predominant cultivated species [4]. Also known as one of the ancient crops, sesame is commonly farmed in Asia and Africa. India, China, Sudan, Nigeria, Myanmar are leading countries in the production of sesame seed [1,4,5]. The total world production is 6.1 million tons in 2016, about 65% of which has been processed as a sesame oil [6].

Sesame seeds are mainly classified based on their color and texture of the seed coat. The color of the seeds differs among white, brown, gold, violet and black while the texture varies as rough or smooth. Another classification is made size of the seed, weighed ranging 2-3.5 g/1000 seeds [7].

Sesame seed mainly comprises lipid, protein, carbohydrate and other minor constituents such as moisture, ash, dietary fibers, vitamins, minerals and lignans. Lipid ranges from 43.4% to 58.8%, is the major fraction of sesame seed [8], and is followed by protein and carbohydrate ranging from 16.7% to 27.4% and 18% to 20%, respectively. The percentage of moisture and ash content is up to 5% in the sesame seeds [9]. Sesame seed has been valued both nutritional quality (up to 20% protein) and a good source of energy because of its high oil content in human life for thousands of years [1].

Oleic (C18:1) (39.1%), linoleic (C18:2) (40.0%), palmitic (C16:0) (9.4%), stearic (C18:0) (4.76) and linolenic (C18:3) (0.46%) acids are the fatty acids found in sesame seeds [1]. Even though sesame oil comprises high levels of unsaturated fatty acids (80-85%) as compared to saturated fatty acids, which is lower level, it is much more stable against oxidative deterioration than other vegetable oils. This stability is attributed to some minor components because of being rich in bioactive components such as lignans, tocopherols and, also browning reaction products, having antioxidant activity as a result of roasting [4].

Lignans, described as an oxidative coupling product of β-hydroxyphenylpropane, are characteristic components in the lipid fraction of sesame seed [7]. They play a role in the

inhibition of oil oxidation and providing stability to oil [10]. Sesamin and sesamolin are main lignans naturally present in sesame seed, their composition changes between 0.07% to 0.61% and 0.02% to 0.48%, respectively [7]. On the other hand, sesamol is found in a comparatively lower amount in sesame seeds [9]. Sesamin has a common lignan form of the β-β' (8-8') linked product of two alcohol radicals. In addition to sesame seed, it exists in other plants with small amounts, but in sesames with large amounts [1]. Experiments have shown that sesamin exerts functional and beneficial effects to health, such as antioxidant, anticarcinogenic, antihypertensive and lipid lowering functions [11]. However, sesamin does not have antioxidative property alone; its metabolites exhibit strong antioxidant activity [10, 14]. According to the studies, sesamin metabolites containing catechol form show stronger activity to prevent reactive oxygen species and inhibit lipid peroxidation than sesamin [13]. Episesamin, the artifact product of sesamin, obtained during the purification stage of sesame oil production displays more potent activity than pure sesame [1]. Sesamolin has a distinctive structure including one acetal bridge along with sesamin structure [1]. Similar to sesamin, it has weak or no antioxidant activity, but its metabolites have, due to containing phenolic hydroxyl groups. As a result of hydrolysis of sesamolin, owing to thermally instability, it can be converted to sesamol and other products during heating. Moreover, almost all sesamolin turns into sesaminol, a new phenolic lignan, in the bleaching process of unroasted sesame oil. Sesamolin is also produced during roasting of sesame seeds [14] and frying [15]. Therefore, it is noticed that sesamolin acts as a pioneer of the sesamol and sesaminol in these processes. Sesamol and sesaminol are minor lignans in lipid fraction of sesame, with potent antioxidant ability. Another compound, sesamolinol is present in low amounts and, however, thanks to hydroxyl group included, it displays antioxidant activity like the other lignans [4]. Lignan contents in sesame seeds show big differences with respect to sesame varieties [1].

Tocopherols (α, β, γ, and δ) and tocotrienols (α, β, γ, and δ) are also important groups existing in the lipid fraction of sesame and they provide high stability to sesame oil together with lignans. Among them, γ -tocopherol is the most abundant tocopherol, accounting for 56.9-99.3 mg/kg, while α-tocopherol and δ-tocopherol have lower amounts, whose concentrations change between 0.67-6.35 mg/kg and 0.034-0.175 mg/kg in sesame seeds [16]. γ-Tocopherol is a much stronger antioxidant activity, even though it contains a lesser amount of vitamin E than α-tocopherol. There are many beneficial effects on health such as prevention of aging and proliferation of human cancer cells [17]. Among phytosterols in sesame seeds, β-

sitosterol is the abundant one, followed by campesterol, Δ^5-avenasterol, stigmasterol and campestanol. It is known that phytosterols are not only related to decreasing cholesterol absorption, the risk of certain types of cancer and cardiovascular disease but also have positive impacts on human diet [18].

Sesame seeds are a good source of minerals and vitamins, especially B group vitamins. According to USDA report, in this group, niacin has the highest concentration (4.515 mg/100 g dry basis) and, followed by thiamin (0.791 mg/100 g dry basis), riboflavin (0.247 mg/100g dry basis), choline (25.6 mg/100 g) and vitamin E, as α-tocopherol (0.25 mg/100 g dry basis). The minerals found in sesame seeds calcium, iron, magnesium, phosphorus, potassium, sodium, zinc and copper. Sesame seed is rich in calcium (975 mg/100 g dry basis), phosphorus (468 mg/100 g dry basis), potassium (468 mg/100 g dry basis) and magnesium (351 mg/100 g dry basis). In addition to that, iron, sodium, zinc, copper present lower amounts those are 14.55 mg/100 g dry basis, 11 mg/100 g dry basis, 7.75 mg/100 g dry basis, 4.082 mg/100 g dry basis, respectively [19].

Sesame seed is composed of approximately 20% protein [7]. Amino acid profile in sesame seeds includes mostly in glutamic acid (200 mg/g protein), arginine (140 mg/g protein), aspartic acid (91 mg/g protein), leucine (75 mg/g protein), but slightly lower in valine (54 mg/g protein), alanine, phenylalanine (51 mg/g protein); serine (47 mg/g protein), isoleucine, proline (42 mg/g protein), tyrosine, threonine (39 mg/g protein), lysine (31 mg/g protein), histidine (29 mg/g protein), cysteine (25 mg/g protein) and tryptophan (18 mg/g protein) [7].

The carbohydrate fraction of sesame contains mainly as dietary fiber but also soluble sugar with a small amount. It is reported that the amount of soluble sugar in sesame seeds represents 2.48% of dry matter. Additionally, sesame contains 19.33% dry matter of total fibers and 13.96% of those was insoluble fibers [20].

Sesame seed, either unroasted or roasted, is mostly used in bakery goods and confectionery products such as decorating on bread and cookies in Asian countries and, it is also consumed as a seasoning in India [1]. Additionally, sesame oil is used as both raw and roasted oil, but the latter has a distinct flavor on account of seeds previously roasted. Sesame seeds supply a great yield of oil when compared with many other seed oil [21]. About 65% of the total world production is consumed as sesame oil [4]. Raw sesame oil is widely consumed in

noddle products or gravy sauce in Korea and other Asian countries. Moreover, its oil is utilized for cooking oil and salad dressing because of having characteristic taste and color. Another usage of sesame oil is in the production of margarine, mixing with different seed oils. Tahini or tahina, known as sesame paste, is another product obtained after dehulling, roasting and grinding steps of the seeds [1]. Cosmetics, chemicals and pharmaceuticals are also the fields using sesame seeds and its oil, apart from food applications [1,22].

1.2. Roasting

Sesame seed, along with its oil, has been an attractive foodstuff in human life for many years and utilized in various ways throughout the world due to its desirable flavor and nutritive value. Roasting is the key step for revealing distinctive flavor, enhancing color and texture of sesame seeds [23]. Sesame roasting is generally performed at 150-200°C for 10-20 min [1]. Expectedly, heat treatment provides a pleasant aroma and appreciated taste for consumers. Studies have identified that there are over 400 flavor components which are pyrazines, pyridines, pyrroles, thiazoles, thiophenes, and furans in roasted sesame seeds [1,24,25]. In addition to that, roasting process not only provides desirable consequences to foods but also leads to some reactions such as Maillard reaction, sugar degradation, protein denaturation, lipid oxidation and vitamin degradation, as well [3]. As a result of these reactions, formation of new compounds having antioxidant activity, a desirable outcome, is possible, however, undesirable changes may also appear, giving rise to nutritional losses and formation of potentially toxic compounds [3,26]. The scope of this study is to investigate the formation of Maillard reaction products in roasted sesame seeds, thereby, it is not addressed on other reactions in the following sections.

1.3. Maillard Reaction

Maillard reaction was discovered by Louis Camille Maillard for the first time in 1912 that amino acids and sugars resulting in brown color during heating [27]. Since that time Maillard reaction has drawn attention of food scientists as it improves color, flavor and aroma. Apart from its positive effects in foods, Maillard reaction leads to loss of nutritional value [28] and, also formation of mutagenic and toxic compounds like 5-hydroxymethylfurfural, furan, acrylamide in foods [29–31]. Among the chemical reactions occurring in foods during thermal process, Maillard reaction is an important topic that should be controlled in terms of food safety and quality. Presence of reactants and precursors determine the reaction pathway

and neo-compounds formed. The reactants taking part in Maillard reaction are amino acids, amines, peptides, protein, ammonia together with reducing sugar, carbonyl compounds, while the influencing factors are pH, temperature, oxygen, light, moisture, heavy metal ions [32].

The Maillard reaction is a complicated reaction system having diverse reaction pathways and it is divided into three stages as early, advanced and final stages to simplify by Hodge and other scientists [33,34]. The Hodge scheme is still commonly utilized to comprehend each main step of the Maillard reaction (Figure 1.1).

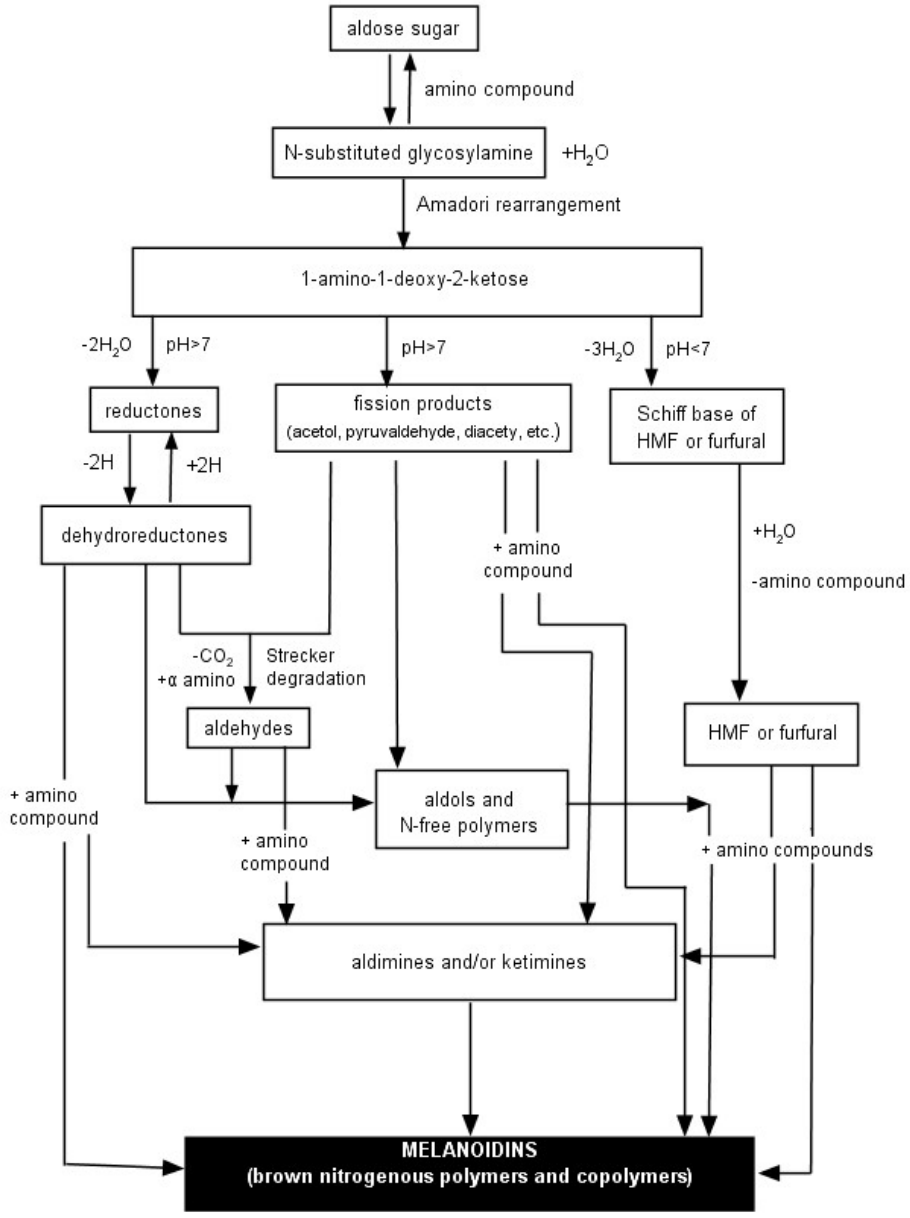


Figure 1.1. Representation of Maillard reaction pathways, adopted from [33]

The Maillard reaction is initiated by condensation of an amine with a carbonyl compound inducing the formation of Schiff base that is unstable imine form, and its cyclic form of N-glycosylamine. Following that, it rearranges to Amadori compound (1-amino-1-deoxy-ketose), in case the source of carbonyl compound is an aldose sugar (Figure 1.2). If the carbonyl compound is a ketose sugar, this rearrangement yields to Heyns compound, named as 2-amino-2-deoxy-aldose (Figure 1.3). These reactions account for the early stage of the Maillard reaction [35].

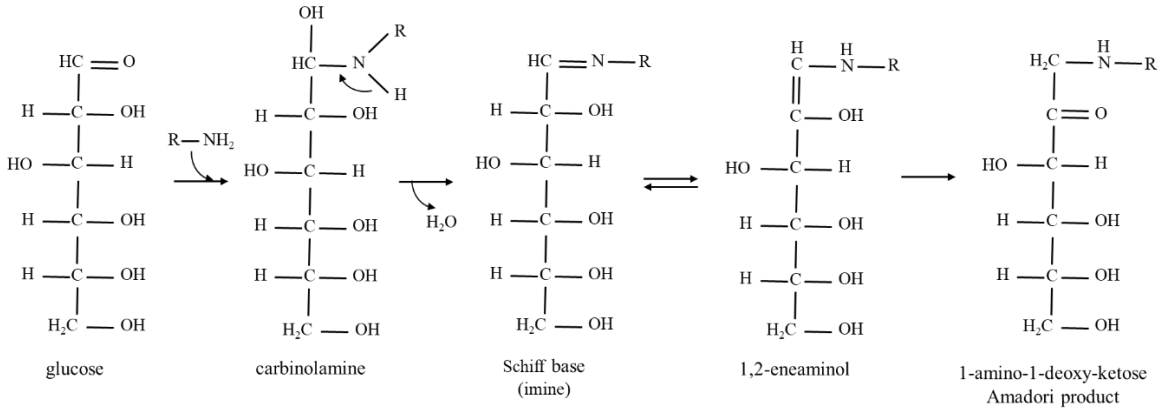


Figure 1.2. Formation of Amadori rearrangement, adopted from [36]

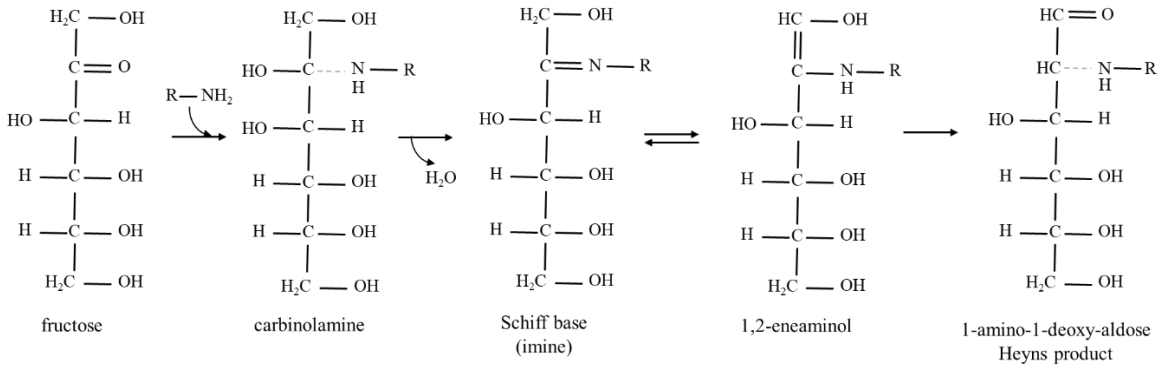


Figure 1.3. Formation of Heyns rearrangement, adopted from [36]

Amadori compounds, known as the first stable product, could be quantitated via degrading to furoyl derivatives through acid hydrolysis [37]. N-ε-fructosyllysine, Amadori product of lysine, considered as the early stage product of Maillard reaction. Furosine, an acid derivative of N-ε-fructosyllysine, is used for evaluation of heat load in processed foods such as cookies, jams and infant foods [38,39] and loss of lysine is monitored with the formation of furosine [40].

In the course of advanced stage, depending on pH, degradation of Amadori product leads to the formation of α-dicarbonyl compounds such as methylglyoxal (MG), glyoxal (GO), glucosone (G), diacetyl (DA), 3-deoxyglucosone (3-DG) and 1-deoxyglucosone (1-DG) [34,41]. In the case of at lower pH, 1,2-enolization route, forming 1,2 eneaminol from ketosamines is favored, inducing the formation of 3-DG via water elimination and amino acid regeneration with hydrolysis and, also formation of 5-hydroxymethylfurfural (HMF) through dehydration of sugars. On the other hand, under alkaline conditions, 2,3-enolization reaction occurs and its intermediates called as 2,3-eneaminol are generated from fructosamine, followed by decomposition to 1-DG via retro-Michael reaction (Figure 1.4) [36,42]. Moreover, 1-DG plays an important role in the formation of aroma compounds [43]. Diacetyl, for instance, is a flavor compound in butter, resulting from 1-DG with the removal of a water molecule [44]. It is considered that 1-DG and 3-DG contribute to the formation of MG [41].

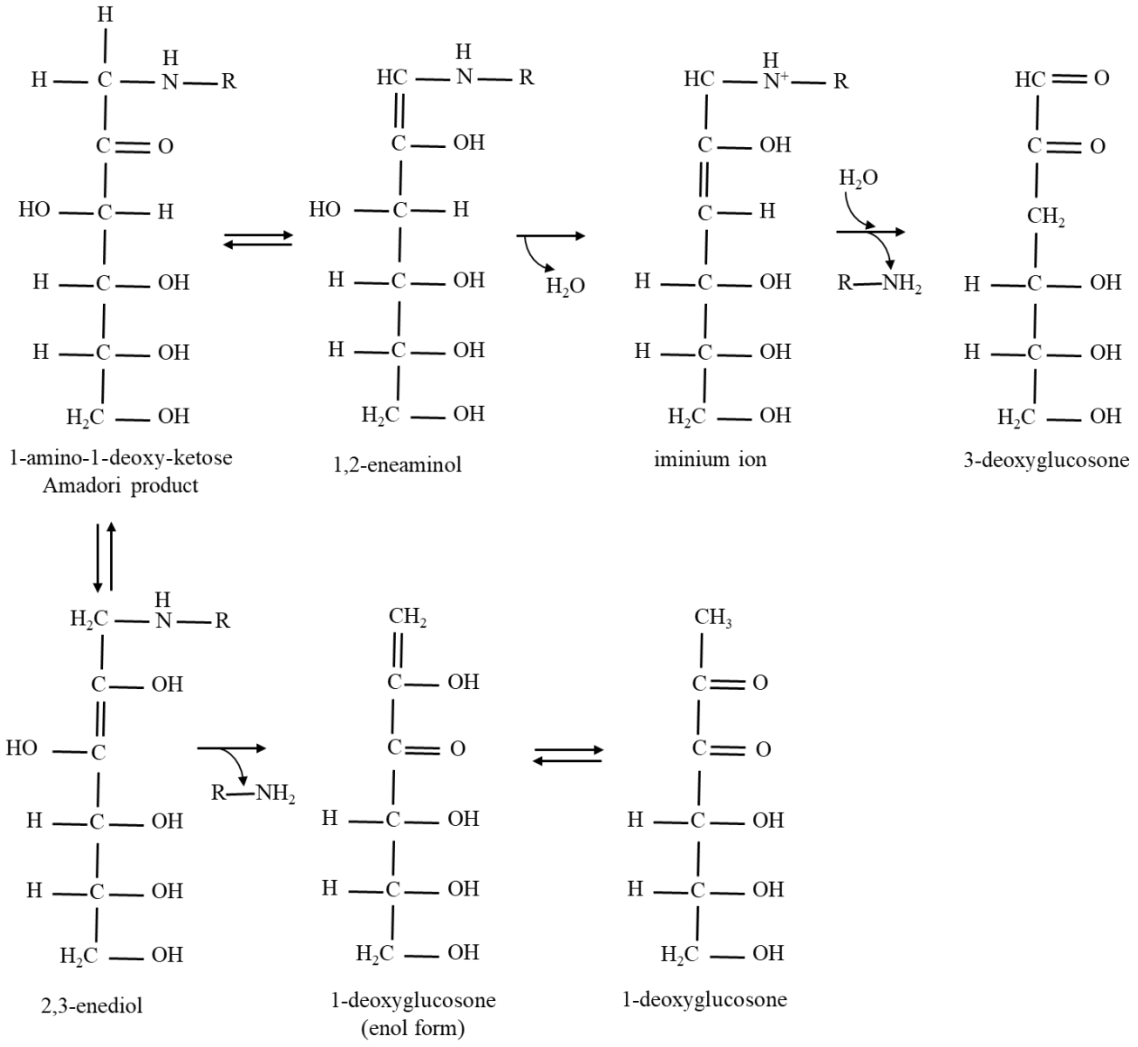


Figure 1.4. Formation of 3-deoxyglucosone and 1-deoxyglucosone through degradation of Amadori product, adopted from [36]

α-Dicarbonyl compounds are not only formed by degradation of Amadori products but also generated by degradation sugars in caramelization, even if there are no amines in reaction medium [45]. In addition to that, oxidation of polyunsaturated fatty acids is another probable mechanism, which could induce the formation of glyoxal and methylglyoxal [46]. It can be deduced from that α-dicarbonyl compounds are the common products of these reactions. To discriminate the source of these compounds is only possible with multiresponse kinetic modelling [47–50]. Additionally, analysing of α-dicarbonyl compounds is very difficult because of being highly reactive compounds. Therefore, this problem could be handled by using a trapping agent in order to derivatization [51].

α-Dicarbonyl compounds present in miscellaneous food products like bakery products, beverages, baby foods, honey, cocoa and coffee at different amounts [52–54]. Also, they are involved in carbonyl stress in vivo and thereby causing protein and DNA modifications [55]. Regarding that α-dicarbonyl compounds, 3-DG has more importance since it is responsible from HMF formation. HMF is a common product formed by caramelization (by dehydration of hexose sugars) or Maillard reaction as a result of heating [45,56]. During 1,2-enolization pathway in Maillard reaction, positively charged amino group promotes in switching the balance to the enol, which converts to glycosulose-3-ene that is followed by cyclodehydration to form HMF [57]. The content of HMF is used as a marker of thermal load applied to many foods rich in carbohydrates and indicates unsuitable storage conditions, as well [56]. From this point of view, honey, fruits, coffee and milk are considered as a chemical index for HMF in foods. Also, HMF level in foods such as cookies, bread, cereals demonstrates the heating process applied to the food [56].

α-Dicarbonyl compounds induce the modification of protein bound amino acids and subsequently form advanced glycation end products (AGEs) [34]. The reactions between reducing carbohydrates and amines are referred to 'glycation', while it is named as 'lipation' if carbonyl compounds originate from lipid peroxidation [58]. The term glycation is used for modification of reactive sides of amino acids such as lysine and arginine and also with their reaction of α-dicarbonyl compounds, resulting in the formation of AGEs. If lipation occurs, on the other hand, the resultant products are called advanced lipoxidation end products (ALEs).

Among AGE/ALEs formed, N-ε-carboxymethyllysine (CML) is one of the well-known products and AGE determined in lens proteins and collagens for the first time [59]. The reaction of GO and MG with lysine residues generates CML and N-ε-carboxyethyllysine (CEL), respectively. In addition, CML can be produced through Namiki pathway [60]. In this route, sugar part of Schiff base formed via reaction with reducing sugar and amine yields glycoaldehyde alkylimine by separating sugar parts of it. Then, this compound oxidizes and produces glyoxal which is followed by reaction with lysine residue leading to CML formation [61]. Another possible pathway resulting in CML formation is the oxidation of N-ε-fructosyllysine, which is formed at the early stage of Maillard reaction [59]. CML has been discovered in a broad range of foods such as dairy products, cereals, coffee, meat, fruits, vegetables and snacks at different concentrations. It is in high concentrations in dairy

products (5143.66 mg/kg protein), whereas fruit and vegetables contain at a lower level (26.62 mg/kg protein) [62].

Pyrraline and pentosidine are also given as an example for AGEs. Pyrraline is produced from the reaction between lysine residue and 3-DG [63] and found in high concentrations in food products [34]. Pentosidine is generated through the addition of a lysine and arginine side chains to a C_5 precursor resulting from carbohydrate degradation [64]. Moreover, arginine residue is able to form argypyrimidine molecule by reacting with MG [65]. In case of linking between two protein and α-dicarbonyl compound, lysine dimers are formed, which are GOLD (glyoxal-methyl-dimer), MOLD (methylglyoxal-methyl-dimer) and DOLD (3-deoxyglucosone-methyl-dimer) [66].

Presence of AGEs in foods possesses a potential risk on individuals because of its link to various chronic diseases like diabetes, diabetic nephropathy and Alzheimer's disease [62,67,68]. However, there is a debate on whether or not dietary AGEs cause for concern about human health recently [69].

In the final stage, the degradation of Amadori product is concluded with the generation of brown nitrogenous compounds, named as melanoidins [33]. Melanoidins are high molecular weight polymers, which are in charge of alterations in color and taste of foods. The structure of melanoidins is complicated because of forming from a combination of different reactive intermediates. Even though its structure has not been clarified yet, it has been revealed that melanoidins possess beneficial effects on health such as showing antioxidant activity, eliminating oxidative stress and metal chelating [70].

One of the important consequences of the Maillard reaction is the formation of toxic compounds such as HMF, acrylamide and furan, named thermal process contaminants.

Presence of HMF in foods might bring about potential health risks. Although there is not any explicit proof about the effects of HMF on humans, *in vitro* data showed that HMF has caused mutagenic effects in DNA [71] and cytotoxic effects on eyes, skin, upper respiratory tract and mucus membranes [56]. Being a metabolite of HMF, 5-sulfoxymethylfurfural, resulting from sulfonation of allylic hydroxyl group has been shown causing genotoxic and mutagenic impacts according to *in vitro* studies [29]. On the other hand, it was concluded

that toxic potential of HMF was low and no adverse effect level for HMF was found comparably higher than estimated daily intake [72]. Additionally, HMF undergoes degradation reactions that are oxidation, decarboxylation, dehydration and condensation in further steps [56].

Acrylamide was first reported to be found in thermally treated foods by Swedish National Food Administration in 2002. After acrylamide was categorized as probably carcinogenic to humans by International Agency for Research on Cancer (IARC) [73], many studies were conducted to determine its formation mechanisms. Maillard reaction was found to be the main route for the acrylamide formation in some foods including French fries, potato chips, cereals and bread, which are carbohydrate-based foods [31,74,75]. A study performed by Zyzak et al [76] showed that asparagine was the primary compound responsible from acrylamide formation. Acrylamide can occur from not only the reaction between asparagine and carbonyl compounds but also asparagine alone. However, when asparagine is reacted with carbonyl compounds at heating process, it results in a faster rate of acrylamide formation rather than asparagine itself [77].

In the course of acrylamide formation in Maillard reaction, asparagine reacts with a carbonyl compound generating N-glycosyl-asparagine and subsequently Schiff base. In a dry system, decarboxylation of Schiff base yields to azomethine ylide which can form imine I and imine II [76,77]. During this step, imine I forms the Strecker aldehyde by hydrolyzation, which does not lead to high amounts of acrylamide [78], whereas imine II induces acrylamide formation directly through the 1,2 elimination [79]. Moreover, hydrolysis of imine II results in 3-aminopropionamide (3-APA) formation, which then forms acrylamide via deamination [76].

There are less important pathways contributing to acrylamide production apart from Maillard reaction, as well. One of them is the possibility of acrylamide formation from directly asparagine even lacking carbonyl source [80]. 3-APA is responsible for this route, but the rate of occurrence is lower. Another precursor for acrylamide is acrolein which could be produced via Maillard reaction, carbohydrate degradation and lipid degradation [81]. Firstly, acrolein is converted to acrylic acid by oxidation and then its reaction with ammonia leads to acrylamide [82].

Acrylamide is categorized as probably carcinogenic to humans by IARC. Because of its genotoxic and carcinogenic features, also neurotoxic effects in high doses [73], acrylamide formation leads to great concern in foods, thus, the determination of its level is an important issue for human health.

Furan is one of the thermal process contaminants. It is a colorless liquid having high volatility and is classified as a possible human carcinogen by IARC [83]. Furan particularly presents in heat-treated foods involving brewed coffee, canned and jarred foods, baby foods [84]. According to experimental animal studies, it was determined to cause tumours and liver toxicity [85]. There are several recommended mechanisms of furan formation. Maga suggested as a primary source of furan that degradation of reducing sugars like glucose, fructose and lactose together with amines or alone by Maillard reaction [86]. Some amino acids like serine, cysteine, aspartic acid, alanine and threonine are precursors of furan. Among them, serine and cysteine, which can form acetaldehyde and glycolaldehyde, are able to produce furan via aldol condensation. On the other hand, aspartic acid, alanine and threonine are capable of merely acetaldehyde, thus, it is necessary to provide glycolaldehyde source for furan formation [87]. It is also considered that oxidation of polyunsaturated fatty acid (PUFA) is one of the possible pathways in the formation of furan [88]. In this way, after formation of lipid hydroperoxides resulting from PUFA through enzymatically or nonenzymatically, homolytic cleavages of PUFA hydroperoxides lead to the formation of 4-hydroxy-2-butenal that is highly toxic compound, which then may be the reason of furan [87]. Besides, carbohydrate degradation could bring about the generation of furan [88]. It is known that ascorbic acid and its derivatives like dehydroascorbic acid are the precursors of furan formation [88].

1.4. Sugar Degradation

Sugar degradation is initiated via an isomerization reaction [89]. Sugar isomerization and degradation are the indicators of caramelization reaction [90]. These reactions might be predominant than Maillard reaction with respect to conditions of the reaction medium, as in heated milk [91]. For initiating epimerization and dehydration along with isomerization of sugars, opening ring and subsequent enolization reaction are needful. This case is also related to epimerization, namely interconversion of aldose and ketose group, C-2 and C-3. The configuration of sugars by enolization and epimerization is known as ‘Lobry de Bruyn-Alberda van Ekenstein transformation’ [92]. This reaction occurs rapidly in alkaline medium

while it is observed in acidic medium to a lesser extent as well [93]. In addition, it was reported that the interconversion of glucose and fructose was in a remarkable amount when heating of sugar based and dry conditions [48,49]. Aldose and ketose sugars undergo isomerization through 1,2-enolization and, resulting in their intermediate 1,2-enediol. Being a reversible reaction, enolization provides an equilibrium medium for D-glucose, D-mannose and D-fructose (Figure 1.5) [89].

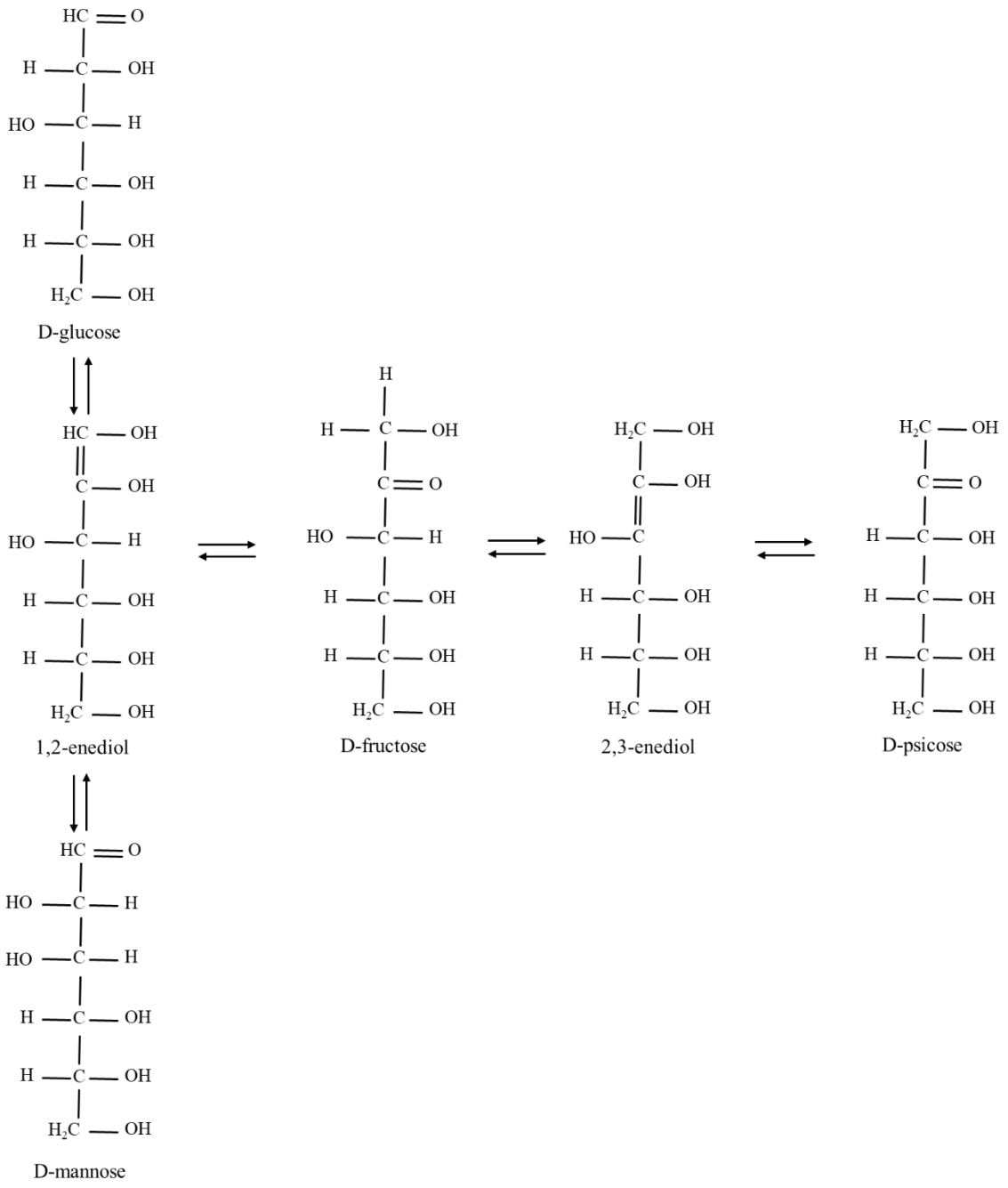


Figure 1.5. Lobry de Bruyn-Alberda van Ekenstein transformation [89]

Dehydration means the elimination of one water molecule from carbon structure of sugars. Dehydration increases when heating particularly under dry conditions and, also modest pH conditions. In the case of one molecule water is removed from glucose or fructose, 3-DG formation occurs. Then, dehydration of 3-DG produces 3,4-dideoxyglucosone (3,4-DG). Finally, when one molecule of water is removed from 3,4-DG, HMF is produced, which means the removal of three water molecule from hexose sugars in total [36,94]. Locas and Yaylayan [95] showed that HMF is also produced through fructofuranosyl cation resulting from sucrose degradation under dry heating conditions. Accordingly, HMF formation through fructofuranosyl cation was higher than that of 3-DG [95]. Elimination of one water molecule from fructose through 2,3-enolization gives rise to 1-DG [90]. Isomerization of 1-DG acts a significant role in the improvement of flavour and color [36].

Shorter chain α-dicarbonyl compounds such as glyoxal, methylglyoxal and diacetyl are produced via fragmentation in alkaline medium and also during food processing [45]. Similarly, it was stated that the formation of α-dicarbonyl compounds was observed in cookies [50].

Glyoxal is not only formed from Amadori product degradation but also from aldose sugars like glucose. Moreover, retro-aldolization and subsequent oxidation of imines could be responsible for glyoxal formation as well [57].

For the formation of methylglyoxal, it was recommended that it is formed through the fragmentation of Schiff base and then the generation of free radicals [96]. Hollnagel and Kroh [45] declared that MG was produced by cleavage of bonds, C_3 and C_4, of 1-DG. According to another study, MG formation also emerged from 3-DG via retro-aldol fragmentation [41].

Diacetyl mainly results from 1-DG isomerization. Besides, its formation facilitated in the presence of amines during Maillard reaction because when glycine was added to glucose, it contributed to more diacetyl generation [45].

2. EFFECT OF ROASTING ON THE FORMATION OF MAILLARD REACTION PRODUCTS

2.1. Introduction

The nature of sesame seeds is convenient for the reactions induced by heat treatment. Among the chemical reactions occurring in foods during heating, Maillard reaction is important that should be investigated due to its both positive and negative impacts. In this section, it was investigated on the Maillard reaction in sesame seeds induced by roasting and evaluated the level of reaction products mentioned before.

2.2. Materials and Methods

2.2.1. Chemicals and Consumables

High purity (>99%) D-sucrose, D-glucose and D-fructose were obtained from Sigma-Aldrich (Diesenhofen, Germany). All amino acids (>98%) were purchased from Merck Co. (Darmstadt, Germany). 3-Deoxyglucosone (75%), quinoxaline (99%), 2-methylquinoxaline (97%), methylglyoxal (40%), 2,3-dimethylquinoxaline (97%), o-phenylenediamine (98%), diethylenetriaminepentaacetic acid (DETAPAC) (98%) and sodium borohydride powder (≥98%) were purchased from Sigma-Aldrich (Steinheim, Germany), whereas furosine standard was purchased from Neosystem Laboratoire (Strasbourg, France). 5-hydroxymethylfurfural (98%) was purchased from Acros (Geel, Begium). Formic acid (98%), methanol and acetonitrile were obtained from JT Baker (Deventer, Holland). Potassium hexacyanoferrate, zinc sulfate, disodium hydrogen phosphate anhydrous, sodium dihydrogen phosphate dihydrate, sodium hydroxide, boric acid, hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany). The Carrez I and Carrez II solutions were prepared by dissolving 15 g of potassium hexacyanoferrate and 30 g of zinc sulfate in 100 ml of water, respectively. Syringe filters (nylon, 0.45 μm), Oasis HLB and Oasis MCX cartridges were supplied by Waters (Millford, MA). Ultrapure water was used throughout the experiments (Mili Q-System, Milipore, Milford, MA).

2.2.2. Roasting of Sesame Seeds

Sesame (Sesamum indicum L.), originating from Nigeria, was purchased from a local market (Ankara, Turkey). Ten grams of sesame seeds were placed in a petri dish as a homogeneous thin layer (3 mm thickness) and roasted in an oven (Memmert UN 55, Germany) at 150, 180,

200, 220°C for different temperatures ranging between 2.5 and 30 min. After left to ambient temperature, the samples were thoroughly ground and stored at -18°C prior to analysis. All samples were roasted in triplicate.

2.2.3. Extraction of Roasted Sesame Samples

One gram of ground sample was triple extracted with 20 mL of water (10, 5, 5 mL), and vortexed for 3 min in each step. Supernatants were centrifuged at 5000 ×g for 3 min in each step and transferred to in a test tube. Then, the tube was centrifuged at 5000 x g for 3 min to obtain a clear extract. The analysis of sugar, free amino acids, HMF, acrylamide and α-dicarbonyl compounds were performed by using the extracts.

2.2.4. Acid Hydrolysis

In order to analyse furosine and protein bound lysine, 100 mg of ground sesame samples were weighed into a glass tube and 5 mL of 8 N HCl added onto it. After the headspace of the tubes was flushed with nitrogen gas, screw caps firmly were closed. Hydrolysis was carried out in an oven at 110°C for 23 h and the hydrolysates were subsequently filtered through filter paper.

2.2.5. Analysis of Sugar

A part of extract of the sesame samples was precipitated by mixing Carrez clarification and, centrifuged at 10000 ×g for 3 min. The clear extract was passed through Oasis HLB cartridge conditioned previously with 1 mL of methanol and 1 mL of water. After discarded the first 8 drops of the eluent, the rest was taken into an autosampler vial for analysis. The analysis was performed as described previously [49].

2.2.6. Analysis of Free Amino Acids and Protein Bound Lysine

For the determination of free amino acids of sesame samples, a part of extract was blended with an equal volume of acetonitrile:water (80:20, v/v) and the mixture was centrifuged at 10000 ×g for 3 min. After passed through a 0.45 μm filter, the filtrate collected into a vial.

Fifty μL of acid hydrolysates, which was obtained as aforementioned was added to a glass tube to analyze protein bound lysine. Then the hydrolysed sample was dried under nitrogen gas, the final content was dissolved in 1 mL of an acetonitrile:water (80:20, v/v) and taken

into a vial by passing through a nylon syringe filter (0.45 μm) and 10 μL was injected into LC–MS/MS system. The analysis of free amino acids and protein bound lysine in roasted sesame samples was implemented with some modifications according to the method described previously [97]. Chromatographic separation was performed on Synchronis-HILIC column (100 × 2.1 mm, 3 μm) at 40°C using a gradient mixture of 0.5% formic acid and 5 mM ammonium formate in water (A) and 0.5% formic acid and 5 mM ammonium formate in 90% acetonitrile (B) at a flow rate of 0.7 mL/min. The eluent composition starting with 100% of B retained for 3 min and linearly decreased to 70% in 4 min. Then, it was linearly decreased to 20% in 10 sec and retained until the end of 10^{th} min. It was linearly increased to its initial conditions (100% of B) in 1 min and retained under this conditions for 4 min. Doing so, the total chromatographic run was completed in 15 min. Theanine was used as an internal standard at concentration of 0.5 mg/L. Waters TQD LC–MS/MS system was operated in positive ionization mode using the following interface parameters: source temperature of 120°C, desolvation temperature of 350°C, collision energy 12 V, desolvation gas flow of 900 L/h, capillary voltage of 3.5 kV, cone voltage of 20 V, and extractor voltage of 3 V. Data acquisition was performed by monitoring m/z ratio of 133.0 for asparagine and 87.0 and 74.0 for its product ions. Quantification was performed by means of external calibration curves built for asparagine in a range between 0.25 and 1 mg/L.

2.2.7. Analysis of 5-Hydroxymethylfurfural

After the extract centrifugated at 10000 ×g for 3 min, the mixture was filtered through 0.45 μm nylon filter and collected into a vial. The analysis of HMF was performed with respect to a previously described by Kocadağlı et al [98]. The filtered extract was injected into Agilent 1200 HPLC system (Waldbronn, Germany) and the quantification of HMF was based on the external calibration curve built ranged between 0.5 and 10 μg/mL.

2.2.8. Analysis of Acrylamide

An extraction procedure was achieved as described previously [99]. Acrylamide content in samples was executed by a Waters Acquity H Class UPLC system operated in positive mode. Chromatographic separation was performed in Hypercarb (100 × 2.1 mm, 3 μm) column at 50°C and 0.1% of formic acid solution was used as the mobile phase at a flow rate of 0.2 mL/min. The analysis was performed as described by Kocadağlı et al [100].

2.2.9. Analysis of Furan

For the analysis of furan, an array of experiments was performed. After roasting and grinding steps, 1 g of sesame samples were weighed into headspace vials and sealed immediately. The content of furan was determined as described by Mogol and Gökmen [101].

2.2.10. Analysis of Furosine

200 µL of the acid hydrolysates were put into a glass tube and purged with nitrogen gas. Then the residue dissolved in 1 mL of deionized water, passed through an Oasis HLB cartridge preconditioned with 1 mL methanol and 1 mL water. Drops, except for the first eight were taken into a vial. Furosine content of the samples was determined as described by Gökmen et al [102].

2.2.11. Analysis of N-ε-Carboxymethyllysine and N-ε-Carboxyethyllysine

The extraction procedure according to the method described by Charissou et al [103] was performed with some modifications. Quantification was carried out through a matrix-matched calibration curve. The samples roasted at 150°C for 5 min was used as a blank matrix. Calibration solutions of CML and CEL with concentrations in the range of 0-20 µg/mL were prepared in the blank matrix, then analysed by using Waters TQD LC–MS/MS. The analysis of CML was carried out with respect to a method described by Akıllıoğlu and Gökmen [104].

2.2.12. Analysis of α-Dicarbonyl Compounds

Extraction was performed as described above. Derivatization of α-dicarbonyl compounds was performed with o-phenylenediamine previously described analytical procedure with some modifications [52]. The coextracted colloids were precipitated by mixing with acetonitrile. Two hundred µL of the combined extract was diluted with 800 µL of the mixture of acetonitrile:water (5:3, v/v), and centrifuged at 15000 ×g for 5 min. For derivatization; five hundred µL of supernatant was mixed with 150 µL of 0.2% o-phenylenediamine solution containing 11 mM diethylenetriaminepentaacetic acid and 150 µL of 0.5 M sodium phosphate buffer (pH 7). The mixture was immediately filtered through 0.45 µm syringe filter into an autosampler vial. It was kept at room temperature, at dark for 2 h prior to LC-MS/MS analysis. Analysis of α-dicarbonyl compounds was performed a method expressed by Kocadağlı and Gökmen with some slight modifications [53]. Waters TQD LC–MS/MS

system operated in positive ionization mode was used. Chromatographic separation was performed in Waters Acquity UPLC BEH C18 column (2.1 × 100 mm, 1.7 μm) at 60°C using mobile phase consisting of 0.1% formic acid in water: 0.1% formic acid in acetonitrile (90:10, v/v) at a flow rate of 0.40 mL/min. MS system was using the following interface parameters: Source temperature of 130°C, desolvation temperature of 400°C, collision gas flow of 0.20 mL/ min, desolvation gas flow of 800 L/min, capillary voltage of 3 kV, cone voltage of 20 V, and extractor voltage of 3 V. Acquisition was performed by monitoring m/z ratios for quinoxaline derivatives as following: 235.2 for 3-DG and 1-DG, 145 for MG, 159.2 for DA. 5-methylquinoxaline was used as an internal standard. The MRM ions of the quinoxaline derivatives of α-dicarbonyl compounds were used for quantitation. The concentrations of quinoxaline derivatives were calculated by means of external calibration curves in the range between 0.02 and 2 mg/L. Working solutions of glucosone and 3-deoxyglucosone in the concentration range between 0.01 and 2.0 mg/L were derivatized and analyzed as described above to build its external calibration curve. All working solutions were prepared in acetonitrile−water (50:50, v/v).

2.2.13. Analysis of Color

Color measurements of roasted sesame seeds were performed by using computer-vision-based image analysis technique as described previously [105]. Color values of sesame seeds were given as L* (lightness), a* (redness), and b* (yellowness) and, also pictures of the roasted samples.

2.2.14. Statistical Analysis

Experimental data was reported as mean ± standard deviation. All analytical determinations were carried out in triplicates. Significance of differences among roasted samples was statistically analyzed by using one-way ANOVA Duncan's test ($p<0.05$) by using SPSS Version 16.0.

2.3. Results and Discussion

2.3.1. Changes in Color of Sesame Seeds During Roasting

The Maillard reaction plays a key role in browning development due to formation of melanoidins. As browning is simultaneously developed together with formation of thermal process contaminants, determination of the color changes during roasting under different

conditions is of importance. For this purpose, computer-based image analysis was performed in order to obtain L*, a*, b* values for the samples roasted at 150, 180, 200 and 220°C for different temperatures. As shown in Figure 2.1, color of roasted sesame seeds indicated the degree of roasting resulting in yellowish, brownish, brown and dark brown color with increased temperature and time. However, sesame roasted after at 200°C for 20 min and 220°C for 10 min had burnt appearance with dark brown color.

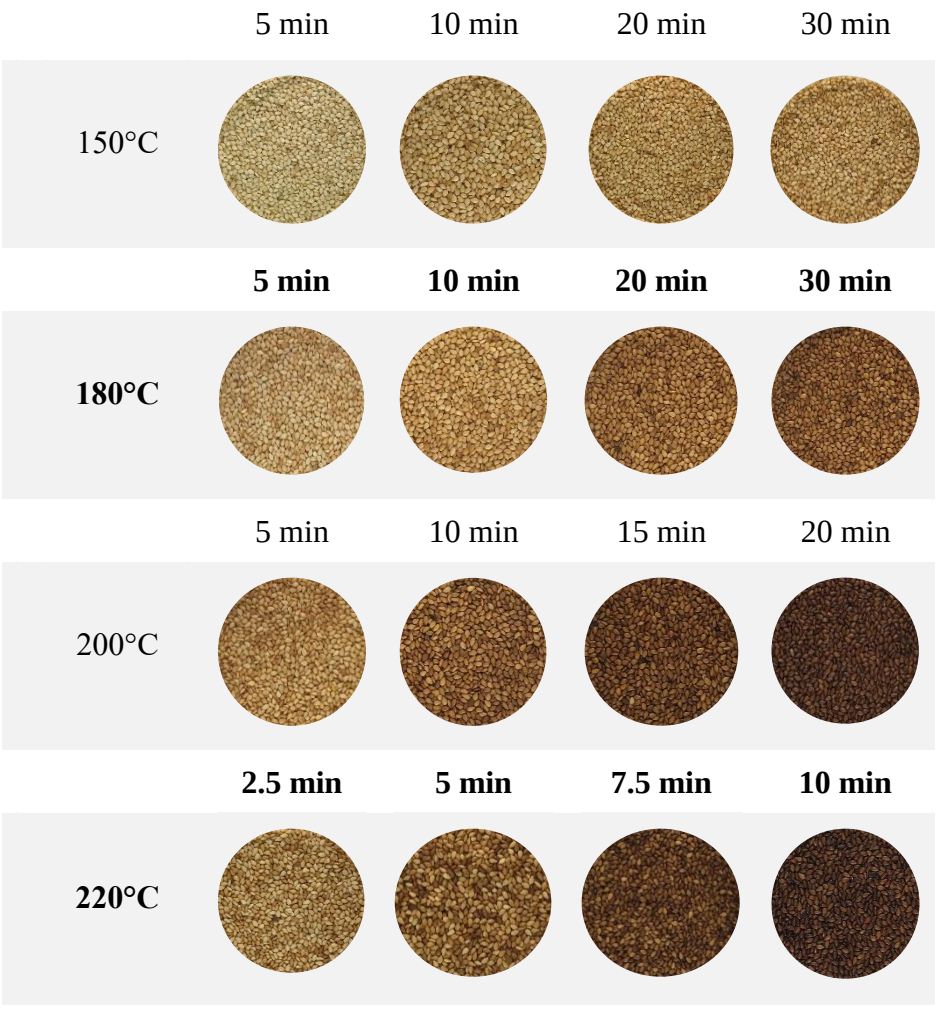


Figure 2.1. Appearance of sesame seeds roasted at different temperatures and times

Table 2.1 gives L*, a*, b* values obtained for the samples roasted at different temperatures and times. As represented, L* (lightness) values of sesame seeds decreased with the increase of roasting temperature and time indicating darker color. However, a* values inclined to increase within the progress of roasting owing to the formation of brown pigments via Maillard reaction. The values of a* (redness) increased significantly ($p<0.05$) for sesame seeds roasted at 150°C and 180°C, subsequently decreased after roasting at 200°C and 220°C

for 15 min and 7.5 min, respectively. On the other hand, b* (yellowness) values increased to a particular roasting time at 150°C and 180°C, but it consistently decreased by roasting at temperatures higher than 200°C, indicating the loss of yellowness and production of brownness at those temperatures.

Kahyaoğlu and Kaya [106] roasted sesame seeds at 120, 150 and 180°C up to 120 min, and they reported that L* value of sesame seeds constantly increased at 120°C during roasting, however, a decline in L* values was observed for the seeds roasted at higher roasting temperatures (150°C and 180°C). On the contrary to our results, they pointed out that increasing a* values well correlated with decreasing L* values according to roasting conditions. Additionally, they concluded that b* values increased as a result of an increase in roasting temperatures.

Table 2.1. Changes in color values in sesame seeds during roasting

Temperature (°C)	Time (min)	L*	a*	b*
150	5	65.5 ± 0.0^{j}	1.3 ± 0.0^{a}	24.5 ± 0.0^{e}
	10	57.1 ± 0.3^{i}	5.2 ± 0.0^{b}	28.2 ± 0.1^{i}
	20	55.7 ± 0.0^{h}	5.9 ± 0.0^{c}	29.6 ± 0.0^{k}
	30	56.9 ± 0.2^{i}	6.5 ± 0.0^{d}	29.1 ± 0.0^{j}
180	5	61.6 ± 0.2^{k}	5.8 ± 0.1^{a}	26.4 ± 0.1^{e}
	10	57.2 ± 0.0^{i}	8.5 ± 0.0^{b}	30.4 ± 0.0^{i}
	20	45.3 ± 0.0^{h}	11.0 ± 0.0^{c}	28.0 ± 0.0^{k}
	30	38.9 ± 0.2^{i}	11.4 ± 0.0^{d}	24.6 ± 0.1^{j}
200	5	55.6 ± 0.2^{h}	8.1 ± 0.0^{f}	29.7 ± 0.1^{k}
	10	40.6 ± 0.0^{e}	10.8 ± 0.0^{k}	24.9 ± 0.0^{f}
	15	28.7 ± 0.1^{d}	10.1 ± 0.1^{j}	19.3 ± 0.1^{d}
	20	22.7 ± 0.1^{b}	8.4 ± 0.0^{g}	12.0 ± 0.1^{b}
220	2.5	51.9 ± 0.1^{g}	6.5 ± 0.0^{d}	27.7 ± 0.0^{a}
	5	41.3 ± 0.1^{f}	8.8 ± 0.0^{h}	26.0 ± 0.0^{c}
	7.5	28.2 ± 0.0^{c}	9.3 ± 0.0^{i}	18.1 ± 0.0^{g}
	10	21.4 ± 0.0^{a}	7.8 ± 0.1^{e}	10.7 ± 0.1^{h}

Values are expressed as mean ± standard deviation. Different letters within the same column indicate statistically differences ($p < 0.05$).

2.3.2. Degradation of Sugars and Amino Acids

Sugars and amino acids are reactants of the Maillard reaction and sugar degradation, therefore, changes in the concentration of them were examined after roasting. Sucrose is the

only detectable sugar in sesame seeds where initial concentration was 2.25±0.1 g/100 g seeds. The loss of sucrose was 9%, 22%, 80% and 76% at the end of the roasting time for each temperature at 150, 180, 200 and 220°C, respectively. Glucose and fructose could not be found in raw and roasted sesame seeds. Roasting induced a significant decrease ($p<0.05$) in the sucrose content at 200°C and 220°C throughout the process and it reached to 0.45±0.05 g/100 g and 0.53±0.04 g/100 g seeds, respectively, at the end of roasting. On the other hand, at 150°C, a slight decrease was observed during roasting of sesame seeds, however, it took 20 min at 180°C (1.75±0.14 g/100 g seeds). Changes in the concentration of sucrose were presented in Figure 2.2.

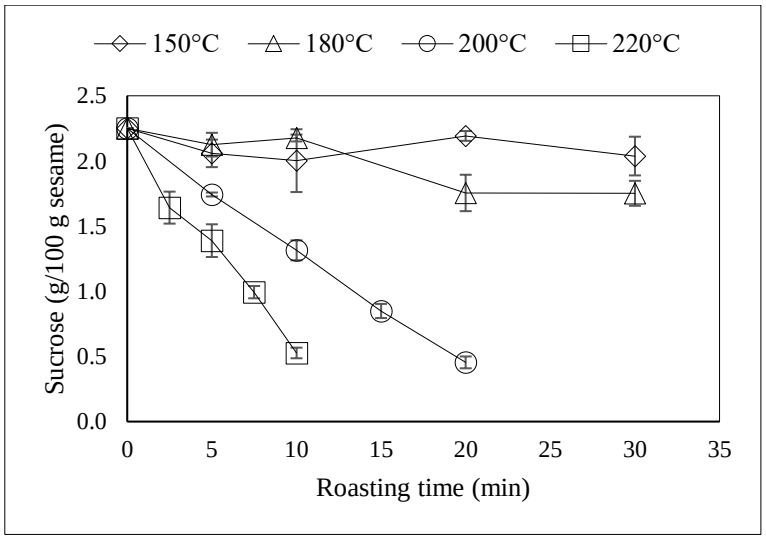


Figure 2.2. Changes in the concentration of sucrose in sesame seeds during roasting (g/100 g sesame)

Amino acids, both free and protein bound form could take part in a diverse reaction in foods, mainly Maillard reaction. Changes in the total free amino acids content were given in Figure 2.3. The concentration of total free amino acids diminished gradually ($p<0.05$) at higher temperatures such as 200°C and 220°C, where nearly 93% of which was lost after roasted at these temperatures for 20 min and 10 min, respectively. This reduction was 47% and 78% when roasting at 150°C and 180°C for 30 min. Profile of individual amino acids and their alteration in the concentrations, along with protein bound lysine were shown in Table 2.2. A considerable ($p<0.05$) decrease was observed in the concentration of protein bound amino acids as roasting time and temperature were increased, especially at higher temperatures (Figure 2.4). The reason for the decrease in amino acid concentration is that it could participate in chemical reactions particularly Maillard reaction.

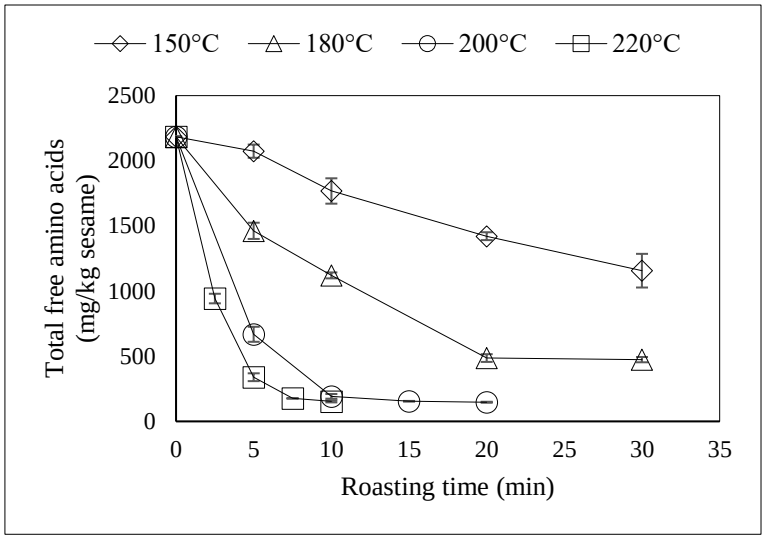


Figure 2.3. Changes in the concentration of total free amino acids in sesame seeds during roasting (mg/kg sesame)

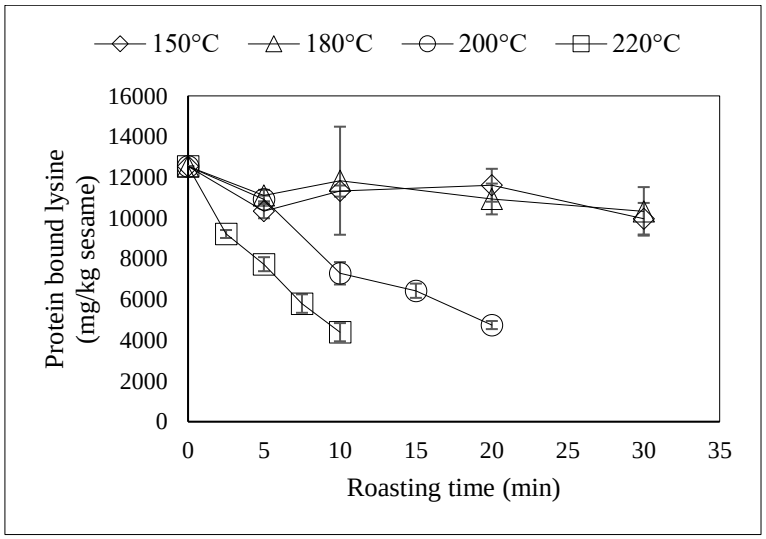


Figure 2.4. Changes in the concentration of protein bound lysine in sesame seeds during roasting (mg/kg sesame)

Table 2.2. Changes in the concentration of free amino acids and protein bound lysine in sesame seeds during roasting (mg/kg sesame)

	150°C 5 min	150°C 10 min	150°C 20 min	150°C 30 min	180°C 5 min	180°C 10 min	180°C 20 min	180°C 30 min	200°C 5 min	200°C 10 min	200°C 15 min	200°C 20 min	220°C 2.5 min	220°C 5 min	220°C 7.5 min	220°C 10 min
Ala	163.4 ±1.3	145.8 ±9.4	110.0 ±7.7	91.9 ±19.2	126.8 ±8.9	98.6 ±1.7	29.3 ±10.3	13.9 ±6.5	64.6 ±8.0	9.7 ±4.5	6.3 ±2.2	2.3 ±2.1	110.4 ±12.6	32.8 ±2.1	5.2 ±6.3	3.9 ±2.6
Arg	274.9 ±20.4	253.0 ±29.6	237.0 ±30.7	230.2 ±25.8	248.9 ±29.3	263.7 ±6.8	222.2 ±13.8	234.2 ±4.5	107.0 ±3.4	100.0 ±6.7	96.7 ±1.8	97.3 ±5.2	134.0 ±4.0	119.5 ±8.4	112.3 ±5.4	93.1 ±1.9
Asn	251.7 ±7.3	207.9 ±5.6	172.0 ±5.9	156.2 ±19.0	180.3 ±13.6	134.8 ±6.2	28.6 ±8.6	20.4 ±6.6	62.5 ±12.7	4.6 ±2.6	0.0	0.0	102.6 ±10.6	18.2 ±7.0	0.0	0.0
Gaba	110.9 ±6.4	93.3 ±9.0	81.9 ±15.6	46.3 ±14.3	77.9 ±7.2	63.3 ±10.7	23.5 ±0.4	9.6 ±4.3	117.3 ±15.2	0.0	0.0	0.0	160.9 ±5.3	87.8 ±6.8	0.0	0.0
Glu	259.2 ±21.8	171.6 ±32.3	141.6 ±0.7	69.7 ±19.0	164.4 ±34.4	40.1 ±24.1	14.5 ±1.9	0.0	37.6 ±1.4	2.3 ±0.5	0.0	0.0	53.5 ±15.0	0.0	0.0	0.0
His	115.8 ±7.9	92.6 ±10.6	89.3 ±2.3	73.5 ±4.0	88.7 ±2.3	76.1 ±8.0	51.5 ±2.9	60.5 ±0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ile	49.5 ±7.7	42.4 ±5.5	33.2 ±7.7	31.2 ±6.3	34.3 ±5.7	28.8 ±4.7	4.0 ±4.4	3.9 ±2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Leu	103.5 ±7.5	76.7 ±8.0	65.6 ±1.4	49.6 ±5.3	67.0 ±8.2	51.1 ±8.0	3.5 ±3.2	3.8 ±1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lys	75.0 ±18.5	54.0 ±7.3	34.5 ±3.4	43.5 ±11.3	59.2 ±7.3	47.5 ±3.6	41.8 ±2.9	45.6 ±10.0	61.3 ±10.0	50.1 ±4.3	45.0 ±3.3	45.9 ±8.7	61.3 ±5.6	57.2 ±5.2	55.7 ±2.9	50.1 ±3.8
Met	24.8 ±2.0	25.5 ±3.4	18.3 ±3.4	15.0 ±0.3	16.5 ±2.1	8.5 ±0.8	0.7 ±0.2	0.3 ±0.3	0.2 ±0.5	0.0	0.0	0.0	3.6 ±0.7	0.0	0.0	0.0
Phe	245.0 ±8.8	202.5 ±6.9	166.5 ±6.8	148.8 ±20.6	174.6 ±13.6	127.3 ±8.5	24.9 ±1.7	13.9 ±11.7	51.7 ±12.8	25.8 ±46.7	0.0	0.0	90.3 ±5.2	1.3 ±1.7	0.0	0.0
Pro	65.0 ±4.9	52.2 ±2.7	30.0 ±14.0	19.9 ±2.6	18.8 ±5.9	15.3 ±1.7	0.4 ±0.0	0.3 ±0.4	17.4 ±8.7	1.1 ±0.6	0.0	0.0	34.2 ±1.7	5.9 ±1.3	0.0	0.0
Ser	58.7 ±5.5	59.4 ±5.5	51.2 ±1.7	6.2 ±9.6	10.3 ±3.4	16.9 ±31.1	15.4 ±15.1	19.0 ±6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Thr	42.4 ±6.1	37.4 ±7.2	35.6 ±4.3	28.0 ±6.5	31.1 ±12.6	21.1 ±2.3	7.9 ±0.0	10.8 ±3.3	8.5 ±4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Trp	45.1 ±2.2	45.3 ±1.9	36.6 ±3.0	35.4 ±3.2	37.0 ±3.2	30.4 ±0.5	8.3 ±2.2	6.5 ±3.2	44.9 ±3.7	0.2 ±0.3	0.0	0.0	61.8 ±5.9	13.4 ±4.3	0.0	0.0
Tyr	159.0 ±4.4	125.1 ±3.4	107.5 ±6.9	111.1 ±20.1	125.6 ±6.3	86.5 ±8.7	7.1 ±1.6	1.8 ±1.5	102.8 ±9.8	7.5 ±2.3	7.0 ±4.9	1.7 ±2.4	127.4 ±28.3	1.0 ±1.5	5.9 ±2.8	0.0
Val	26.4 ±0.0	12.1 ±5.7	21.8 ±2.1	16.2 ±3.0	19.7 ±4.8	17.4 ±4.3	4.6 ±1.7	2.4 ±1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Protein bound Lys	10338.5 ±348.5	11326.9 ±272.7	11610.4 ±808.2	9967.8 ±776.1	11104.4 ±281.4	11834.5 ±2653.8	10936.6 ±757.1	10328.6 ±1191.8	10913.2 ±188.8	7287.0 ±550.6	6431.0 ±350.3	4745.9 ±199.0	9216.6 ±195.3	7734.4 ±343.9	5800.4 ±454.0	4394.1 ±447.6

2.3.3. Formation of 5-Hydroxymethylfurfural

Figure 2.5 illustrates HMF formation in sesame seeds roasted at 150, 180, 200 and 220°C for applied temperatures. Formation of HMF showed an increasing trend during roasting at all temperatures except 150°C. HMF formation was relatively less at 150°C compared to that of higher roasting temperatures. However, when the temperature was raised, HMF content in sesame seeds significantly ($p<0.05$) increased to 75.6±8.5, 60.5±3.4 and 39.8±1.1 mg/kg at 180, 200 and 220°C, respectively. HMF reached the highest level at 180°C, which was almost 18 times higher than that of at 150°C. An increase in temperature promoted the formation of HMF during roasting, but the amount of HMF was found to be higher concentration due to the fact that roasting time was longer at 180°C. As indicated before, HMF is generally used as a heat load indicator in a wide range of foods such as bakery products, breakfast cereals, coffee and honey [94]. Thereby, HMF formation in sesame seeds could also be monitored to investigate the heating intensity applied during roasting. According to the results provided by Agila and Barringer [107], increasing both the temperature and time during roasting of almonds showed an increase in HMF concentration, reaching to a maximum level, 905 μg/L, in almonds roasted at 177°C for 20 min. Likewise, it was reported by Fallico [108] that HMF content of hazelnuts rapidly increased during the progress of roasting at a constant temperature. In a similar study, HMF formation in roasted hazelnuts was highly affected by the increase in roasting time and temperature [109]. Since sesame seeds are mostly used in various bakery products, that are subjected to elevated temperatures, the formation of HMF in sesame seeds under these conditions should be considered.

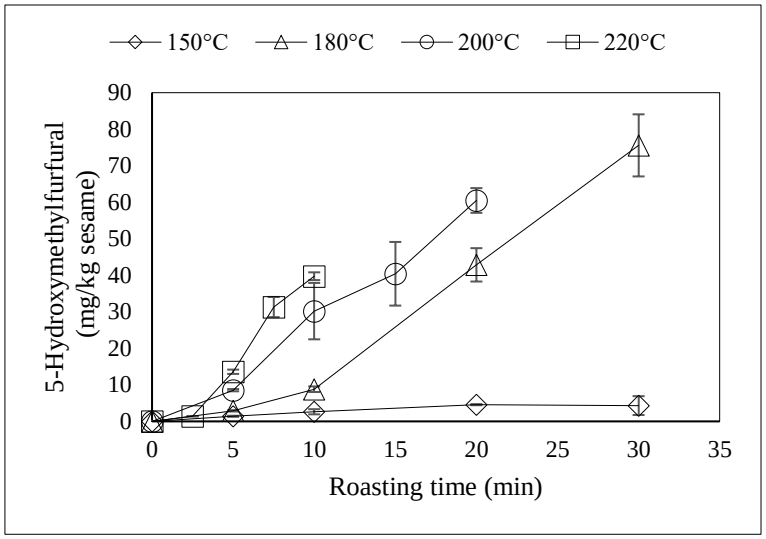


Figure 2.5. Formation of 5-hydroxymethylfurfural (HMF) in sesame seeds during roasting (mg/kg sesame)

2.3.4. Formation of Acrylamide

Effect of roasting on acrylamide levels, which is recognized a probable human carcinogen, was also determined in sesame seeds. As shown in Figure 2.6, acrylamide formation in sesame seeds was facilitated as a result of increasing the roasting temperature to a certain extent. The concentration of acrylamide in sesame seed was found to be increased during roasting at 150°C and 180°C for 20 min reaching the content of 306.1±90.4 and 590.8±151.7 μg/kg, respectively, subsequently decreased gradually as roasting proceeded. At higher temperatures, this interval was shorter, it took 10 min at 200°C and 5 min at 220°C, attained to 633.0±49.4 and 656.2±59.1 μg/kg, respectively. Then, acrylamide content in sesame seeds drastically ($p<0.05$) decreased when the roasting time was prolonged at those temperatures. This substantial reduction in acrylamide is the net result of acrylamide formation/elimination kinetics. As it is known, both formation and elimination of acrylamide progress simultaneously during heating of foods and observed levels of acrylamide in foods is the net amount. As the amounts of precursors of acrylamide play a key role for the determination of dominant reaction, acrylamide formation is dominant in the presence of asparagine or carbonyl compounds, however, its elimination becomes dominant in the lack of any precursor. According to this, during roasting of sesame seeds, acrylamide formation was predominant until to a certain roasting degree, whereas acrylamide elimination became predominant as roasting proceeded. It was noticed from these results that this type of kinetic pattern was similar to roasted coffee [98,110]. Kocadağlı et al [98] reported that maximum

acrylamide concentration was 468 μg/kg in coffee beans roasted at 220°C for 5 min. They concluded that free asparagine was the limiting reactant in green coffee, thus, owing to the lack of free asparagine, a sudden decline in acrylamide concentration was monitored after 5 min roasting. It was also reported that acrylamide was formed in other seeds roasted at elevated temperatures. A study revealed that acrylamide formed in almonds ranging from no detectable levels to 236 μg/kg when almonds were roasted at 130°C for 2.5-40 min. However, acrylamide concentration changed between 715-1044 μg/kg in almond roasted at 150°C for 15-30 min [111]. For roasted hazelnuts, this level was found ranging between 14-22 μg/kg [112].

Hereby, acrylamide content in roasted sesame seeds was found as comparably higher than common acrylamide-rich foods such as potato crisp, snacks and French fries (332-550 μg/kg) depending on heating conditions and levels of reaction precursors [113]. It is known that free asparagine is the main precursor for occurrence of acrylamide in heated foods. For understanding the effect of asparagine on acrylamide formation in sesame seeds, the changes of free asparagine contents in roasted samples were displayed in Figure 2.7. The amount of asparagine diminished drastically ($p<0.05$) in the course of roasting and it was completely run out in samples roasted at 200°C and 220°C. Owing to the deficiency of free asparagine, a dramatic decline ($p<0.05$) in acrylamide content of roasted sesame seeds was observed during roasting. It can be clearly seen from these findings that the changes in asparagine and acrylamide concentration well correlated. Thus, it could be stated that the quantity of free asparagine is the limiting precursor for the acrylamide generation during roasting of sesame seeds. Namely, an abrupt reduction in acrylamide level of roasted sesame seeds was due to insufficient level of asparagine as the roasting temperature and time increased.

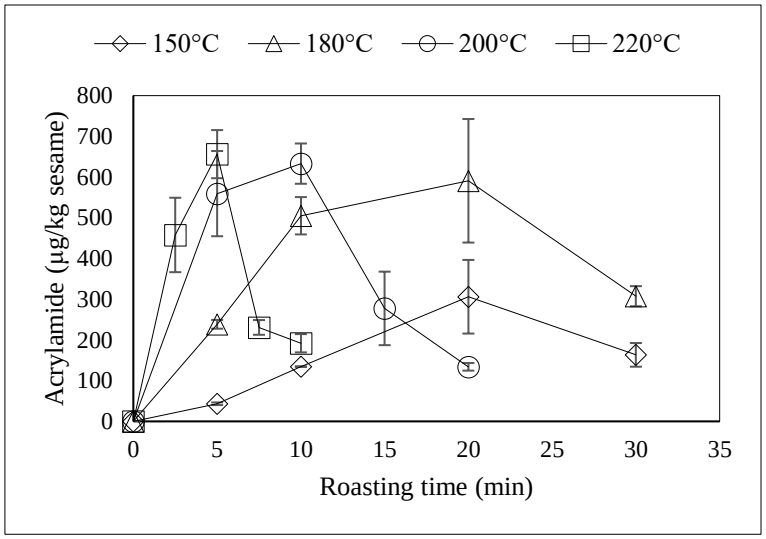


Figure 2.6. Formation of acrylamide in sesame seeds during roasting (µg/kg sesame)

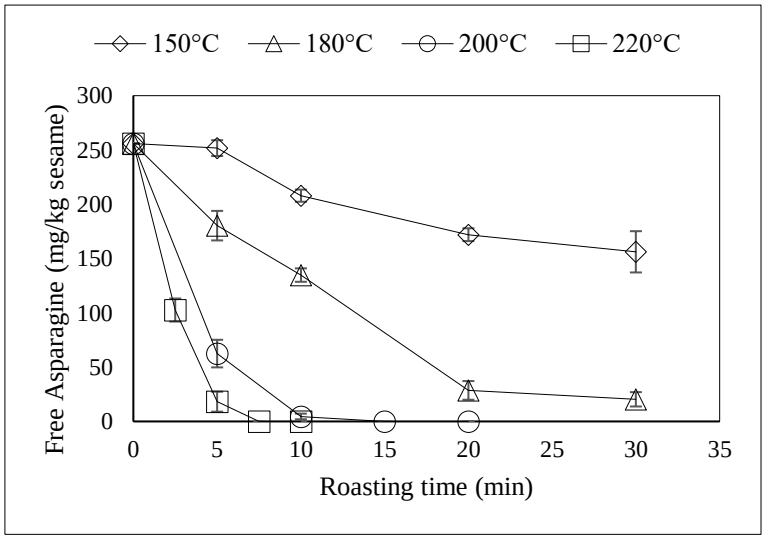


Figure 2.7. Formation of free asparagine in sesame seeds during roasting (mg/kg sesame)

2.3.5. Formation of Furosine

N-ε-fructosyllysine is an early glycation marker, indicating the progress of Maillard reaction. Furosine, the compound produced through N-ε-fructosyllysine during acid hydrolysis, was analyzed in roasted sesame seeds in order to monitor the progress of Maillard reaction during roasting. The furosine concentration yielded to a maximum value of 307.3±0.5 mg/kg in sesame seeds roasted at 150°C for 5 min and it was followed by a substantial decrease ($p<0.05$) when the thermal load increased (Figure 2.8). The maximum concentrations were 50.2±14.8, 29.5±0.9 and 44.4±0.9 mg/kg at 180, 200 and 220°C for initial roasting temperatures, respectively. After that time, furosine levels followed a decreasing trend and,

but did not change significantly ($p>0.05$) during roasting of sesame seeds at those temperatures. The reason for the decline in furosine contents as a result of increasing temperature might be its possible conversion to other compounds by degradation or oxidation of Amadori product. Furosine might be degraded or oxidized to advanced glycation end products like CML, during overheating. Similar to our findings, furosine concentrations were analyzed in both raw and roasted hazelnuts, and a drastic decrease ($p<0.05$) in its content was observed after roasting at 150°C for 30 min (from 39.4 ± 2.6 mg/kg to 32.5±3.9 mg/kg for Tombul variety and from 75.7±1.0 to 33.7±0.1 mg/kg for Levant variety) [114].

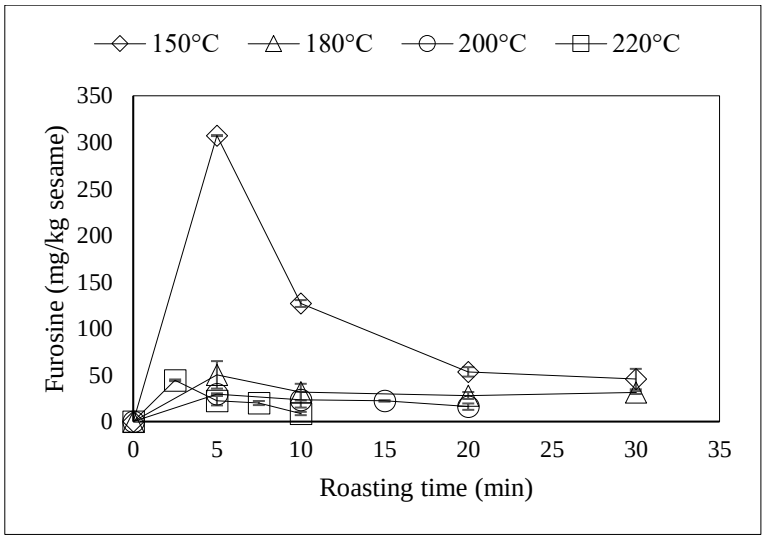
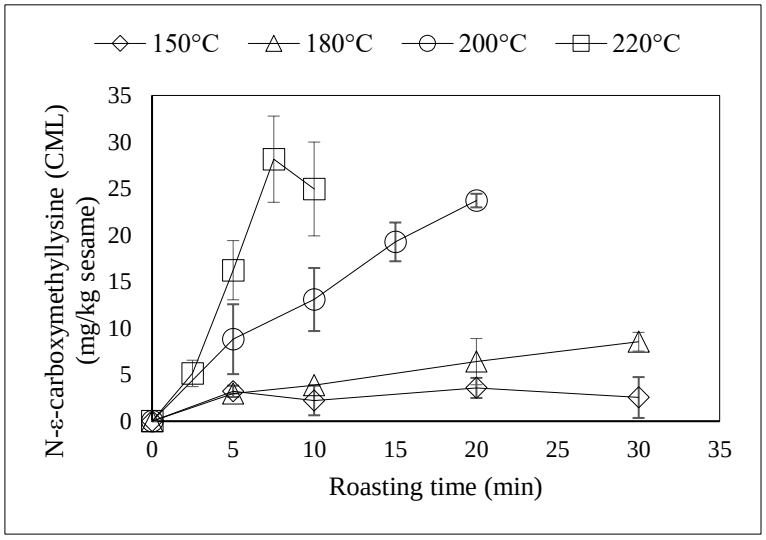


Figure 2.8. Formation of furosine in sesame seeds during roasting (mg/kg sesame)

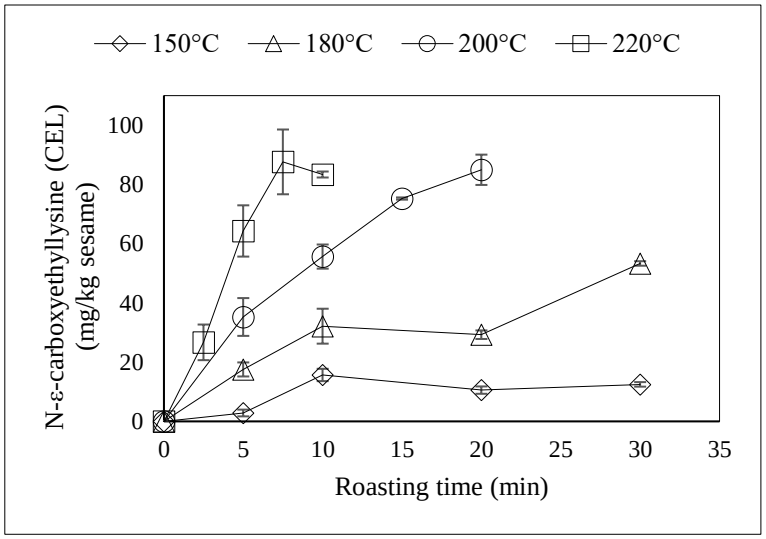
2.3.6. Formation of N-ε-Carboxymethyllysine and N-ε-Carboxyethyllysine

Figure 2.9 shows the concentration of CML and CEL, indicators of advanced glycation, formed at all temperature-time conditions during roasting of sesame seeds. The maximum level of CML was 28.2±4.6 mg/kg after roasting at 220°C for 7.5 min. Additionally, CML concentration reached a maximum value of 2.5±2.2, 8.5±1.0 and 23.7±0.7 mg/kg during roasting of sesame seeds at 150, 180 and 200°C at the end of roasting, respectively. Obviously, the amount of furosine in roasted sesame seeds was higher significantly than that of CML, representing the predominance of the early stage of Maillard reaction. According to a study conducted in commercial roasted peanuts, CML concentration was reported as about 4 times lower than furosine concentrations [115]. In another study performed with a wide range of food samples, CML concentrations varied between 137-424 mg/kg [62].

Accordingly, it can be stated that the amount of CML in roasted sesame seeds was comparably low with respect to many food materials. However, during production of tahina, which is produced from sesame seeds by roasting and grinding, a remarkable increase was observed in CML formation after roasting (115°C for 2 h) and sterilization stages (100°C for 30 min), reaching to almost 17 mg/kg in the final product [23]. Consequently, it could be interfered that CML formation was highly promoted by heating at lower temperatures for longer times. The trend of CEL formation, meanwhile, was similar to CML, but its amount was higher than that of CML, which was attained 87.6±10.9 mg/kg in samples roasted at 220°C for 7.5 min. Similarly, Zhang et al [116] reported that CEL levels (4.26 ± 1.38 mg/kg) were higher than that of CML (7.70 ± 2.56 mg/kg) in almonds roasted at 132°C for 22 min. Additionally, in sponge cakes, it was also found to be higher CEL formation regardless of sugar types used [117].



(a)



(b)

Figure 2.9. Formation of AGEs: (a) N-ε-carboxymethyllysine (CML), (b) N-ε-carboxyethyllysine (CEL) in sesame seeds during roasting (mg/kg sesame)

2.3.7. Formation of Furan

Furan, a heat-induced contaminant, was monitored in roasted sesame seeds (Table 2.3) and as a result, only trace amount of furan (<LOQ) was observed in sesame seeds in consequence of roasting at 150°C. On the other hand, furan could not also be detected at 180°C and 200°C for 10 min. However, the concentration of furan reached to 28.2±11.1 ng/g at 180°C after roasting for 30 min and 254.0±28.8 ng/g at 200°C after roasting for 20 min. During roasting at 220°C after 5 min, furan formation increased and attained to the highest level, 264.4±13.0 ng/g in sesame seeds when the roasting was completed. Similar to our findings, roasting did not lead to a substantial increase in furan concentration in hazelnuts at very low temperatures, 50°C. However, when hazelnuts were roasted at temperatures exceeding 120°C, it was attained a significant raise in hazelnuts, whose composition is akin to sesame seed [118]. As mentioned before, furan is formed through the thermal degradation of sugars directly or together with amino acids, thermal degradation of certain amino acids and thermal oxidation of polyunsaturated fatty acids. Considering that sesame seeds involve PUFAs such as linoleic and linolenic acid, furan formation is expected during roasting of sesame seeds owing to these precursors. Nevertheless, the risk of furan formation could be relatively low during roasting due to the fact that antioxidants such as sesamol, sesamin and sesamolinol in sesame seeds have good capability for prevention of PUFAs oxidation. Additionally, highly volatility of furan should also be considered for the observed values in roasted sesame

seeds. According to Scientific Report announced by EFSA, baby foods contained the lowest levels of furan (with an average of 3.2 ng/g), while this level was the highest for brewed coffee and roasted coffee with 45 ng/g and 3660 ng/g, respectively [119]. In view of such information, it could be said that furan may not cause concern in sesame seeds roasting conditions applied in general.

Table 2.3. Changes in furan concentration in sesame seeds during roasting (ng/g sesame)

Temperature (°C)	Time (min)	Furan (ng/g)
150	5	<LOQ
	10	<LOQ
	20	<LOQ
	30	<LOQ
180	5	<LOQ
	10	<LOQ
	20	18.4±0.9[a]
	30	28.2±11.1[b]
200	5	<LOQ
	10	<LOQ
	15	151.9±24.7[a]
	20	254.0±28.8[b]
220	2.5	<LOQ
	5	<LOQ
	7.5	49.7±10.9[a]
	10	264.4±13.0[b]

Data are given as mean ± standard deviation. Different letters within same column indicate statistically differences ($p < 0.05$). LOQ: limit of quantification.

2.3.8. Formation of α-Dicarbonyl Compounds

α-Dicarbonyl compounds are one of the intermediates formed during thermal processing of foods and their formation arise mainly from Maillard reaction, sugar degradation and lipid oxidation. 1-DG and DA could not be detected in unroasted sesame seeds while 3-DG and MG were found, which might be emerged from storage conditions of nontreated sesame seeds and during shipping period. As they are highly reactive compounds, no matter what their quantities are in foods, they can modify reactive sides of protein chains, inducing loss of nutritional value [34]. Since levels of these compounds in foods are important, α-dicarbonyl compounds formed during roasting of sesame seeds were monitored. It was observed that roasting process gave rise to the formation of 3-DG, 1-DG, MG and DA in sesame seeds. The changes in their concentrations are illustrated in Figure 2.10. According

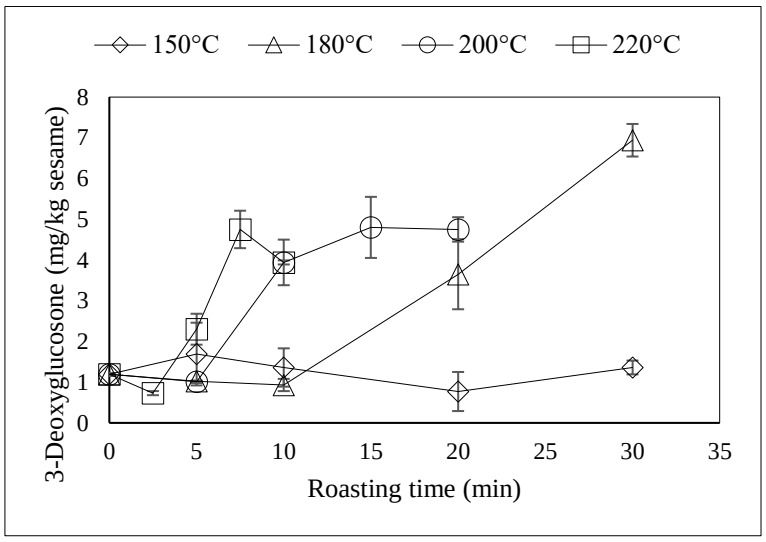
to the results, a minor change in the amount of 3-DG was monitored during roasting at 150°C, whereas it increased gradually ($p<0.05$) with time and reached to 6.9±0.4 and 4.8±0.3 mg/kg in sesame seeds roasted at 180°C and 200°C after roasting for 30 and 20 min, respectively. Differently, at 220°C, the trend of 3-DG formation increased within roasting time of 7.5 min and subsequently decreased remarkably ($p<0.05$), reaching to 3.9±0.1 mg/kg after 10 min. Nonetheless, 3-DG content of roasted sesame seeds was comparably lower than most of processed food items such as honey, vinegar, jams, jellies, sweeteners, candies, bread and cookies [52].

1-DG was also formed in sesame seeds at all roasting temperatures and the maximum concentrations roasted at 150, 180, 200 and 220°C were found as 1.05±0.20, 0.61±0.16, 0.85±0.13 and 0.72±0.13 mg/kg after roasting for 5 min, 5 min, 20 min and 7.5 min, respectively. However, the content did not exhibit a particular change under those conditions. The reason for that might be the measurement uncertainty in the amount of 1-DG due to its known reactivity, therefore, showing no accumulation under the present in the course of roasting [120].

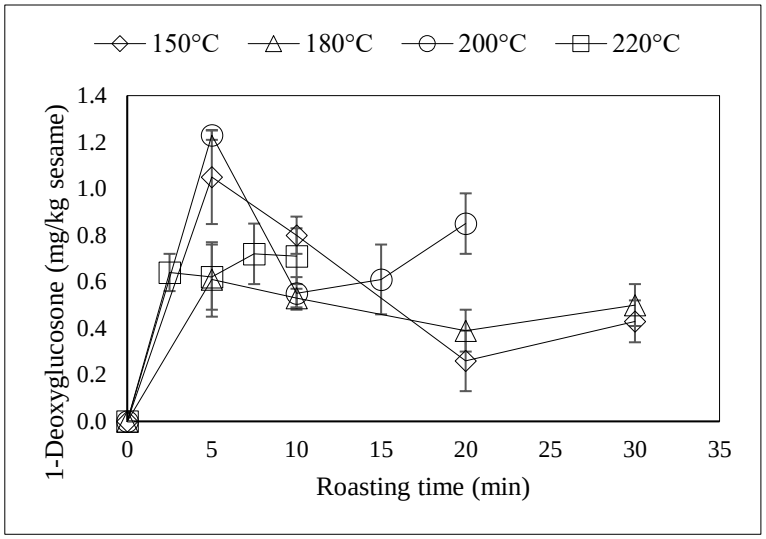
MG concentration reached the maximum concentration after 10 min of roasting at 220°C, attaining 5.7±0.9 mg/kg. MG content of hazelnuts, which is rich in oleic acid, was reported as 4.2±0.3 mg/kg and 4.8±0.2 mg/kg in Tombul and Levant quality hazelnuts roasted at 150°C for 30 min, respectively [114]. It could be clearly shown that these levels were close to the maximum concentration found in sesame seeds. On the other hand, according to a study conducting with olive oils, MG level in olive oils was found as 0.61±0.3 mg/kg, which means almost 7-fold lower than that of hazelnuts and sesame seeds. Based upon these results, it could be considered that MG formation might arise from other fraction rather than lipids during roasting of sesame seeds. Moreover, MG levels in heat treated fish oils such as cod liver, tuna and salmon oils were measured to be higher than vegetable oils such as corn, olive and soybean oils because fish oils contain more polyunsaturated fatty acids in comparison to vegetable oils [46].

DA levels increased to a certain extent and reached 1.2±0.2 mg/kg and 1.2±0.19 mg/kg in sesame seeds roasted at 200°C for 20 min and 220°C for 7.5 min, respectively, although a decreasing step ($p<0.05$) was observed for the roasting temperatures at 150°C and 180°C.

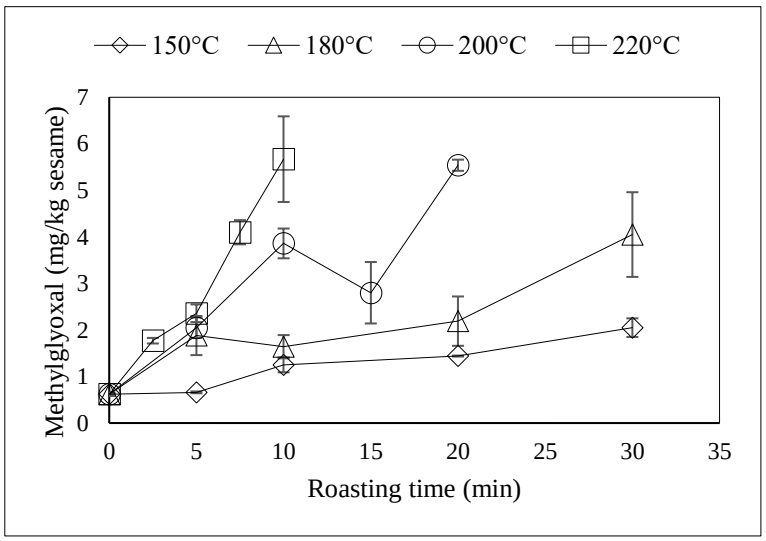
GO and MG, which are shorter chain dicarbonyl compounds, are known to yield through sugar degradation, Maillard reaction and, also lipid oxidation [45]. In sesame seeds, which consist mostly of lipid fraction, lipid oxidation might also contribute to the occurrence of carbonyl compounds. However, the effect of lipid oxidation on the formation of dicarbonyl compounds could not be evaluated during roasting of sesame seeds, as it is merely achieved by model system assays. Yoshida and Takagi [14] reported that they observed no alteration in the fatty acid composition of sesame oil prepared at different roasting conditions (160-250°C). In a different study to determine oxidative stability of sesame oil prepared from sesame seeds roasted under diverse conditions, it was found that conjugated dienoic acid value was lower in sesame seeds roasted at higher temperature for longer time, but, more sesamol was specified in sesame oil [121]. As mentioned previously, these findings have proved that sesame seeds are less susceptible to oxidation during roasting, thanks to the fatty acid profile and the presence of antioxidants. In the light of these findings, it can be concluded that dicarbonyl compounds in roasted sesame seeds were mainly formed through Maillard reaction and caramelization.



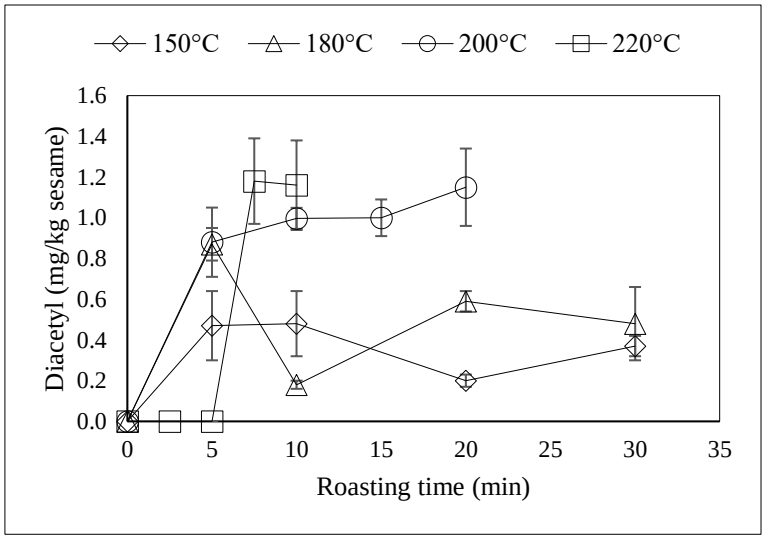
(a)


150°C
180°C
200°C
220°C
1-Deoxyglucosone (mg/kg sesame)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
Roasting time (min)

(b)


150°C
180°C
200°C
220°C
Methylglyoxal (mg/kg sesame)
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
35
Roasting time (min)

(c)



(d)

Figure 2.10. Formation of α-dicarbonyl compounds: (a) 3-deoxyglucosone (3-DG), (b) 1-deoxyglucosone (1-DG), (c) methylglyoxal (MG), (d) diacetyl (DA) in sesame seeds during roasting (mg/kg sesame)

2.4. Conclusion

The results of this study revealed that the roasting process led to the formation of Maillard reaction products in sesame seeds. To the best of our knowledge, this is the first comprehensive report providing an insight to the presence of heat-induced compounds in roasted sesame seeds. Formation of thermal process contaminants including α-dicarbonyl compounds, HMF, acrylamide and furan in sesame seeds were induced by roasting. In addition to thermal process contaminants, glycation markers such as furosine, CML and CEL were also formed in sesame seeds as a result of the roasting process. In detail, the results obtained from roasted sesame seeds at different temperatures created a typical Maillard reaction picture. Formation of α-dicarbonyl compounds, HMF and acrylamide were highly promoted by more heat load. In addition, it was observed in this study that at least 10 min of roasting at 180°C and 200°C was needed for furan formation in sesame seeds, while this time was more than 5 min at 220°C. Interestingly, the results showed that acrylamide levels in sesame seeds roasted at 200°C exceeded the acrylamide content of many heat-treated foods. Additionally, the loss of essential amino acids like lysine and arginine occurred as one of the consequences of Maillard reaction. To conclude, sesame seed and its oil are consumed through bakery goods, confectionery products as well as cooking oil, tahini or salad dressing. Considering that they are subjected to heat treatment before consumption,

thermal processing conditions applied and the contribution of sesame seeds to daily intake levels of thermal process contaminants is important.

3. MULTIRESPONSE KINETIC MODELLING OF MAILLARD REACTION AND CARAMELIZATION IN SESAME SEEDS

3.1. Introduction

The reaction products as a result of roasting of sesame seeds could not be arisen from only one reaction pathway. Rather, there are various reactions responsible for the formation and elimination of these products. During roasting process, Maillard reaction and caramelization take place together, thereby, it occurs parallel and consecutive reactions impressing each other, namely discrimination of some common intermediates is too hard in a complex food matrix [122]. Therefore, in order to control the products and determine important steps quantitively, it is required a kinetic approach to reveal the reaction mechanism. Regarding one response kinetic model, it does not enlighten the whole mechanism. However, multiresponse kinetic modelling allows for consideration all the reactants, intermediates and products simultaneously; thus, it enables to estimate reaction parameters precisely [122,123].

In this section, it was aimed to explain how Maillard reaction and caramelization during sesame roasting impact on different reaction products by building multiresponse kinetic models. For this purpose, two different models were proposed, which one was related with dicarbonyl compounds and glycation markers, and the other was formation of HMF and acrylamide. The main reactants and products analysed in the previous section were utilized to create kinetic models and, it was evaluated reaction mechanism obtained along with estimated kinetic parameters in detail.

3.2. Multiresponse Kinetic Modelling of Dicarbonyl Compounds and Glycation Markers

3.2.1. Kinetic Data Analysis

For the kinetic modelling of glycation markers and dicarbonyl compounds in sesame seeds during roasting, data of reactants and products (roasted at 180, 200 and 220°C for 2.5-30 min) obtained from the previous chapter was used. The reactants were sucrose and protein bound lysine while the products were dicarbonyl compounds (1-DG, 3-DG, MG), furosine, CML and CEL. Their concentrations were stated as μmol/kg sesame seed.

A kinetic model was suggested including formation of α-dicarbonyl compounds and glycation markers through Maillard reaction and caramelization appearing during roasting of sesame seeds (Figure 3.1).

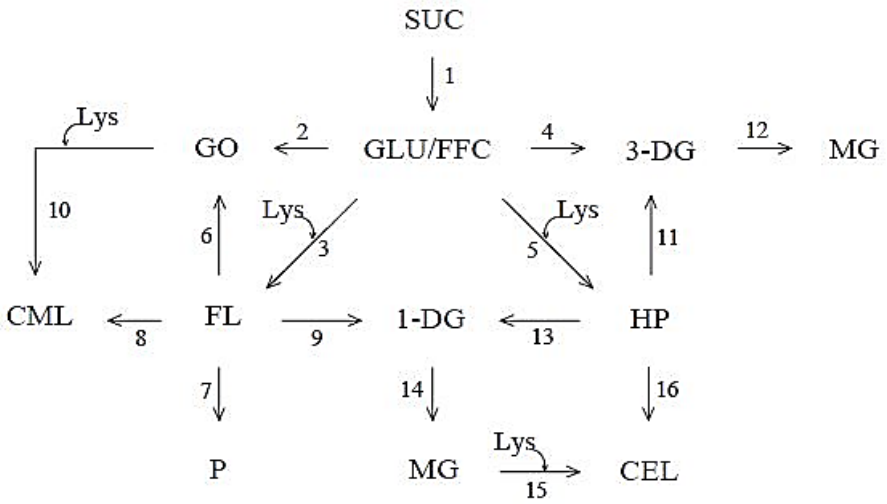


Figure 3.1. Proposed kinetic model for α-dicarbonyl compounds and glycation markers through Maillard reaction and caramelization appearing during roasting of sesame seeds. SUC, sucrose; GLU, glucose; FFC, fructofuranosyl cation; FL, N-ε-fructosyllysine; HP, Heyns product; 3-DG, 3-deoxyglucosone; 1-DG, 1-deoxyglucosone; MG, methylglyoxal; GO, glyoxal; CML, N-ε-carboxymethyllysine; CEL, N-ε-carboxyethyllysine; Lys, protein bound lysine; P, product.

For each reaction step, a reaction rate constant (k) was given and reaction network was described by building a differential equation. Then, each of them was solved by numerical integration to figure out the reaction mechanism. In this way, it is possible to observe linking between reactants and products. Parameter estimation was determined via using Athena Visual Studio software (v.14.2) with non-linear regression for each temperature. The estimated parameters and experimental data were compared to evaluate whether the kinetic model was appropriate with goodness of fit and posterior probability criterion [124].

$$\frac{d[SUC]}{dt} = -k_1[SUC]$$

$$\frac{d[GLU/FFC]}{dt} = k_1[SUC] - (k_3 + k_5)[GLU/FFC][Lys] - (k_2 + k_4)[GLU/FFC]$$

$$\frac{d[FL]}{dt} = (k_3)[GLU/FFC][Lys] - (k_6 + k_7 + k_8 + k_9)[FL]$$

$$\frac{d[CML]}{dt} = k_8[FL] + k_{10}[GO][Lys]$$

$$\frac{d[3-DG]}{dt} = k_4[GLU/FFC] + k_{11}[HP] - k_{12}[3-DG]$$

$$\frac{d[1-DG]}{dt} = k_9[FL] + k_{13}[HP] - k_{14}[1-DG]$$

$$\frac{d[MG]}{dt} = k_{12}[3-DG] + k_{14}[1-DG] - k_{15}[MG][Lys]$$

$$\frac{d[CEL]}{dt} = k_{16}[HP] + k_{15}[MG][Lys]$$

$$\frac{d[Lys]}{dt} = -(k_3 + k_5)[GLU/FFC][Lys] - k_{10}[GO][Lys] - k_{15}[MG][Lys]$$

$$\frac{d[GO]}{dt} = k_2[GLU/FFC] + k_6[FL] - k_{10}[GO][Lys]$$

$$\frac{d[HP]}{dt} = k_5[GLU/FFC][Lys] - (k_{11} + k_{13} + k_{16})[HP]$$

$$\frac{d[P]}{dt} = k_7[FL]$$

In order to determine the temperature dependence of the reactions, activation energies, E_a (kJ/mol) was calculated by building the Arrhenius equation

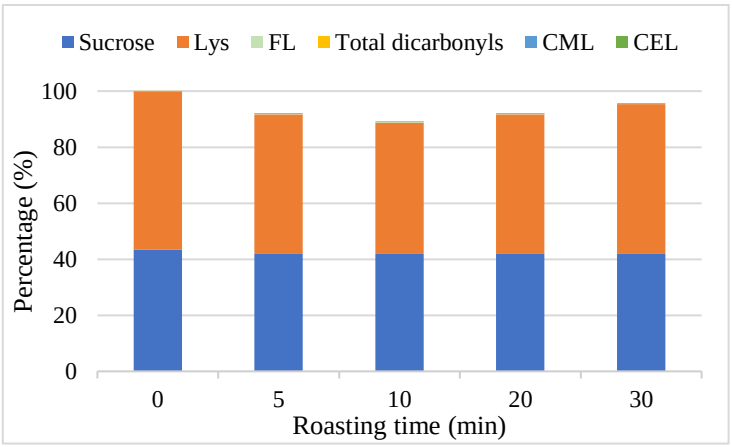
$$k(T) = A \times \exp\left(\frac{E_a}{RT}\right)$$

where R is the gas constant (8.3145×10^{-3} kJ/mol K), T is the temperature, k is the reaction rate constant and A is the preexponential factor. In order to calculate the activation energy (E_a) for each individual reaction, a plot of lnk (T) versus 1/T was used, whose slope gives E_a.

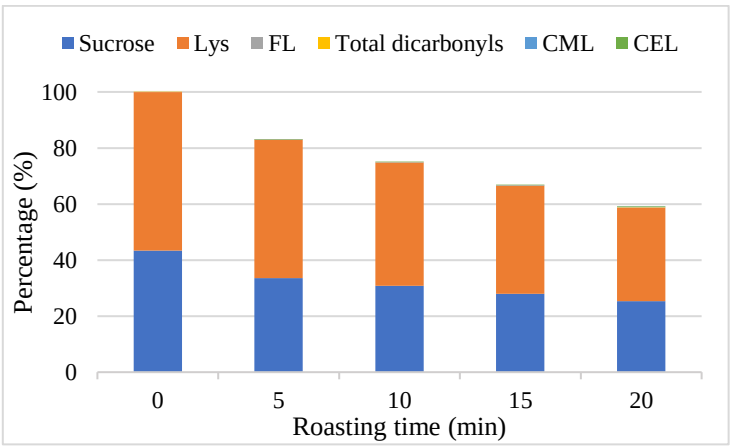
3.3. Results and Discussion

3.3.1. The Mass Balance

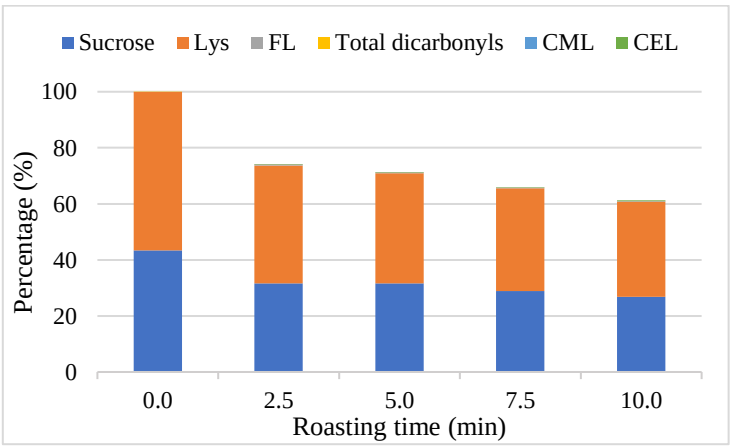
The mass balances of the reactants and the products calculating as the relative ratio of each compound (%) for all roasting temperature and time conditions were presented in Figure 3.2.



(a)



(b)



(c)

Figure 3.2. Mass balance (%) of reactants and products during roasting of sesame seed (a) 180°C (b) 200°C (c) 220°C.

As shown in Figure 3.2, total moles of reactants and products diminished within the progress of roasting. At 180°C, the recovery at 5-30 min of roasting found in the range of 90-95%. Meanwhile, the recovery at 200°C was 83% and 59% after roasting for 5 min and 20 min, respectively. Besides, the total moles of these compounds were 74% and 61% for 2.5 and 10 min of roasting at 220°C, respectively. Due to these results, a gradual decrease in total moles of the determined compounds indicated the significance of early and advanced stages of the Maillard reaction together with the progress of caramelization. Accordingly, the inconsistency in the mass balance might be consequences of the not quantified compounds, such as melanoidins, which are one of the final stage products in Maillard reactions [96,122].

3.3.2. Kinetic Modelling

Reactants, intermediates and water content found in foods is not uniformly dispersed; therefore, kinetic modelling of real foods is a demanding duty. The changes in water during thermal process must be incorporated into the model. However, heat and mass transfer coefficients of water were neglected in the model as the amount of water in sesame seed is very limited.

Model discrimination for (1) sucrose degradation and formation of Amadori and Heyns product, (2) α-dicarbonyl compounds and their reaction of amino acids, (3) CML and CEL formation and their reaction of amino acids was drawn to obtain the appropriate model characterizing the experimental data. For this purpose, the comprehensive reaction mechanism was performed and illustrated in Figure 3.3. As could be seen from the results, some of the kinetic model fits could not be well estimated, and which varied based on the roasting temperature (Figure 3.4). This caused to be unavoidable making a revision in the model.

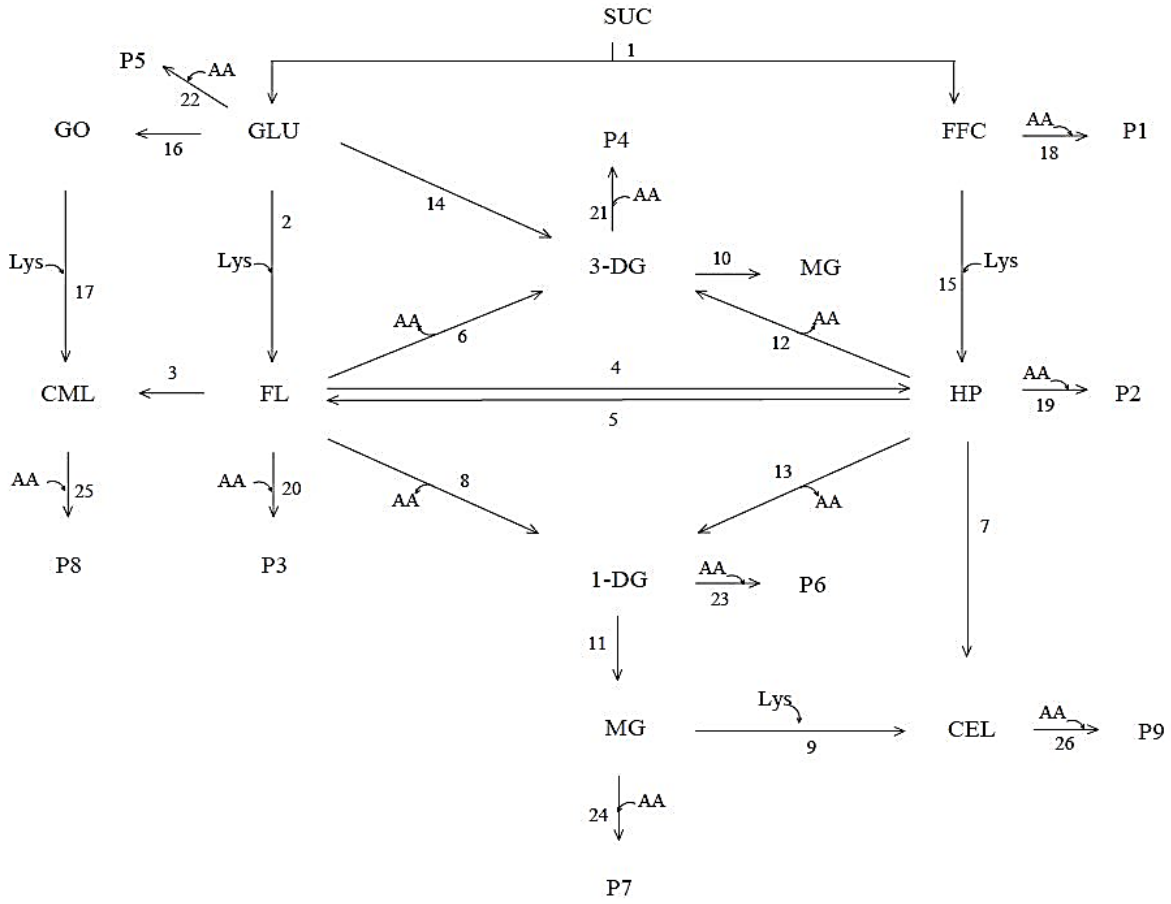
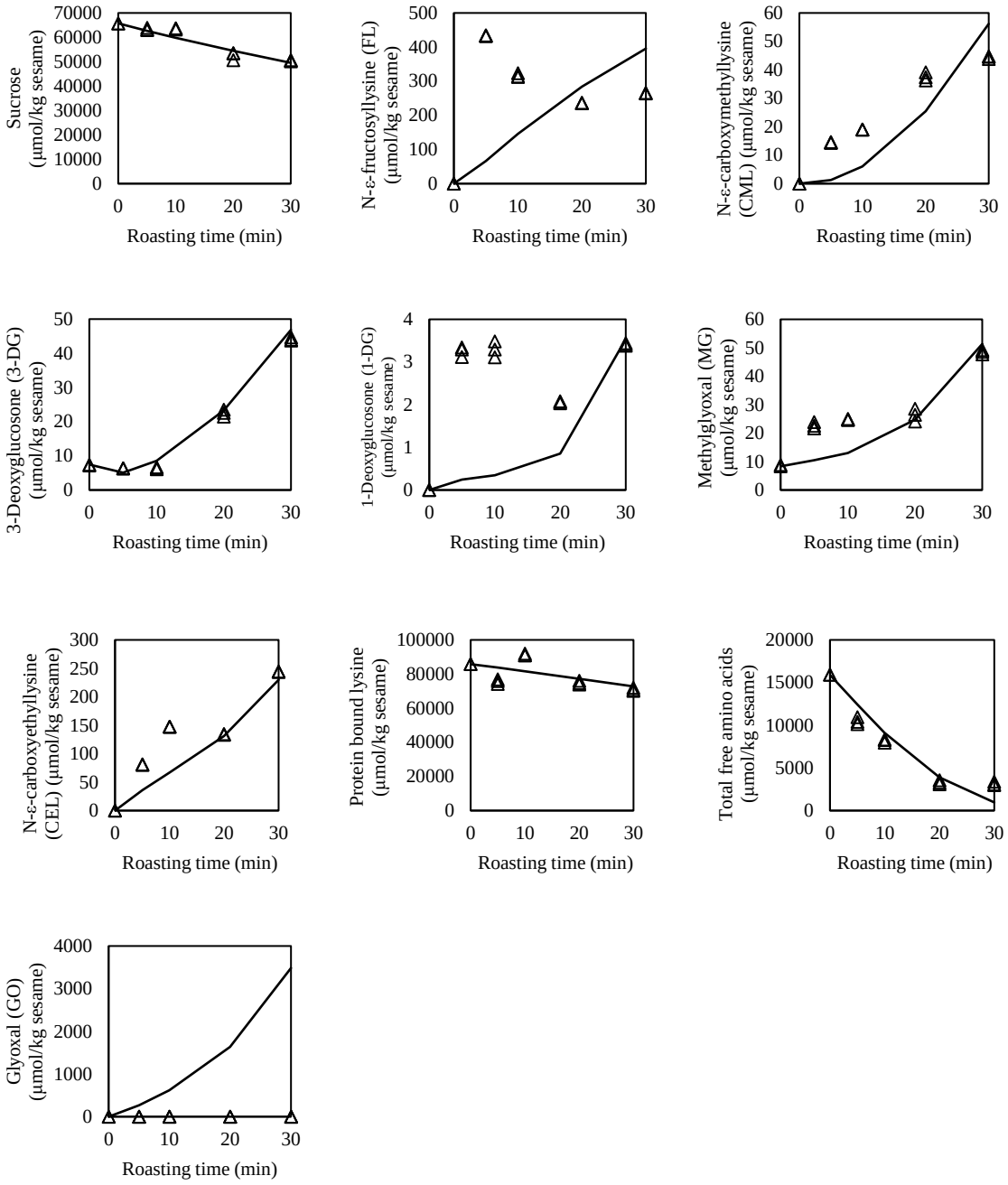
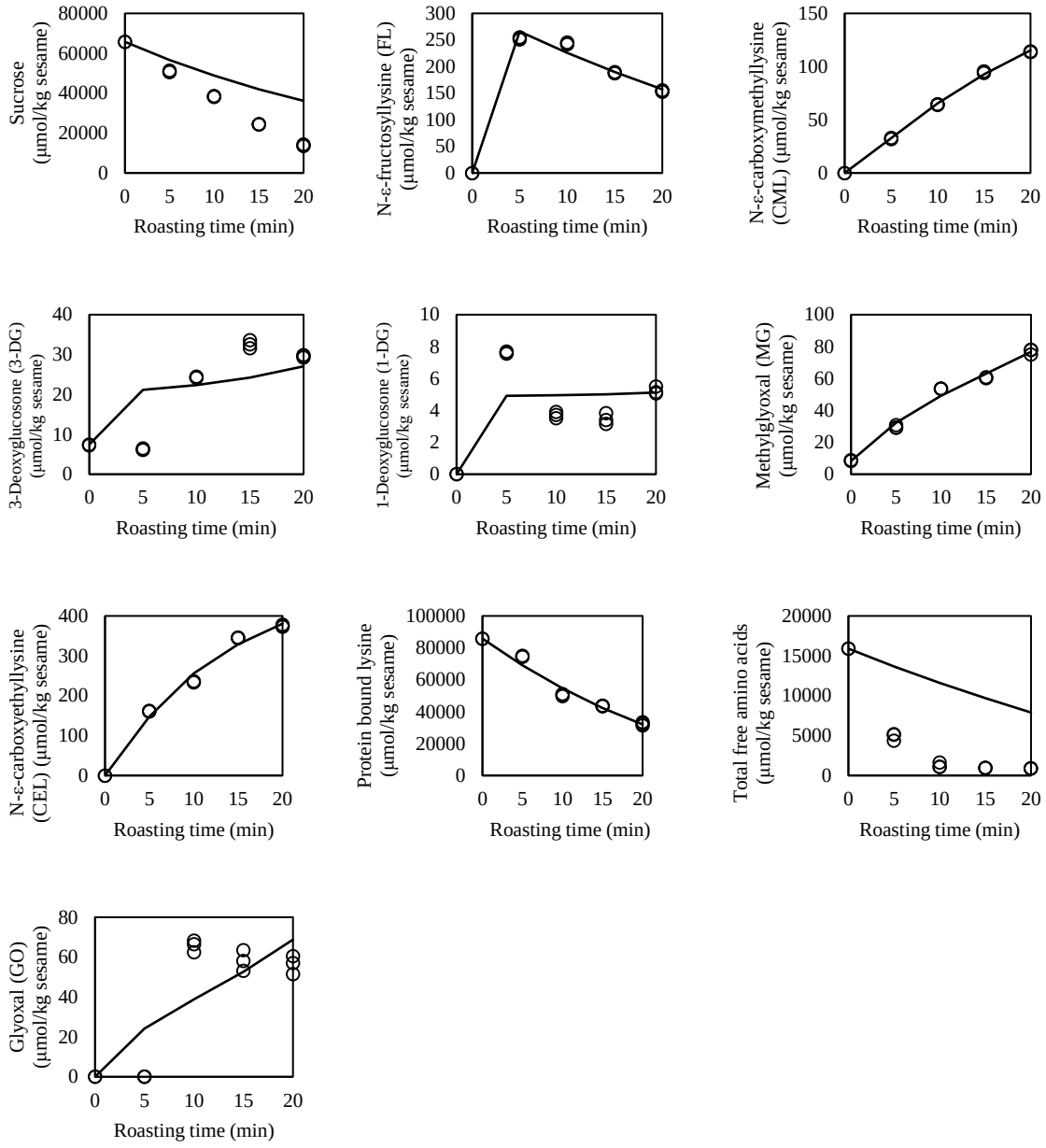


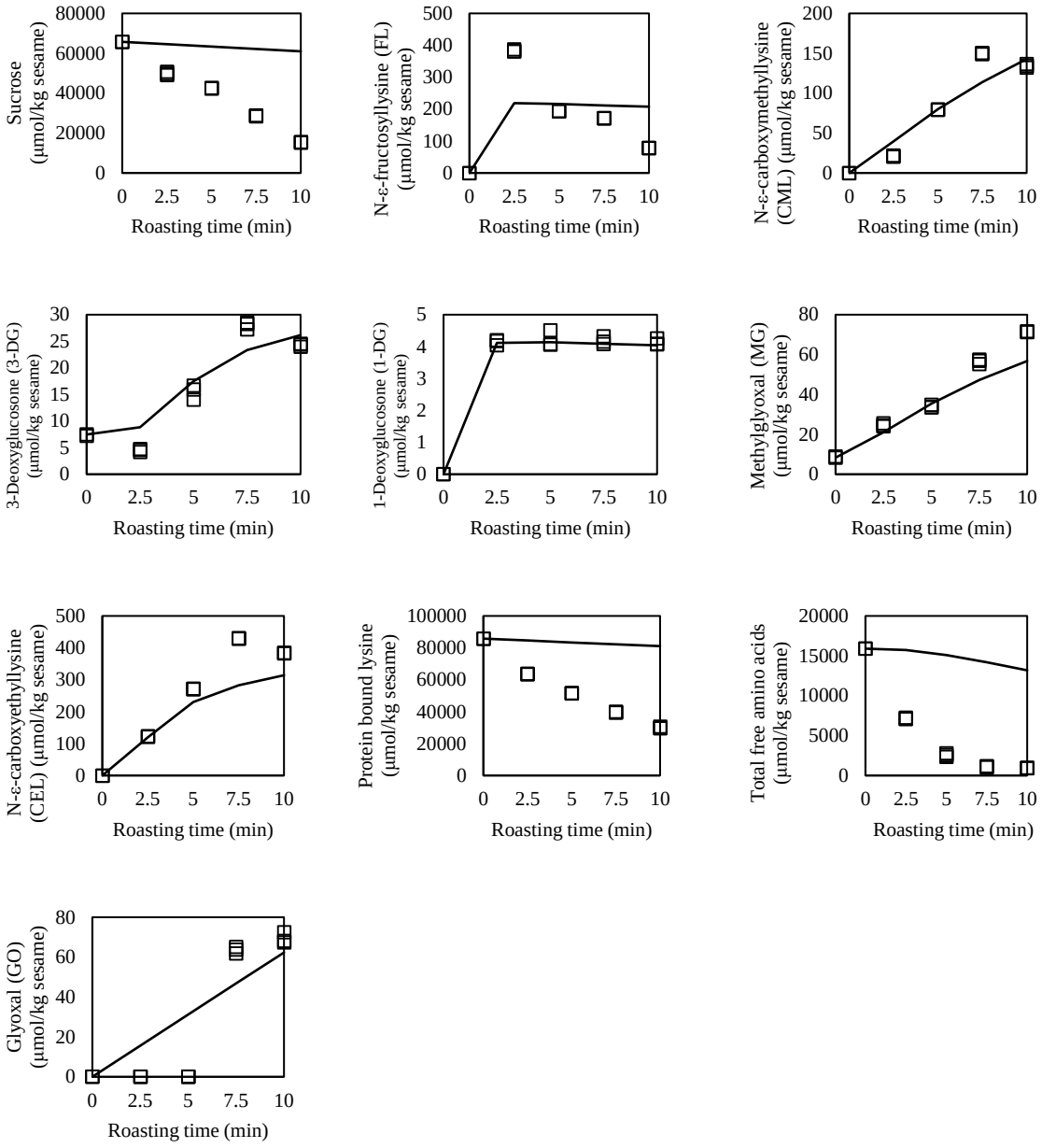
Figure 3.3. Comprehensive kinetic model for α-dicarbonyl compounds and glycation markers through Maillard reaction and caramelization appearing during roasting of sesame seeds. SUC, sucrose; GLU, glucose; FFC, fructofuranosyl cation; FL, N-ε-fructosyllysine; HP, Heyns product; 3-DG, 3-deoxyglucosone; 1-DG, 1- deoxyglucosone; MG, methylglyoxal; GO, glyoxal; CML, N-ε-carboxymethyllysine; CEL, N-ε-carboxyethyllysine; Lys, protein bound lysine; AA, total free amino acids; P, product.


Sucrose (μmol/kg sesame)
70000
60000
50000
40000
30000
20000
10000
0
0 10 20 30
Roasting time (min)
N-ε-fructosyllysine (FL) (μmol/kg sesame)
500
400
300
200
100
0
0 10 20 30
Roasting time (min)
N-ε-carboxymethyllysine (CML) (μmol/kg sesame)
60
50
40
30
20
10
0
0 10 20 30
Roasting time (min)
3-Deoxyglucosone (3-DG) (μmol/kg sesame)
50
40
30
20
10
0
0 10 20 30
Roasting time (min)
1-Deoxyglucosone (1-DG) (μmol/kg sesame)
4
3
2
1
0
0 10 20 30
Roasting time (min)
Methylglyoxal (MG) (μmol/kg sesame)
60
50
40
30
20
10
0
0 10 20 30
Roasting time (min)
N-ε-carboxyethyllysine (CEL) (μmol/kg sesame)
300
250
200
150
100
50
0
0 10 20 30
Roasting time (min)
Protein bound lysine (μmol/kg sesame)
100000
80000
60000
40000
20000
0
0 10 20 30
Roasting time (min)
Total free amino acids (μmol/kg sesame)
20000
15000
10000
5000
0
0 10 20 30
Roasting time (min)
Glyoxal (GO) (μmol/kg sesame)
4000
3000
2000
1000
0
0 10 20 30
Roasting time (min)

(a)


Sucrose (μmol/kg sesame)
80000
60000
40000
20000
0
0 5 10 15 20
Roasting time (min)
N-ε-fructosyllysine (FL) (μmol/kg sesame)
300
250
200
150
100
50
0
0 5 10 15 20
Roasting time (min)
N-ε-carboxymethyllysine (CML) (μmol/kg sesame)
150
100
50
0
0 5 10 15 20
Roasting time (min)
3-Deoxyglucosone (3-DG) (μmol/kg sesame)
40
30
20
10
0
0 5 10 15 20
Roasting time (min)
1-Deoxyglucosone (1-DG) (μmol/kg sesame)
10
8
6
4
2
0
0 5 10 15 20
Roasting time (min)
Methylglyoxal (MG) (μmol/kg sesame)
100
80
60
40
20
0
0 5 10 15 20
Roasting time (min)
N-ε-carboxyethyllysine (CEL) (μmol/kg sesame)
400
300
200
100
0
0 5 10 15 20
Roasting time (min)
Protein bound lysine (μmol/kg sesame)
100000
80000
60000
40000
20000
0
0 5 10 15 20
Roasting time (min)
Total free amino acids (μmol/kg sesame)
20000
15000
10000
5000
0
0 5 10 15 20
Roasting time (min)
Glyoxal (GO) (μmol/kg sesame)
80
60
40
20
0
0 5 10 15 20
Roasting time (min)

(b)



(c)

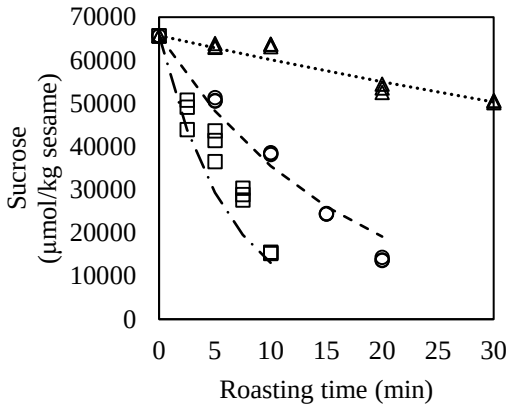
Figure 3.4. Model fits, provided according to comprehensive kinetic model to the experimental data (a) at 180°C, (b) at 200°C, (c) at 220°C.

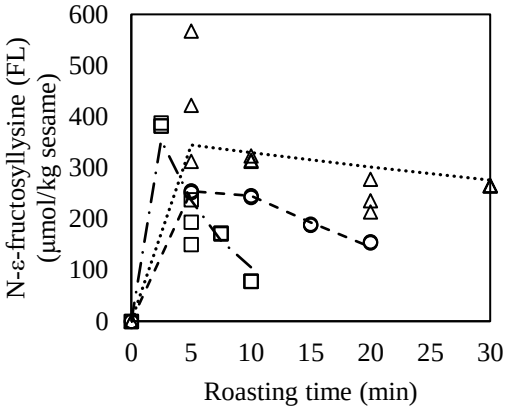
Considered the fits for the comprehensive model network, some of the reaction steps were excluded or included. Accordingly, Heyns product formed from not only presence of fructose but also from glucose under baking conditions [125]. Thus, interconversion of Amadori (N-ε-fructosyllysine) and Heyns product was involved in the reaction network. However, degradation of Heyns product (P2) was excluded from the model to reduce unknown parameters because it could not be defined precisely and, also not given an

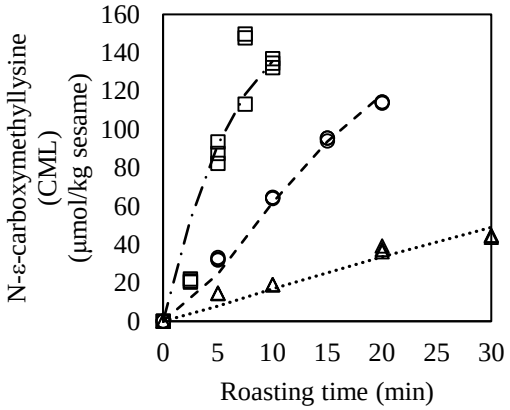
appropriate model. In addition to that, involvement in degradation products of dicarbonyl compounds (P4, P6, P7) with the reaction of amino acids, which lead to formation of various products resulted in not well prediction of fit because of not measurable compounds. Hence, they were omitted from the comprehensive model. Finally, by excluding the degradation parameters of CML and CEL (P8, P9) was achieved the best fitting kinetic model.

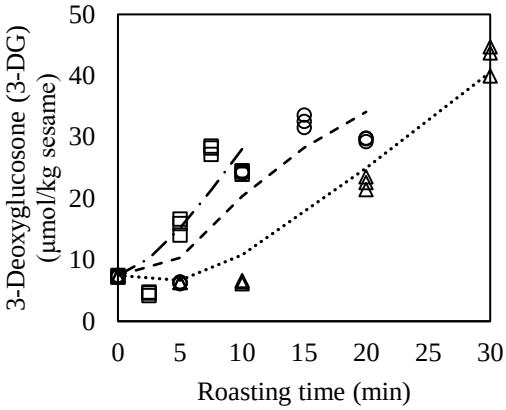
The proposed reaction mechanism for kinetics of glycation products and dicarbonyl compounds was acquired by excluding or including certain steps from the comprehensive model. Thus, the reaction network was simplified, and the estimation parameters were specified precisely. This ensured to unveil the important or predominant pathways in the model.

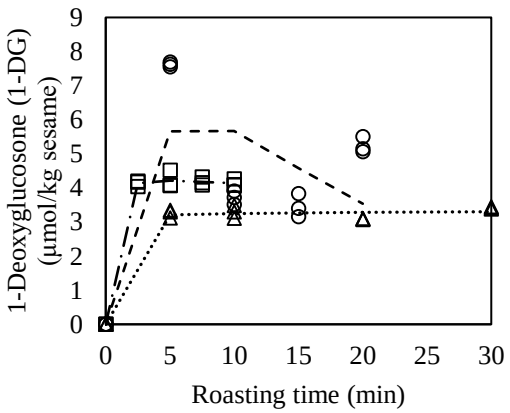
The proposed model was involved the sucrose degradation into glucose and fructofuranosyl cation, formation of Amadori and Heyns products from sucrose degradation products, formation of α-dicarbonyl compounds pathways and CML and CEL formation through Amadori/Heyns product or dicarbonyl compounds. Differential equations were set up and solved, model fits for predicted data were obtained afterwards (Figure 3.5).

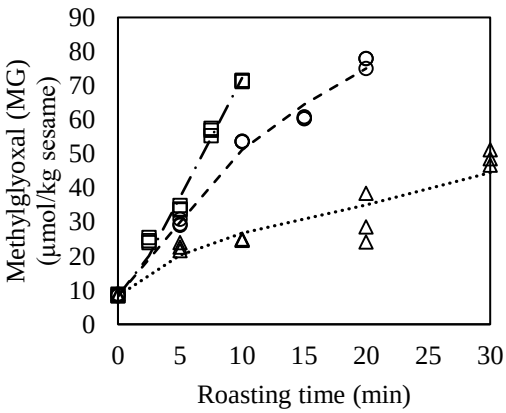

Sucrose (µmol/kg sesame)
70000
60000
50000
40000
30000
20000
10000
0
0 5 10 15 20 25 30
Roasting time (min)


N-ε-fructosyllysine (FL) (µmol/kg sesame)
600
500
400
300
200
100
0
0 5 10 15 20 25 30
Roasting time (min)


N-ε-carboxymethyllysine (CML) (µmol/kg sesame)
160
140
120
100
80
60
40
20
0
0 5 10 15 20 25 30
Roasting time (min)


3-Deoxyglucosone (3-DG) (µmol/kg sesame)
50
40
30
20
10
0
0 5 10 15 20 25 30
Roasting time (min)


1-Deoxyglucosone (1-DG) (µmol/kg sesame)
9
8
7
6
5
4
3
2
1
0
0 5 10 15 20 25 30
Roasting time (min)


Methylglyoxal (MG) (µmol/kg sesame)
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30
Roasting time (min)

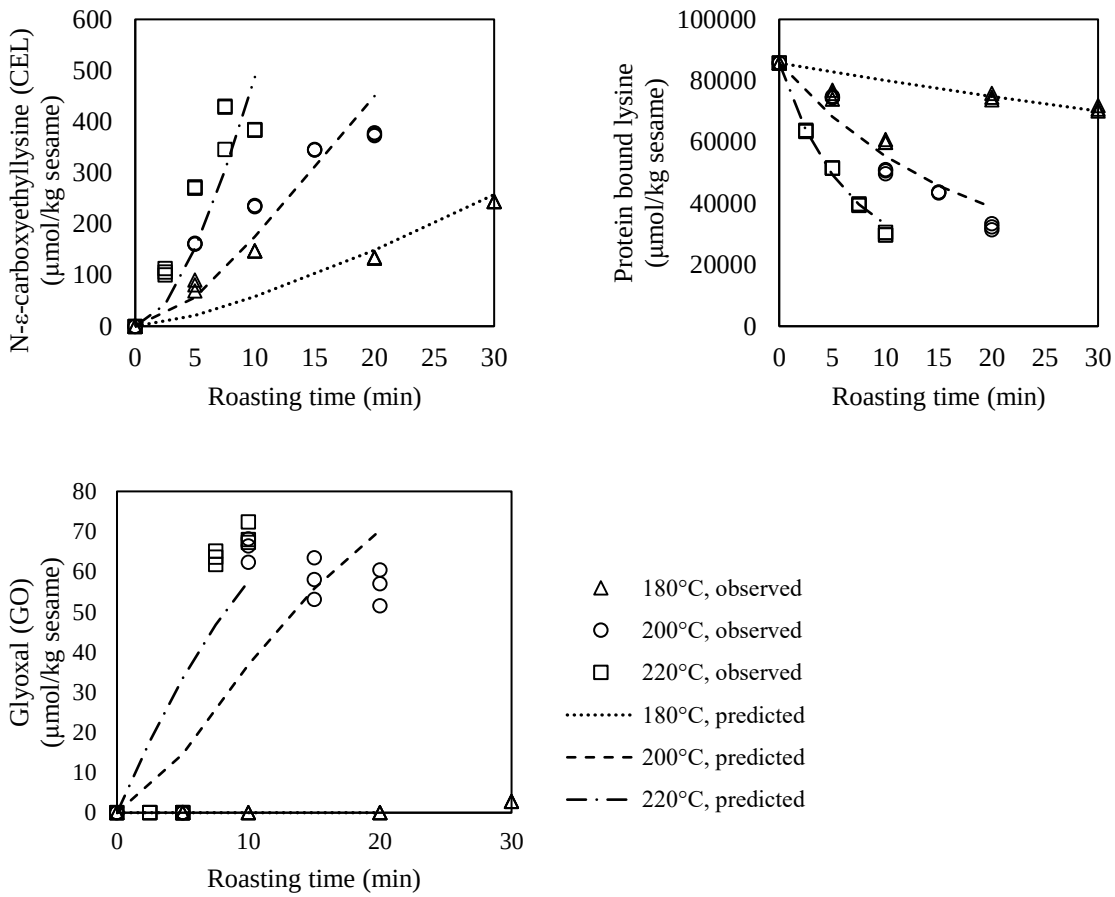


Figure 3.5. Kinetic model fit (lines) to the experimental data (markers) of reactants and products during roasting of sesame seeds.

Table 3.1. Reaction rate constants, their 95% highest posterior density (HPD) intervals, activation energies (E_a) and coefficient of determination (R^2) for sesame seeds at selected roasting temperatures.

	Elementary reaction step	Rate constant	180°C		200°C		220°C		E_a	R^2
			k	HPD	k	HPD	k	HPD	(kJ/mol)	
1	SUC → GLU/FFC	$min^{-1} \times 10^3$	8.9	±0.95	61.7	±4.5	161.4	±7.2	135	0.972
2	GLU → GO	$min^{-1} \times 10^3$	0	±0	0	±0	168.1	±43.3	-82	0.729
3	GLU + Lys → FL	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	14.8	±8.0	1.14	±0.13	0.67	±0.07	145	0.891
4	GLU → 3-DG	$min^{-1} \times 10^3$	0	±0	511	±241	14.6	±41.1	-345	0.848
5	FFC + Lys → HP	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	2.8	ind*	38.2	ind*	2.1	ind*	-10	0.004
6	FL → GO	$min^{-1} \times 10^3$	0	±0	17.3	±3.1	0	±0	-5	0.006
7	FL → P	$min^{-1} \times 10^3$	1347	±247	172	±31	4916	ind*	57	0.130
8	FL → CML	$min^{-1} \times 10^3$	5.3	±0.7	29	±0.9	54	±6.5	108	0.940
9	FL → 1-DG	$min^{-1} \times 10^3$	21	±4.8	77	±13.3	13	±3.0	-21	0.058
10	GO + Lys → CML	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	0	±0	0.0030	±0.00063	0.0094	±0.0034	-546	0.699
11	HP → 3-DG	$min^{-1} \times 10^3$	2.8	ind*	0.39	±0.20	0.075	±0.089	-169	0.999
12	3-DG → MG	$min^{-1} \times 10^3$	123.2	±79.4	500	±263	18.8	±110.2	-84	0.303
13	HP → 1-DG	$min^{-1} \times 10^3$	0.88	±0.60	0.02	±0.18	0.13	±0.04	-92	0.271
14	1-DG → MG	$min^{-1} \times 10^3$	2363	±491	3455	±1274	1578	±404	-18	0.244
15	MG + Lys → CEL	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	0.0037	±0.0007	0.00939	±0.00124	0.027	±0.004	91	0.995
16	HP → CEL	$min^{-1} \times 10^3$	0.00098	±0.00024	0.00080	±0.00015	1.96	±0.33	348	0.708

*ind: Indeterminate.

The reaction rate constants for each roasting temperature were given in Table 3.1, with ±95% HPD. Excluding for k_5, k_7 and k_{11}, the rest of rate constants of the reaction steps were determined in ±95% HPD interval. The reason of the uncertainty in these steps might be arisen from some unquantifiable compounds such as HP, fructofuranosyl cation and degradation product of N-ε-fructosyllysine. Even so, these compounds were not omitted from the model because it was not obtained better model fits under this situation.

The activation energy for each elementary step was shown in Table 3.1. Generally, the activation energies of the chemical reactions in food systems vary around 120 kJ/mol [91]. This was proved in a study of glucose/glycine model system [126]. Evaluating the results in this study, degradation of sucrose into glucose and fructofuranosyl cation was fairly temperature dependent (E_a; 135 kJ/mol). FL degraded preferably into CML (E_a; 108 kJ/mol) rather than GO and another reaction product as the roasting temperature increased. As for CEL, it was shown that formation of CEL through HP appeared to be more important at higher temperatures (E_a; 348 kJ/mol). On the other hand, the reaction between MG and lysine residue for CEL formation was highly temperature dependent (E_a; 91 kJ/mol). It could be deduced from that CEL occurred mostly from MG and lysine. Since Maillard reaction and caramelization consist of a diverse complex mechanism, some of the activation energies of reaction steps were inconsistent with Arrhenius equation defining temperature dependence. Additionally, most of activation energies of chemical reactions were found as negative value. This might be attributed to reactions that having no barriers. Maillard reaction comprises of complex reaction stages, but in order to simplify the model, it was assumed that some of these stages took place in a single step despite of the fact that they were composed of several steps. This led to accumulation of intermediate products providing free energy to the reaction. Hence, these kinds of reactions able to proceed without potential barrier [127].

3.3.3. Reaction Network Model

In dry conditions and at high heating temperatures, sucrose breakdowns into glucose and fructofuranosyl cation rather than its hydrolysis to glucose and fructose [95]. For this reason, formation of fructofuranosyl cation and glucose through sucrose in dry pyrolytic conditions was incorporated into the model. However, the addition steps of their degradation products with the reaction of amino acids (P1 and P5) did not give a good fit in glucose and fructofuranosyl cation because they are unquantifiable compounds, hereby were removed from the model.

Maillard reaction is a condensation of an amine with a carbonyl compound inducing the formation of Schiff base. In case of an aldose sugar as a carbonyl compound, formation of Schiff base is followed by rearrangement to Amadori product [35]. If Amadori product reacted with lysine, an amino acid, then Amadori product of lysine occurs, named as N-ε-fructosyllysine [40]. Therefore, formation of FL through with the reaction of glucose and protein bound lysine was added to the reaction system. On the other hand, interaction

between the fructofuranosyl cation and protein bound lysine induces forming of HP [95], and which was also included in the model. Since their formation occurs readily, these reaction steps were presumed to a single reaction step. However, the step of the interconversion of FL and HP was excluded as the reaction rate was found in lower bound. The estimated reaction rate constants of FL formation (k_3) were 14.8×10^{-3}, 1.14×10^{-3} and 0.67×10^{-3} kg.μmol^{-1}.min^{-1} for 180, 200 and 220°C, respectively. On the other hand, the rate constants of HP formation (k_5) were 2.8×10^{-3}, 38.2×10^{-3} and 2.1×10^{-3} kg.μmol^{-1}.min^{-1} for 180, 200 and 220°C, respectively. FL formation was the fast step at 180°C, which indicates the early stage of Maillard reaction while HP formation became predominant as the reaction proceeded. However, HP formation (k_5) could not be estimated precisely within ±95% HPD interval and, this might be resulted from that HP could not be quantified experimentally.

Degradation of Amadori product results in 3-DG and 1-DG formation [128]. During degradation, amino acids are regenerated, however, its data was removed from the model to obtain a good estimated data. The formation rate of 3-DG from FL was estimated to be zero or in lower bound; hence it was not included in the reaction mechanism. The reason is that amino acids regeneration occurs via hydrolysis, but the roasted sesame seeds have highly dry condition. On the other hand, 3-DG formation through HP decreased with the roasting temperature increased. However, the rate constant (k_{11}) for roasting at 180°C and 220°C could not be estimated in ±95% HPD interval. Apart from HP, glucose degradation contributed to the formation of 3-DG, but the reaction rate constant (k_4) was estimated as zero at 180°C. As the roasting temperature increased, the rate constant increased, afterwards decreased. Contrary to these results, Taş and Gökmen [109] reported that the rate of 3-DG formation through HP increased when the roasting temperature was increased (from 150°C to 170°C) and degradation step of Amadori product and glucose were not significant pathways compared with that of HP degradation. The reason for that might be different roasting temperature applied. Thus, the reaction behaviour might change with a rise in temperature.

As for 1-DG, when compared with the rate constant of FL (k_9) and HP (k_{13}) pathway for each roasting temperature, it was shown that formation of 1-DG mainly proceeded with FL degradation. Namely, Amadori product degradation played an important role in comparison with HP in 1-DG formation in this model.

Hollnagel and Kroh proposed that MG could be emerged from retro-aldolization reaction of mainly 1-DG and, also 3-DG [45]. According to the findings in the proposed kinetic model, the rate constant of MG formation through 1-DG (k_{14}) was comparatively higher than that of 3-DG. However, MG generation from 3-DG was not estimated with an appropriate certainty at 220°C. It was deduced from the results that 1-DG was found to be a pioneer for the formation of MG during roasting of sesame seed. This could be linked that the reactivity of 1-DG is higher than 3-DG [129]. Similar to results of that study, the formation of MG via 3-DG was of minor importance during kinetic modelling of glucose/flour system [49]. Likewise, the same consequence was reported in a kinetic model of Maillard reaction and caramelization during roasting of hazelnut [109].

GO formation consists of two possible pathways; the first way is from glucose by retro-aldol scission [41] and, the second way is from hydrolysis of Schiff base [51]. The latter pathway was simplified to a single step by disregarding rearrangement stage and, the formation of GO was regarded from only N-ε-fructosyllysine. In addition to that, GO generation through FL was included in the proposed model to achieve the best model fitting to the estimated data. The formation and degradation rate constants of GO (k_2, k_6, k_{10}) was fixed to be zero at 180°C because it was not detected any formation at that temperature. At the roasting temperature was 200°C, the formation rate of GO through glucose was estimated to be zero whereas FL pathway became predominant. However, at the roasting temperature was 220°C, glucose for GO formation was found to be quantitively important while the formation rate of GO through FL was estimated to be zero. Additionally, the model fit for GO was not given well estimated because of the limited of data points in GO. The degradation step of FL (k_7) was found to be highest for each roasting temperature, even though the reaction rate constant at 220°C was not estimated with high precision. Despite all these, the model fits and reaction rate constants together with estimated data imprecisely were acceptable.

CML formation can result from the reaction with glyoxal and lysine residue [61], and oxidation of N-ε-fructosyllysine [59]. According to the kinetic model, the reaction rate constant for CML formation through glyoxal (k_{10}) was estimated as zero at 180°C and, for roasting temperatures at 200°C and 220°C, the rate constant found to be quite lower compared with FL pathway. In view of these findings, it could be stated that CML formation from FL (k_8) was the predominant step.

CEL, is a homologue of CML, can be mostly formed as a result of the reaction between MG and lysine. MG is considered as mainly responsible for CEL formation, the role of other reactants could not be clarified exactly, though [117]. A study conducted by Treibmann et al [125] was noticed that formation of CEL correlated with concentrations of Heyns rearrangement product. Hence, CEL formation through HP was added to the model and both reaction pathways were tested. According to the results, the rate constant of CEL from MG (with a reaction of protein bound lysine) was relatively higher than that of HP for sesame seed roasted at 180°C and 200°C. Nonetheless, when the roasting temperature was 220°C, it was observed that CEL generation from HP became predominant, as the reaction rate constant (k_{16}) was indicated to be the fast step.

3.4. Multiresponse Kinetic Modelling of HMF and Acrylamide Formation

3.4.1. Kinetic Data Analysis

For the kinetic modelling of HMF and acrylamide in sesame seeds during roasting, data of reactants and products (roasted at 180, 200 and 220°C for 2.5-30 min) obtained from the previous chapter was used. The reactants were sucrose and amino acids (free amino acids and asparagine) while the products were 3-DG, HMF and acrylamide. Their concentrations were stated as μmol/kg sesame seed.

A kinetic model was suggested including formation of HMF and acrylamide through Maillard reaction and caramelization appearing during roasting of sesame seeds (Figure 3.7).

For each reaction step, a reaction rate constant (k) was given and reaction network was described by building a differential equation. Then each of them was solved by numerical integration to figure out the reaction mechanism. In this way, it is possible to observe linking between reactants and products. Parameter estimation was determined via using Athena Visual Studio software (v.14.2) with non-linear regression for each temperature. The estimated parameters and experimental data were compared to evaluate whether the kinetic model was appropriate with goodness of fit and posterior probability criterion [124].

$$\frac{d[SUC]}{dt} = -k_1[SUC]$$

$$\frac{d[GLU]}{dt} = k_1[SUC] - k_2[GLU][AA] - k_8[GLU][ASN] - k_5[GLU]$$

$$\frac{d[FFC]}{dt} = k_1[SUC] - k_3[FFC]$$

$$\frac{d[HMF]}{dt} = k_3[FFC] + k_6[3-DG] - k_7[HMF][ASN] - k_4[HMF]$$

$$\frac{d[3-DG]}{dt} = k_5[GLU] - (k_6 + k_{11})[3-DG]$$

$$\frac{d[ACR]}{dt} = k_7[HMF][ASN] + k_8[GLU][ASN] - k_{10}[ASN]$$

$$\frac{d[ASN]}{dt} = -k_7[HMF][ASN] - k_8[GLU][ASN] - k_9[ACR]$$

$$\frac{d[AA]}{dt} = -k_2[GLU][AA]$$

$$\frac{d[MRP]}{dt} = k_2[GLU][AA]$$

$$\frac{d[P_1]}{dt} = k_4[HMF]$$

$$\frac{d[P_2]}{dt} = k_9[ACR]$$

$$\frac{d[P_3]}{dt} = k_{10}[ASN]$$

$$\frac{d[P_4]}{dt} = k_{11}[3-DG]$$

In order to determine the temperature dependence of the reactions, activation energies, E_a (kJ/mol) were calculated by building the Arrhenius equation

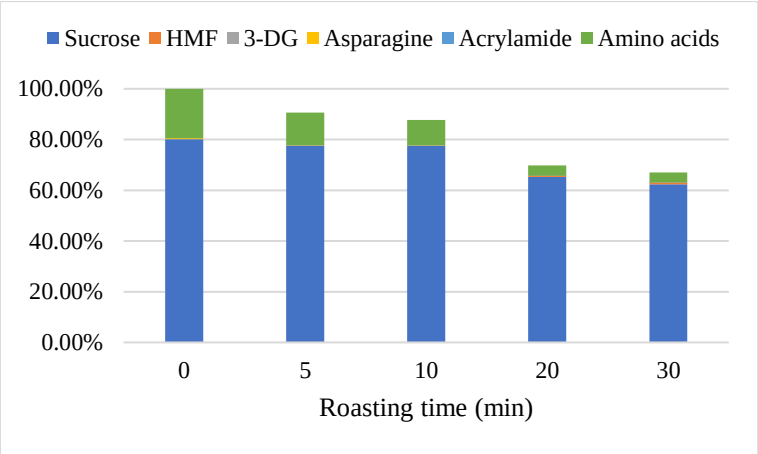
$$k(T) = A \times \exp\left(\frac{E_a}{RT}\right)$$

where R is the gas constant (8.3145×10^{-3} kJ/mol K), T is the temperature, k is the reaction rate constant and A is the preexponential factor. In order to calculate the activation energy (E_a) for each individual reaction, a plot of lnk (T) versus 1/T was used, whose slope gives E_a.

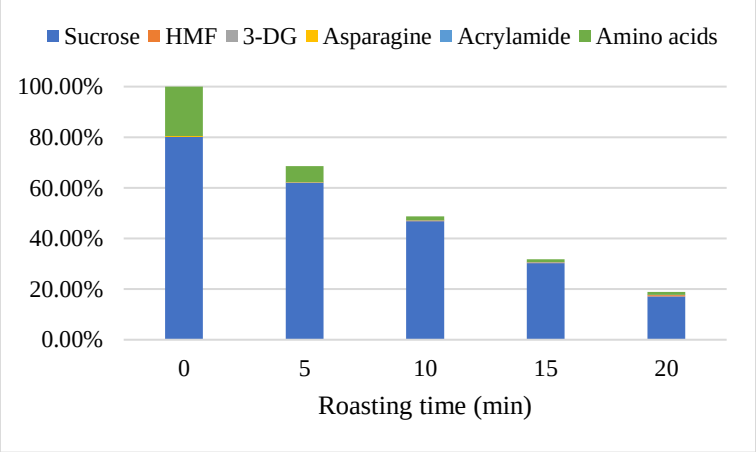
3.5. Results and Discussion

3.5.1. The Mass Balance

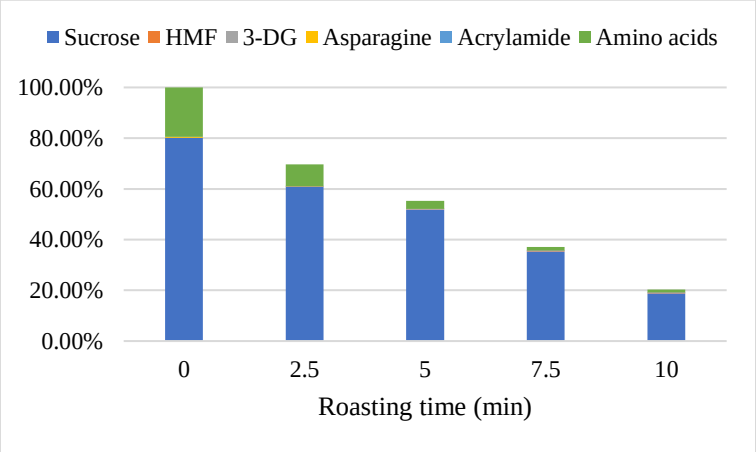
The mass balances of the reactants and the products calculating as the relative ratio of each compound (%) for all roasting temperature and time conditions were presented in Figure 3.6.



(a)



(b)



(c)

Figure 3.6. Mass balance (%) of reactants and products during roasting of sesame seed (a) 180°C (b) 200°C (c) 220°C.

As shown in Figure 3.6, total moles of reactants and the products declined within the progress of roasting. At 180°C, the recovery after 5 min of roasting was 90% while it was found as 67% at the end of 30 min. Besides, the recovery at 200°C was 68% and 19% after roasting for 5 min and 20 min, respectively. The total moles of these compounds were 70% and 20% for 2.5 and 10 min of roasting at 220°C, respectively. These results indicated that a gradual decrease in total moles of the compounds marked the changes of progress in early and advanced stage of Maillard reaction and, also caramelization. Melanoidins, which is one of the not identified final products in Maillard reaction might be the reason for inconsistency in the mass balance [96,122].

3.5.2. Kinetic Modelling

Reactants, intermediates and water content found in foods is not uniformly dispersed; therefore, kinetic modelling of real foods is a demanding duty. The changes in water during thermal process should be incorporated into the model. However, heat and mass transfer coefficients of water were neglected in this model as the amount of water in sesame seeds was very limited.

Model discrimination for (1) sucrose degradation and HMF formation, (2) formation and elimination of 3-DG, (3) formation of acrylamide was drawn to obtain the appropriate model characterizing the experimental data. For this purpose, the mechanistic reaction mechanism was performed and illustrated in Figure 3.7. According to the results, the model fits of acrylamide could not be well estimated for the roasting temperature at 200°C and 220°C (Figure 3.8). It was necessary a revision to obtain a compatible model. By making model discrimination, some reaction steps, which were illustrated in grey, were excluded.

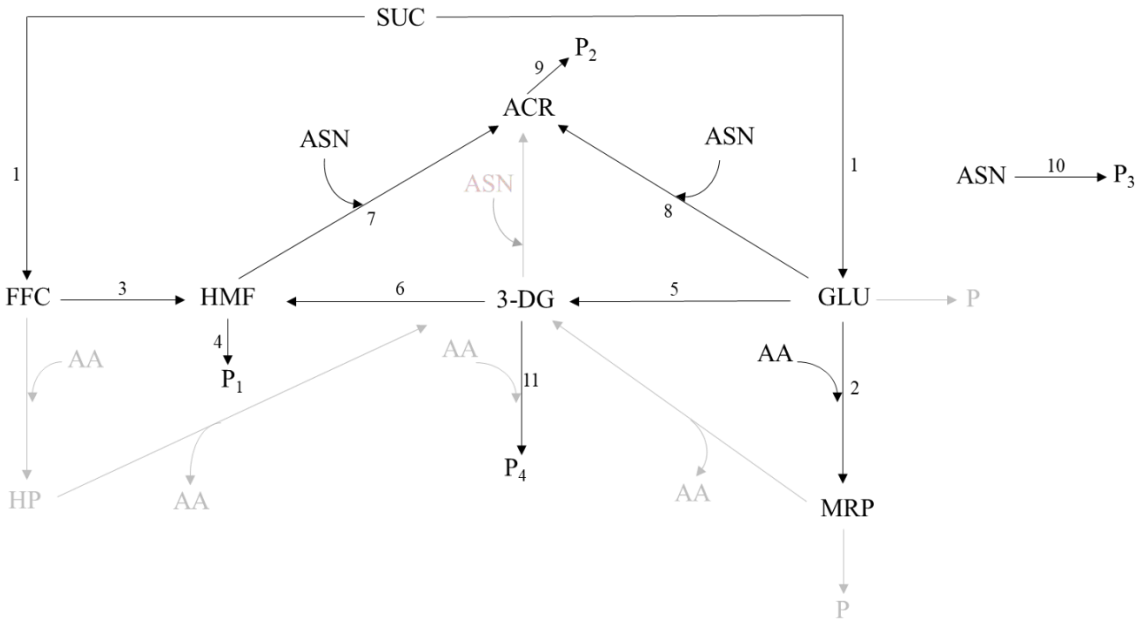
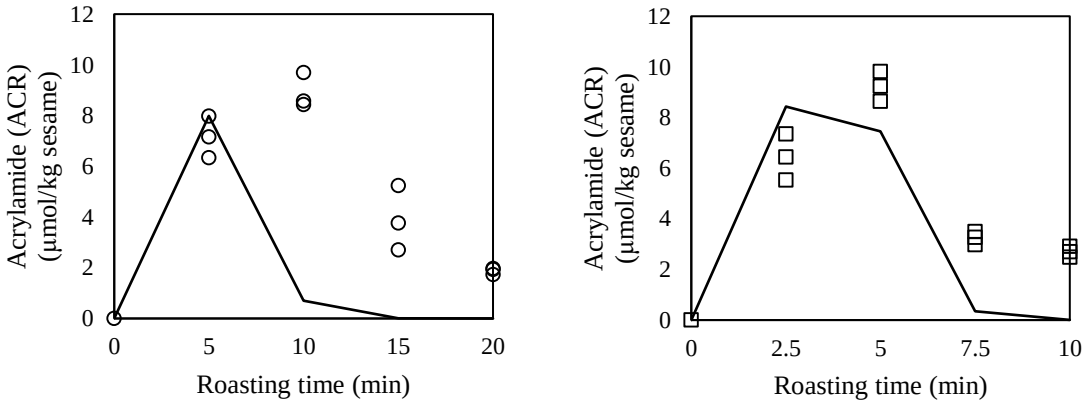


Figure 3.7. Mechanistic model of HMF and acrylamide formation from Maillard reaction and caramelization during roasting of sesame seeds. SUC, sucrose; GLU, glucose; FFC, fructofuranosyl cation; MRP, Maillard reaction product; HP, Heyns product; 3-DG, 3-deoxyglucosone; ASN, asparagine; ACR, acrylamide; AA, total free amino acids; P, products.

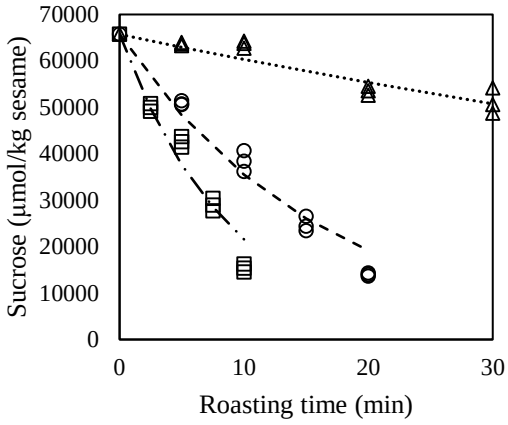


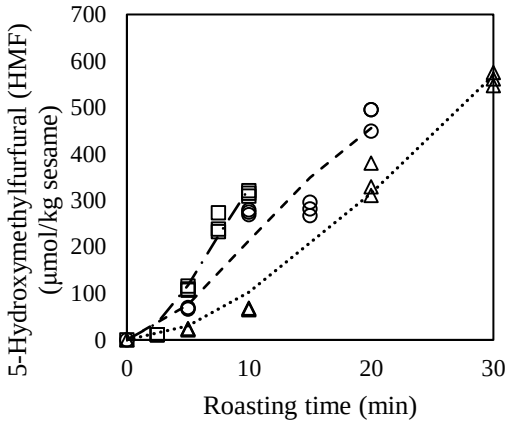
(a) (b)

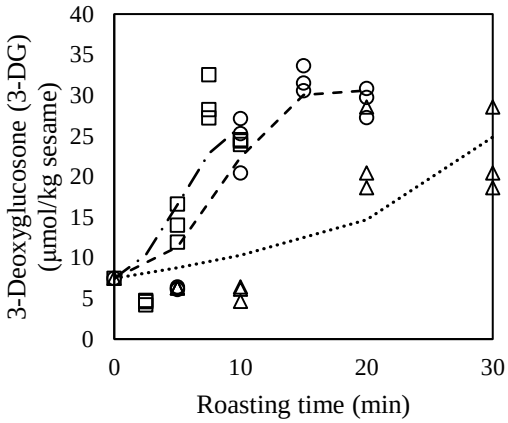
Figure 3.8. Model fits indicating acrylamide formation, obtained according to mechanistic kinetic model. Straight lines represent model fit according to estimated data. (a) Open circular (○) marker assigned acrylamide formation to the experimental data at 200°C; (b) open square (□) marker assigned acrylamide formation to the experimental data at 220°C.

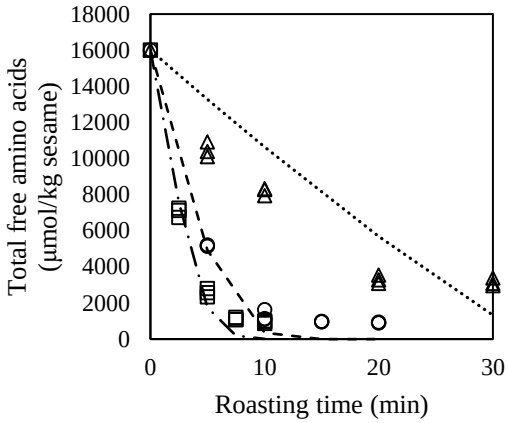
By excluding the certain steps from the mechanistic model, the reaction mechanism for the formation of HMF and acrylamide was acquired. Since the reaction network was simplified, the estimation parameters were specified precisely, and model fit was obtained describing the observed data. This ensured to unveil the important or predominant pathways in the model.

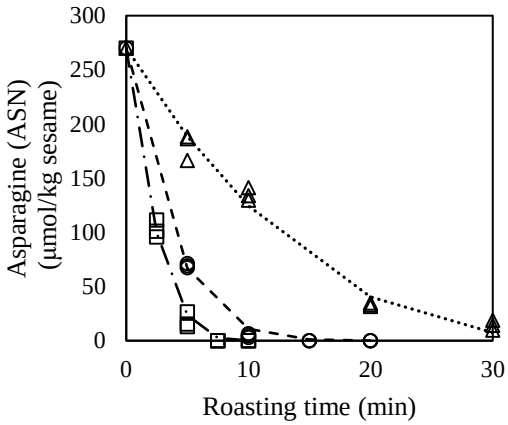
The mechanistic model was involved in sucrose degradation into glucose and fructofuranosyl cation, formation of 3-DG from glucose or HP, HMF formation through fructofuranosyl cation or HP, acrylamide formation through the reaction of ASN with HMF and glucose or 3-DG, degradation products of these compounds. Differential equations were set up and solved, model fits for predicted data were obtained afterwards (Figure 3.9).


Sucrose (µmol/kg sesame)
70000
60000
50000
40000
30000
20000
10000
0
0
10
20
30
Roasting time (min)


5-Hydroxymethylfurfural (HMF) (µmol/kg sesame)
700
600
500
400
300
200
100
0
0
10
20
30
Roasting time (min)


3-Deoxyglucosone (3-DG) (µmol/kg sesame)
40
35
30
25
20
15
10
5
0
0
10
20
30
Roasting time (min)


Total free amino acids (µmol/kg sesame)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
10
20
30
Roasting time (min)


Asparagine (ASN) (µmol/kg sesame)
300
250
200
150
100
50
0
0
10
20
30
Roasting time (min)

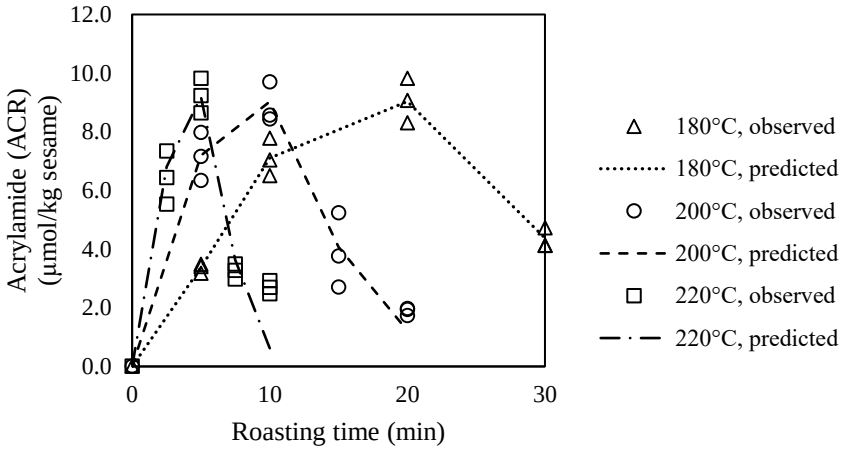


Figure 3.9. Kinetic model fit (lines) to the experimental data (markers) of reactants and products during roasting of sesame seeds.

Table 3.2. Reaction rate constants, their 95% highest posterior density (HPD) intervals, activation energies (E_a) and coefficient of determination (R^2) for sesame seeds at selected roasting temperatures.

	Elementary reaction step	Rate constant	180°C		200°C		220°C		E_a (kJ/mol)	R^2
			k	HPD	k	HPD	k	HPD		
1	SUC → GLU/FFC	$min^{-1} \times 10^3$	8.62	±0.88	61.6	±5.3	111.4	±11.0	120	0.926
2	GLU+AA → MRP	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	1.03	±0.33	0.08	±0.04	0.07	±0.03	-125	0.782
3	FFC → HMF	$min^{-1} \times 10^3$	5.41	±1.16	2.55	±1.18	2.80	±0.71	-31	0.670
4	HMF → P_1	$min^{-1} \times 10^3$	84.1	±31.1	212.6	±136.6	256.7	±121.8	52	0.888
5	GLU → 3-DG	$min^{-1} \times 10^3$	7.20	±3.40	104.4	±57.9	128.6	±175.1	135	0.823
6	3-DG → HMF	$min^{-1} \times 10^3$	0	±0	0	±0	0	±0	-	-
7	HMF+ASN → ACR	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	0.20	±0.04	0.75	±0.28	2.96	±0.93	125	0.999
8	GLU+ ASN → ACR	$kg \times \mu mol^{-1} \times min^{-1} \times 10^3$	0.10	±0.02	0	±0	0	±0	-650	0.771
9	ACR → P_2	$min^{-1} \times 10^3$	348.9	±43.5	278.3	±42.89	1053	±227	50	0.578
10	ASN → P_3	$min^{-1} \times 10^3$	66.0	±6.20	258.5	±10.2	359.8	±24.1	79	0.905
11	3-DG → P_4	$min^{-1} \times 10^3$	0	±0	43559	±9922	77065	±60470	1287	0.786

The reaction rate constants for each roasting temperature were given in Table 3.2, with ±95% HPD. Almost all rate constants of the reaction steps were determined in ±95% HPD interval. The reason of the uncertainty in these steps might arise from some unquantifiable compounds like degradation product of 3-DG. Even so, these compounds were not omitted from the model because the results obtained were not better under these conditions.

The activation energy for each elementary step was shown in Table 3.2. Generally, the activation energies of the chemical reactions vary around 120 kJ/mol [91]. This was proved in a study of glucose/glycine model system [126]. Evaluating the results in this study, degradation of sucrose into glucose and fructofuranosyl cation was fairly temperature dependent (E_a; 120 kJ/mol). Also, 3-DG formation through glucose was highly

temperature dependent (E_a; 135 kJ/mol). As for acrylamide, it was shown that formation of acrylamide through the reaction with HMF and ASN appeared to be more important at higher temperatures (E_a; 125 kJ/mol). Several activation energies of chemical reactions were found as negative value, as in HMF formation from fructofuranosyl cation. This might be attributed to reactions that having no barriers. Maillard reaction comprises of complex reaction stages, but in order to simplify the model, it was assumed that some of these stages took place in a single step despite of the fact that they were composed of several steps. This led to accumulation of intermediate products providing free energy to the reaction. Hence, these kinds of reactions can proceed without potential barrier [127].

3.5.3. Reaction Network Model

Owing to low moisture content, sesame seeds reach high temperatures instantly during heating. As a result of these conditions, sucrose could decompose resulting in the liberating of glucose and fructofuranosyl cation through the cleavage of glycosidic bond. This very reactive cation is the pioneer of HMF at high temperatures and under dry systems [95]. Glucose can contribute to HMF formation as well, but for its formation, dicarbonyl compound such as 3-DG must be generated through Maillard reaction and caramelization [52,95]. Besides, fructofuranosyl cation can also occur from fructose in dry pyrolytic conditions, but it is known to be very difficult under these conditions [95]. Considering all the possible pathways, HMF formation through fructofuranosyl cation and 3-DG were included in the model network.

Expectedly, the rate constant of sucrose degradation increased by increasing temperature. The formation rate of HMF from 3-DG (k_6) was estimated as zero at all temperatures whereas the estimated rate constants of HMF via fructofuranosyl cation (k_3) were 5.41×10^{-3}, 2.55×10^{-3} and 2.80×10^{-3} min^{-1} for 180, 200 and 220°C, respectively. Similarly, it was reported that 3-DG pathway for HMF generation was of kinetically less importance than fructofuranosyl cation during roasting of hazelnut [109]. In addition to that, the degradation rate of HMF (k_4) increased with temperature.

Apart from HMF formation, the interaction of fructofuranosyl cation and amine group gives rise to fructofuranosyl amine which can rearrange into HP [95]. The rate constant for HP via fructofuranosyl cation was found as lower rate bound; for this reason, this pathway was excluded from the model.

Some compounds are tended to degradation and polymerization reactions. Glucose, a product emerging from decomposition of sucrose can form Maillard reaction products (MRPs) by reacting with any of free amino acids. These products are known as flavour and color compounds. Even though MRP was not measured experimentally, it was added to the model to obtain good modelling results. The reaction rate constant of MRP from glucose (k_2) slightly changed with the roasting temperature. Additionally, glucose might decompose to its degradation products. However, this step and, also degradation product of MRP were omitted since they did not fit well to the experimental values.

In the formation 3-DG, MRP and HP pathways occurring from glucose degradation were tested. 3-DG formation through HP was estimated in lower bound, thus this step was excluded to simplify the kinetic model. Additionally, 3-DG formation by the reaction between MRP and amino acids was not included in the model because the fits of model were not estimated well. On the other hand, degradation rate of glucose (k_5) for 3-DG increased as the roasting temperature increased. However, its rate constant at 220°C could not be determined in the 95% HPD interval.

The reaction between dicarbonyl compounds and amino acids is defined as Strecker degradation which plays a role in colour and aroma formation [130]. Furthermore, melanoidins are eventuated as a result of polymerization reaction of α-dicarbonyl compounds [131]. However, by including the reaction of 3-DG with amino acids in the mechanistic model was not compatible experimentally. Therefore, amino acid was excluded in this step. The reaction rate of 3-DG degradation (k_{11}) was found as zero at 180°C, interestingly, it showed a sudden rise at further temperatures.

The primary mechanism of acrylamide generation via the Maillard reaction during heating at high temperatures is the interaction of ASN with a carbonyl compound [31,74,76,77]. There are two pathways responsible for the acrylamide formation, which are defined as a generic amino acid route and a specific amino acid route. In the generic amino acid pathway, firstly the reaction of a reducing sugar with amino acids induces to Schiff base and subsequently rearrangement to Amadori product or Heyns product (depending on an aldose or a ketose sugar). Then, they undergo dehydration and dicarbonyl, hydroxycarbonyl formation occurs afterwards. Lastly, these compounds lead to the formation of acrylamide by reacting with ASN in Strecker degradation. On the other hand, in the specific amino acid

pathway, acrylamide originates from the reaction between reducing sugar and ASN forming Schiff base and it is followed by decarboxylation [132]. In addition, it was reported in a study conducted by Gökmen et al [133], HMF is capable of acrylamide generation in dry system by reacting with ASN. Basically, reducing sugars are known as the primary reactants of acrylamide formation due to providing carbonyl source. However, the detectable level of any reducing sugar could not be observed in roasted sesame seeds. Considering this, HMF owing to its reactivity, could take part in acrylamide formation in sucrose-rich food system. All these probable pathways were involved in the acrylamide formation.

Comparing the formation rate of acrylamide from directly glucose-ASN with 3-DG-ASN, it was observed that 3-DG route was not quantitatively important pathway, thereby this step was excluded from the model network. However, the reaction rate of glucose with ASN (k_8) was rather low at 180°C, and it was estimated as zero with the temperature increased. As for HMF route, the estimated reaction rate (k_7) was 0.20×10^{-3}, 0.75×10^{-3} and 2.96×10^{-3} kg × μmol^{-1} × min^{-1} for 180, 200 and 220°C, respectively. It was clearly seen that the contribution of HMF to acrylamide production was predominant than glucose, unlike most of foods. This is the first study indicating the acrylamide formation through the reaction of HMF with ASN in a real food system.

Apart from involvement to acrylamide formation, ASN could also participate in degradation reaction, thereby form some products like fumaric acid and aspartic acid [134]. The degradation rate of ASN (k_{10}) increased by increasing the roasting temperature. Also, the reaction rate for acrylamide degradation (k_9) found to be quite higher than that of formation and showed an increasing trend with temperature.

3.6. Conclusion

The multiresponse kinetic modelling aimed to enlighten the progress of the Maillard reaction and caramelization during roasting of sesame seeds. For this purpose, two reaction models were created explaining the formation pathways of dicarbonyl compounds, furosine, CML, CEL, HMF and acrylamide. As a result, it was determined which steps were of major or less importance kinetically. The first model involved the degradation of sucrose into glucose and fructofuranosyl cation, formation of Amadori and Heyns products from sucrose degradation products, formation of α-dicarbonyl compounds pathways and CML and CEL formation through Amadori/Heyns product or dicarbonyl compounds. In the second model, the

reaction steps were sucrose degradation into glucose and fructofuranosyl cation, formation of 3-DG from glucose or Heyns product, HMF production from fructofuranosyl cation, acrylamide formation through the reaction of asparagine with HMF or glucose, degradation products of these compounds. It was deduced from the results that HMF formation occurred via fructofuranosyl cation while acrylamide was originated from the reaction of HMF and asparagine, not by specific or general amino acid pathway. HMF due to its reactivity take on a significance in acrylamide formation rather than reducing sugar in dry and sucrose-rich system during heating. To the best of our knowledge, it was shown for the first time that formation of acrylamide was to have progress via HMF route in real food. Additionally, it was concluded that 3-DG was not effective on HMF and acrylamide generation. According to the findings, CML formation by the degradation of Amadori product, fructosyllysine was the dominant pathway. As for CEL, it was formed from the reaction between methylglyoxal and lysine at 180°C and 200°C, while the roasting temperature at 220°C, Heyns product was responsible for CEL formation.

GENERAL CONCLUSION AND DISCUSSION

Investigation of the chemical changes as a result of roasting is of importance in foods. Among these chemical reactions, Maillard reaction is of great significance, as it leads to formation of both beneficial and hazardous compounds, during the roasting of sesame seeds. Sesame seed is mostly consumed after roasting at high temperatures, however, to date, the effect of roasting of sesame seeds on the Maillard reaction products including glycation products and heat-induced contaminants have not been explored in the literature. This thesis, therefore, aimed to investigate the formation of Maillard reaction products during roasting of sesame seeds. In addition to that, understanding the reaction mechanism by performing multiresponse kinetic modelling was also aimed.

Sucrose is the only detectable sugar in sesame seeds and its concentration decreased by increasing the roasting temperature. Similarly, a significant decline was observed in the concentration of total free amino acids, nearly 93% of which consumed at the end of roasting. Expectedly, HMF formation was promoted as the heat load increased and reached to the highest concentration in roasted temperature at 180°C, 75.6±8.5 mg/kg. Acrylamide concentration increased with roasting temperature and time to a certain extent and was followed by a decrease. The reason for that was the simultaneous progress of formation and elimination of acrylamide during heating of foods. In case of lacking in a precursor, especially asparagine, for acrylamide formation, elimination became predominant. It was concluded that this kinetic behaviour was similar to roasted coffee. Also, the changes in asparagine level in sesame seeds showed compatibility with acrylamide formation. Furosine, an early glycation product, reached to the maximum level (307.3±0.5 mg/kg) at 150°C for 5 min and was followed by a decreasing trend. The reason for the decline in furosine levels as a result of increasing temperature might be its possible conversion to other compounds. Furosine might be degraded or oxidized to advanced glycation end products like CML, during overheating. The amount of furosine in roasted sesame seeds was higher significantly than that of CML, representing the predominance of the early stage of Maillard reaction. Furan was found in trace amount in roasted sesame seeds and it yielded to 264.4±13.0 ng/g at the end of the roasting process. Since sesame seeds contain lignans having antioxidant property like sesamol and sesamolinol, the risk of furan formation might be low level. The roasting process led to the formation of α-dicarbonyl compounds which are 3-DG, 1-DG,

MG and DA, but they were found at relatively lower levels. However, their concentrations increased as a result of roasting.

Multiresponse kinetic modelling provides understanding the mechanism of Maillard reaction and caramelization along with by calculating reaction rate constant for each elementary step. For that, a kinetic model is recommended, and model fits are evaluated. According to the findings, sucrose breakdown resulted in the formation of glucose and fructofuranosyl cation in dry system. 1-DG was mainly formed from FL, 3-DG was generated through HP at 180°C while at 200°C and 220°C, glucose pathway was predominant. Also, MG formation via 1-DG was the fast step. In the formation of CML, the rate constant of FL was found as higher than GO. On the other hand, CEL was majorly produced from MG-lysine reaction at 180°C and 200°C.

Under low moisture conditions, HMF was generated through fructofuranosyl cation rather than 3-DG. Interestingly, it was found for acrylamide that the rate constant of the reaction between HMF and ASN was relatively higher than that of GLU and ASN system. Unlike generally known pathways, generic and specific amino acid pathway, it was the first study providing evidence for acrylamide formation through HMF in a real food system.

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APPENDIX

Publications

E. Berk, A. Hamzalıoglu, V. Gökmen, Investigations on the Maillard reaction in sesame (Sesamum indicum L.) seeds induced by roasting, Journal of Agricultural and Food Chemistry, 67 (**2019)** 4923-4930.

HACETTEPE UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING
THESIS/DISSERTATION ORIGINALITY REPORT

HACETTEPE UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING
TO THE DEPARTMENT OF FOOD ENGINEERING

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