Acrylamide Formation in Vegetable Oils and Animal Fats During Heat Treatment

G. Daniali [1], S. Jinap [1, 2, *], P. Hajeb [1], M. Sanny [1], C.P. Tan [3]

[1] Department of Food Science, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
[2] Department of Food Safety, Institute of Food Security, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
[3] Department of Food Technology, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

* Corresponding Author. E-mail: jinap@upm.edu.my, sjinap@gmail.com

Abstract. The method of liquid chromatographic tandem mass spectrometry was utilized and modified to confirm and quantify acrylamide in heating cooking oil and animal fat. Heating asparagine with various cooking oils and animal fat at 180 °C produced varying amounts of acrylamide. The acrylamide in the different cooking oils and animal fat using a constant amount of asparagine was measured. Cooking oils were also examined for peroxide, anisidine and iodine values (or oxidation values). A direct correlation was observed between oxidation values and acrylamide formation in different cooking oils. Significantly less acrylamide was produced in saturated animal fat than in unsaturated cooking oil, with 366 ng/g in lard and 211 ng/g in ghee versus 2447 ng/g in soy oil, followed by palm olein with 1442 ng/g.

Keywords: Acrylamide; Vegetable oils; Animal fats; LC–MS/MS; Oxidation values.

1. Introduction

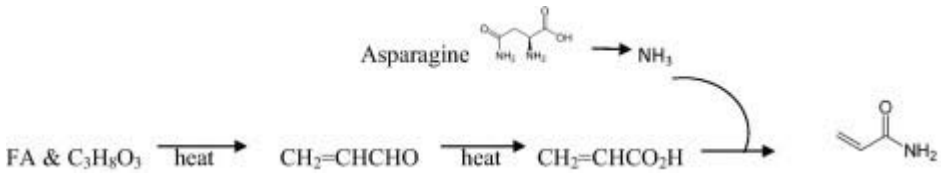
Acrylamide (2-propenamide) is a hydrophilic compound that has been classified as a probable human carcinogen. It is present in numerous fried foods such as potato crisps, French fries, breakfast cereals, coffee beans, snacks and bakery products. Acrylamide is a common toxic compound produced in oil after the frying of food (Matthaus et al., 2004 and Mestdagh et al., 2005).

Acrylamide is mainly produced by the Maillard reaction involving asparagines and reducing (Mottram, Wedzicha, & Dodson, 2002). The Maillard reaction occurs when free amino group with a reducing sugar to form Amadori products. In the next step, the degradation of Amadori products follows; the products are hydrolyzed to form 3-aminopropionamide, which can degrade to a further extent through the elimination of ammonia to form acrylamide when heated. Alternatively, the decarboxylated Schiff base can decompose directly to form acrylamide via elimination of an imine (Zyzak et al., 2003). There are some similarities in the formation of acrylamide, through Maillard and lipid pathway. First, amino acids in both of the reactions are sources of ammonia. Furthermore, both of the pathways require the carbonyl source in order for acrylamide formation to occur (Yasuhara et al., 2003 and Zyzak et al., 2003).

Acrylamide is formed in frying oil due to the degradation of the oil or to the interaction between carbonyl groups and other components (such as amino acids from the food) under high temperature (Aladedunye & Przybylski, 2011). These reactions are found to be related to the degradation and interaction between oxidants and other components and the formation of certain toxic compounds in deep fat frying oil after heat processing (Ou et al., 2010). Also, certain secondary lipid oxidation products may convert amino acids into either their corresponding Strecker aldehydes or vinylogous derivatives, depending on the amount of oxygen present in the reaction (Hidalgo and Zamora, 2007 and Zamora et al., 2007), thereby suggesting that a potential route for the contribution of these secondary lipid oxidation products to acrylamide formation in thermally treated foods. Under

appropriate conditions, oxidized proteins will result in the degradation of asparagine to acrylamide and contribute to the formation of this contaminant during food processing.

Previous studies have shown that degradation products of amino acids can also be produced during the Maillard reaction (Stadler et al., 2004 and Tareke et al., 2002). There are several reports regarding acrylamide formation from asparagine with carbonyl compounds. Heating asparagine with octanal, 2-octanone or 2,3-butanedione may result in the formation of various amounts of acrylamide (Becalski, Lau, Lewis, & Seaman, 2003). Glycolaldehyde and glyceraldehyde produce approximately 2 times and 1.75 times more acrylamide than glucose with asparagine respectively (Yaylayan, Wnorowski, & Perez Locas, 2003). Although according to Zamora and Hidalgo (2008), the presence of primary lipid oxidation products, or even unoxidized lipids under oxidizing conditions, is the only prerequisite needed to observe a positive contribution of lipids to acrylamide formation during food heating. It has been known for over half a century that α-amino acid produces ammonia via Strecker degradation in the presence of a carbonyl compound (Schonberg & Moubasher, 1952). Acrylic acid, which is an oxidation product of acrolein and glycerol, produces a significant amount of acrylamide with ammonia (Yasuhara et al., 2003). A fatty acid (such as pure linoleic acid and linolenic acid hydroperoxides) backbone showed by Ewert, Granvogl, and Schieberle (2014) to be the key precursor structure for acrolein formation. The hypothesized formation mechanisms of acrylamide from amino acids and lipids are shown below:



When oil is heated at temperatures above the smoke point, glycerol is degraded to acrolein and the formation of acrolein is known to increase directly with the increase in unsaturation in the oil. The oil is hydrolyzed into glycerol and fatty acids and acrolein is produced by the elimination of water from glycerol by a heterolytic acid-catalysed carbonium ion mechanism followed by oxidation (Uchida et al., 1999). Acrolein can also be produced as a result of oxidation of polyunsaturated fatty acids and their degradation products. Acrolein is also found to form in vivo by the metal-catalysed oxidation of polyunsaturated fatty acids, including arachidonic acid (Esterbauer, Schaur, & Zollner, 1991).

According to Pedreschi, Kaack, and Granby (2006) the free asparagines and the reducing sugars (acrylamide precursor) can leach out from the surface layer of cut potato to the media. It has also been shown by Mestdagh et al. (2005) that acrylamide precursor could indeed be transferred to the frying oil.

The objectives of this study are to determine the effect of asparagine on the formation of acrylamide in vegetable oils and animal fats and to assess the formation of acrylamide from asparagine in vegetable oils and animal fats having different oxidation values. Further detection of the acrylamide level present in oils has been carried out through the use of the analytical method.

2. Materials and methods

2.1. Materials

Sesame, soy bean, sunflower, corn, olive and palm olein oils, animal fat ghee and lard had been purchased from a local market (Serdang, Malaysia). Isotopic [13C3] acrylamide (isotopic purity, 99%) used as an internal standard was obtained from Cambridge Isotope Laboratories (Andover, MA, USA) at the concentration of 1 mg/ml and diluted to 50 ppb to form a working solution, which was used in the sample, standard and spiking acrylamide preparation. Acrylamide (standard for GC, assay ⩾99.8%) was obtained from Sigma–Aldrich (Hong Kong, China) in powder form, whereas Oasis MCX 3 cc (60 mg) liquid phase and Oasis HLB 3 cc (60 mg) solid phase extraction cartridges were purchased from Waters Corporation (Waters, Milford, MA, USA). Certified reference material

(CRM) toasted bread was purchased from European reference materials (ERM) (Geel, Belgium). Other chemicals were obtained from Fisher Scientific (Leicestershire, UK).

2.2. Experimental design

A model system was designed to study the influence of asparagine concentrations on the formation of acrylamide in cooking oils. Four different concentrations of asparagine were examined (0.1, 0.2, 0.3, 0.5 mg) in two types of vegetable oil (soybean and sunflower oil) and one type of animal fat (lard). The information obtained (the best amount of asparagine, 0.2 mg according to Table 3) was used to determine the acrylamide concentration in different vegetable oils and animal fats (sesame, soy bean, sun flower, corn, olive, palm olein oils, animal fat ghee and lard). Ten grams each of cooking oil and animal fat were mixed with 0.2 mg asparagine, transferred into a Petri dish and heated up at 180 °C (180 °C is the actual temperature in the probe oven when it was set at 188 °C) for 30 min. After cooling, the acrylamide concentration was determined. The experiment was replicated thrice. The oxidation values (peroxide value, iodine value and anisidine value) of the oils were measured before and after heat treatment. Correlations were drawn between the oxidation values and acrylamide formation for both oils and fats.

2.3. Instrumentation

Liquid chromatography–mass spectrometry (LC–MS-MS) analysis was performed on a TSQ Quantum Ultra (Thermo Scientific, San Jose, CA, USA) triple quadrupole mass spectrometer which was connected to an Accela High Speed LC quaternary high pressure pump and an Accela autosampler (Thermo Finnigan, San Jose, CA, USA). An atmospheric pressure chemical ionization (APCI) source was used to produce and introduce ions into the mass spectrometer, equipped with X-calibur software (Thermo Scientific, San Jose, CA, USA) for separation, detection and quantification. The analytical column was a porous graphitic carbon Hypercarb column (2.1 mm × 50 mm ID; 5 μm) (Thermo Electron, Bellafonte, PA, USA) maintained at 45 °C. The mobile phase was 100% water and the flow rate was maintained at 150 μl/min. The injection volume was 10 μl. Acrylamide was analyzed using the APCI in positive ion mode. Selective reaction monitored mode (SRM) was acquired with the characteristic fragmentation transitions m/z 72 > 55 ([M+H–NH3]+) for acrylamide and m/z 75 > 58 for [13C3] acrylamide. The APCI-optimized parameters were: discharge current, 4 μA; capillary temperature, 250 °C; sheath gas pressure, 10 arb and auxiliary gas pressure, 12 arb. Tube lens offset voltages were optimized for acrylamide using the automated optimization procedure in syringe infusion mode provided by the manufacturer. The argon collision gas pressure was adjusted to 2.9e-5 psi (1.5 mTorr) for MS/MS. A spectrophotometer (Spectronic 20 Ginisys, Rockford, IL, USA) with a wavelength range of 340–950 nm and a nominal spectral band width of 20 nm (consistent over the entire wavelength range) was used in the study to determine anisidine values.

2.4. Determination of peroxide values

The primary products of lipid oxidation and hydro peroxides are generally referred to as peroxides. Peroxide values were determined by using conventional iodometric titration with thiosulfate (AOAC, 1984). The sample was suspended in 25 mL of an acetic acid/chloroform (3:2) mixture and 0.5 mL of saturated KI. The resulting mixture was kept in the dark for 5 min, after which 70 mL of distilled water and 1 mL of a 1% (w/v) solution of starch paste were added. The mixture was then titrated with sodium thiosulfate 0.01 N. The POV of the sample was calculated by using the following equation:

S is the titration of sample (mL), B is the titration of blank (mL), while N is the normality of thiosulfate solution and W is the weight of sample (g) (AOAC, 1984).

2.5. Determination of iodine values

Iodine values (IVs) were used to determine the amount of unsaturated fatty acids, which, in the form of double bonds, reacted with iodine compounds. The iodine values of the oils extracted from the commercial samples were determined according to AOCS (1993). Weighed samples were placed in a 500 ml conical flask followed by the addition of 20 ml of carbon tetrachloride and 25 ml of Wijs reagent. A stopper was inserted and it was rotated and placed in the dark for an hour; after which 20 ml of potassium iodide (10% concentration) was added to the flask, followed by 100 ml of pure water. This mixture was titrated with 0.1 M of sodium thiosulfate solution until the yellow color disappeared.

A few drops of starch solution were added before continuing the titration until the blue color disappeared. The IV of the sample was calculated by using the following equation:

C is the concentration of the sodium thiosulfate solution (mol/L), V1 is the volume (mL) of sodium thiosulfate solution used for the blank test, V2 is the volume (mL) of sodium thiosulfate solution used for the sample test and M is the mass (g) of the sample.

2.6. Determination of anisidine values

Anisidine values (AnVs) represented the level of non-volatile aldehydes, primarily 2-alkenes, present in the fat. Solution (a) was prepared by dissolving 0.500 g of oil in trimethylpentane with the volume brought to 25.0 ml with the same solvent using a volumetric flask. Solution (b) was prepared by adding 1.0 ml of a 2.5 g/L solution of p-anisidine in glacial acetic acid and then shaken in a dark place. A reference solution was prepared by adding 5.0 ml of trimethylpentane to 1.0 ml of a 2.5 g/l solution of p-anisidine in glacial acetic acid and then shaken in the dark, until the absorbance of solution (a) at the maximum at 350 nm using trimethylpentane as the compensation liquid was measured. The absorbance of solution (b) was measured at 350 nm exactly 10 min after its preparation using the reference solution as the compensation liquid. The anisidine value was calculated from the expression:

A1 is absorbance of solution (b) at 350 nm, A2 is absorbance of solution (a) at 350 nm and W is the weight of the oil being tested (a) in grams (AOCS, 1993).

2.7. Analysis of acrylamide

2.7.1. Extraction

Modified methods of Ehling et al., 2005 and Daniali et al., 2013 and Lim, Jinap, Sanny, Tan, and Khatib (2013) had been applied to extract acrylamide from the samples. l-asparagine (0.2 g) was weighed and added to 10 mL of oil using a volumetric flask, heated up in a Petri dish and heated in the oven at 180 °C for 30 min. The mixture was stirred with a magnetic stirrer and allowed to cool to room temperature. A 0.5 g sample of the heated mixture of oil and l-asparagine was transferred to a 50 ml centrifuge tube and the volume was adjusted to 10 mL with 50 ppb 13C3-labelled acrylamide as an internal standard. Samples were mixed using a reciprovertical shaker (RS-1, Jeio Tech Co., Gyeonggi-do, Korea) for 30 min at medium speed (ca. 285 pulses/min). The homogenate was centrifuged using a refrigerated centrifuge (3–18 K, Sigma, Gillingham Dorset, UK) at 10,000 rpm (10956 RCF ×g) for 30 min at 4 °C. A syringe filter (0.45 μm) was used to filter an approximately 4 ml aliquot beneath the oil layer. Oasis HLB and Oasis MCX cartridges were conditioned and equilibrated with 3 ml of methanol followed by 3 ml of water before being loaded with the filtrate. The filtrate (2 mL) was passed through the Oasis HLB cartridge (Waters, Milford, MA, USA) gravitationally and discarded. The acrylamide containing fraction from the Oasis HLB cartridge was eluted with 2 ml of water; the eluent was collected and then loaded onto the Oasis MCX cartridge (Waters, Milford, MA, USA). The collected eluent was transferred to an amber vial for LC–MS/MS analysis.

2.7.2. Quantitation of acrylamide

Monomer [13C3] acrylamide was used as internal standard. Acrylamide in the cooking oils was determined from a calibration curve constructed by plotting the peak area ratios (m/z 55 and m/z 58) versus the concentrations of neat acrylamide injected with a constant amount of [13C3] acrylamide (50 ng/mL).

2.8. Validation of the acrylamide determination method

2.8.1. Calibration curve

Acrylamide in the oil samples was quantified using the ion of acrylamide at 72 m/z for acrylamide and the ion of its internal standard at m/z 75 m/z for [13C3]-acrylamide. The calibration curve was constructed by plotting peak area ratios (peak area of ions m/z 72/75) against the corresponding substance concentrations (μg/kg). The acrylamide concentrations in the sample extracts were calculated from the calibration curve by plotting the area ratio of m/z 72/75 ions found in the sample. The LC–MS/MS results were calibrated with two calibration curves determined by seven standard calibration solutions (AOAC, 2002).

2.8.2. Limit of detection (LOD) and limit of quantification (LOQ)

The limit of detection (LOD) and limit of quantification (LOQ) were determined by using the lowest calibrator concentration in seven experiments and were established at a signal/noise ratio (S/N) > 3 and (S/N) > 10 respectively (AOAC, 2002).

2.8.3. Recovery of acrylamide

The recovery of acrylamide from the heated oils was assessed by spiking acrylamide at a range of concentrations (50–5000) μg/kg into different heated oils. Each measurement was performed in seven replications and the recovery result was reported as the mean of the 7 determinations (AOAC, 2002).

2.8.4. Repeatability and reproducibility of acrylamide determination

The repeatability was determined by six analyses of a spiked sample. The levels spiked were 100 μg/kg and 500 μg/kg in one day. The reproducibility was determined by six analyses of a spiked sample on different days. The levels spiked were 100 μg/kg and 500 μg/kg. The repeatability and reproducibility were expressed as relative standard deviations (RSD%), (AOAC, 2002).

2.8.5. Certified reference material

Certified reference materials (CRMs) were reference materials that were homogeneous and stable with respect to one or more specified properties and for which traceability and values of uncertainty at a stated level of confidence had been established where applicable. Toasted bread with a certified value of 425 ng/g acrylamide and uncertainty value of 29 ng/g was obtained from the European commission.

3. Statistical analysis

Analysis of variance (ANOVA) was used to analyze the significance of differences between acrylamide concentrations in different cooking oils. The ANOVA analysis was performed by using Minitab (Release 14 for Windows, Pennsylvania, USA). Significance was determined at the 95% confidence level ($p < 0.05$) whilst Tukey's test was used for further statistical analysis.

4. Results and discussion

Before the method for acrylamide determination was used in this study, it was validated for linearity and recovery to assess its accuracy. The method used had a regression coefficient of 0.9998, equation $Y = 0.0869983 + 0.0170771X$, LOD and LOQ was 2 and 5 μ g/kg respectively. Recovery was used to determine whether analyte detection was affected by differences in the diluent used to prepare the standard curve and the sample matrix. This method showed 104.2, 98.3, 99.6, 107.7 and 100.3% for 50, 100, 500, 1000 and 5000 μg/kg, respectively (Table 1). These recovery values were in the acceptable range according to the AOAC (2002). Repeatability and reproducibility were 3.40–6.25 and 1.08–5.68 on the same day; and were 5.00–7.98 and 0.50–7.86 on different days. These data meet the requirements of the guidelines for standard methodological performance (AOAC, 2002).

The method found that 426 ± 1 ng/g of acrylamide had an uncertainty value of 29 ng/g when it was used on the toasted bread certified reference material (CRM) with a certified acrylamide level of 425 ng/g (Table 5). The repeatability and the reproducibility tested on the same day were found to be 3.40–6.25 and 1.08–5.68; and those on different days 5.00–7.98 and 0.50–7.86 respectively (Table 2). The criteria for confirmation of identity in this method were in agreement with those proposed by Cheng, Kao, Shih, Chou, and Yeh (2009) and Chuang, Chiu, and Chen (2006), which had a detection limit of 3 μg/kg, with the recovery ranged from 95 to 113%. The coefficient of variation ranged from 1.3 to 10.0% for the repeatability test and 3.3 to 6.9% for the reproducibility test. Lucentini et al. (2009) had reported the limit of detection and limit of quantification for acrylamide to be 0.2 ng/ml and 0.8 ng/ml respectively. Repeatability given as RSD was <5 and <15% for the LC–MS/MS. These recent works showed that the present method can be utilized for acrylamide detection in oil samples (Cheng et al., 2009 and Lucentini et al., 2009).

4.1. Acrylamide formation in cooking oil and fat

A model study was designed to determine the optimum amount of asparagines added to be used in the experiment. Soy bean oil, sunflower oil and lard were used. The results found that when

asparagine was heated in the absence of lipid (control), acrylamide was not produced. However, when different concentrations of asparagine were heated with the cooking oil, acrylamide was produced (Table 3). The formation of acrylamide in oil/asparagine reaction mixtures of 0.1 asparagine was significantly different ($P < 0.001$) compared to the other concentrations for both cooking oils and lard i.e. 18,100 ± 200 and 23,200 ± 300 ng/g ($p < 0.001$) for soy bean oil; 17,700 ± 200 and 24,100 ± 300 ng/g for sunflower oil and 324 ± 10 and 408 ± 11 ng/g ($p < 0.001$) for lard. However, there was no significant difference ($p > 0.05$) between the rest of the concentrations when more than 0.2 g of asparagine was added to either oil. Therefore, 0.2 mg of asparagine was used in all experiments.

One of the major chemical reactions occurring in oil during heat processing was lipid oxidation, which started with the formation of hydroperoxide and proceeded via radical mechanisms. The oxidation values in different types of oil before heat treatment were measured (Table 4). The highest peroxide value was found in olive oil (22.8 ± 0.7) and the lowest was in sesame oil (1.9 ± 0.1). The highest iodine value was found in soy oil (120.9 ± 3.5) and the lowest was in ghee (47.5 ± 3.2), whereas the lowest anisidine value was found in ghee (17.4 ± 1.0) and the highest in sesame oil (36.5 ± 2.2). Peroxide value was used to measure peroxide and hydroperoxide, whereas anisidine value determined secondary oxidation products, shown in Table 4 and Table 5 respectively. After the heat treatment of sesame oil, anisidine and peroxide values increased from low levels of 1.9 and 36.5 to 13 and 41 which equaled 84% and 11% changes respectively. The anisidine and peroxide values for soy oil increased from 5.7 and 19.1 to 31and 39, which equaled 81% and 52% changes respectively; whereas those of sunflower increased from 16.5 and 18.4 to 12 and 41, which equaled 41% and 55% changes respectively. The same trend was found in all the oils indicating that the main oxidative event was the formation of peroxide, followed by decomposition of peroxide leading to secondary oxidation.

The iodine value of each oil decreased during heat treatment and the saturation rate increased. The iodine value was from 120.9 to 35 in soy oil, which resulted in a 71% change; from 87.1 to 28 in sunflower oil, which equaled in a 68% change and from 104.8 to 79 in corn oil, which is a 24% change. Oxidation products were found to be unstable compounds, which might have undergone further reactions resulting in the formation of the flavor compounds such as aldehydes, ketones, alcohol, epoxides and hydrocarbons (Capuano et al., 2010, Friedman, 2003 and Mestdagh et al., 2008. Frying produced fatty acid oxidation products that reacted with asparagine and formed acrylamide. Table 5 showed that high concentrations of acrylamide were produced in soy oil (2447 ng/g) followed by palm olein (1442 ng/g), sunflower oil (1226 ng/g), sesame oil (1139 ng/g), olive oil (542 ng/g), corn oil (430 ng/g), lard (366 ng/g) and ghee (211 ng/g). The oils with high primary and secondary oxidant values exhibited higher acrylamide concentrations. When cooking oil was heated up to high temperatures, glycerol was degraded to acrolein (Stevens & Maier, 2008). Due to their high antioxidant contents, olive oil and sesame oil formed less acrylamide than the other oils; as acrylamide was formed by oxidation of acrolein to acrylic acid, which reacted with ammonium coming from nitrogen-containing compounds such as amino acids.

The formation of acrolein had been found to accelerate with increases in insaturation and polyunsaturated acids in the oil according to Uchida et al. (1999). The peroxidation of polyunsaturated fatty acids had been found to generate free acrolein and this was in agreement with the results presented in this study. It would be worthwhile to note that Mestdagh et al. (2005) reported that no significant difference in acrylamide formation was found between the various heating oils after frying French fries. Different frying methods and conditions could have been the cause of this disagreement; for they had used the tubular reactor at 175 °C for 2 min. Similarly, Mestdagh, Meulenaer, and Peteghem (2007) had investigated the oxidation and oil hydrolysis on the formation of acrylamide, and they had concluded that oil degradation products, such as glycerol, mono and diacylglycerols did not significantly influence the acrylamide formation. Totani, Yawata, Takada, and Moriya (2007) claimed that frying oil used in deep frying would not contaminate food stuffs with acrylamide. Both these studies used oxidized cooking oil, which might not have contained acrolein and acrylic acid and therefore acrylamide would not have been produced. Since the boiling points of acrolein and acrylic acid are 53 °C and 141 °C respectively, this would indicate that the compounds

could be unstable and would easily be evaporated (Stevens & Maier, 2008). According to Selke and Frankel (1987) and Matthews, Scanlan, and Libbey (1971) the first products of hydrolyzed oil was glycerol and fatty acids, and acrolein was produced by the elimination of water from glycerol and oxidation of polyunsaturated fatty acids. Acrolein can also be produced as a result of the oxidation of polyunsaturated fatty acids and their degradation products (Matthews et al., 1971 and Selke and Frankel, 1987). Soy oil would be expected to be highly sensitive to oxidation because of the high content of unsaturated fatty acids; whilst some oils with high contents of saturated fatty acids, such as lard, might be expected to be less sensitive.

The dependence of the acrylamide content on oxidation was investigated by correlating the oxidation values presence with acrylamide amounts in different cooking oils, and a positive correlation was observed between peroxide value and acrylamide content ($R2 = 0.75$; $p < 0.05$). It would be noteworthy that both the iodine value and anisidine value correlated with the acrylamide content in cooking oil at ($R2 = 0.85$; $p < 0.05$), (Fig. 1). The anisidine and iodine values represented the levels of aldehydes and unsaturated double bonds respectively. Aldehydes had been found to be major degradation products in unsaturated oils due to their potential to exert toxicological effects, as they would react with the amino groups of proteins and produce acrylamide or aldehydes like acrolein, which would produce acrylamide (Umano and Shibamoto, 1987 and Yen and Wu, 2003).

5. Conclusion

The performance characteristics of the modified methods used in this study indicated that the methods were suitable for confirmatory analysis of acrylamide in cooking oils, as it was in compliance with AOAC (2002). The methods were confirmed suitable with certified reference material (CRM) of acrylamide in toasted bread. Unsaturated cooking oils produced high concentrations of acrylamide and high carbonyl compound content during heat processing. Correlations between the iodine values in the oils and animal fats and their acrylamide contents suggested that oils with more double bonds appeared to have higher acrylamide contents due to their unsaturated structures.

Acknowledgement

The authors would like to thank Universiti Putra Malaysia for sponsoring the research, vote no: Putra Grant 02-02-12-2042RU.

References

1. Aladedunye, F. A., & Przybylski, R. (2011). Antioxidative properties of phenolic acids and interaction with endogenous minor components during frying. European Journal of Lipid Science and Technology, 113(12), 1465–1473.
2. AOAC official methods of analysis (2002). Guidelines for standard method performance requirements. Available in: <www.aoac.org/.../AOAC.../SLV_Guidelines_Dietary_Supplements.pdf>.
3. AOAC. Association of Official Analytical Chemists (1984). Official methods of analysis (14th ed.). Arlington, VA.
4. AOCS (1993). Official methods and recommended practices of the American oil chemists society (4th ed.). Champaign, IL: AOCS Press.
5. Becalski, A., Lau, B. P. Y., Lewis, D., & Seaman, S. W. (2003). Acrylamide in foods: Occurrence, sources, and modeling. Journal of Agricultural and Food Chemistry, 51, 802–808.
6. Capuano, E., Oliviero, T., Acar, Ö. C., Gökmen, V., & Fogliano, V. (2010). Lipid oxidation promotes acrylamide formation in fat-rich model systems. Food Research International, 43, 1021–1026.
7. Cheng, W. C., Kao, Y. M., Shih, D. Y. C., Chou, S. S., & Yeh, A. (2009). Validation of an improved LC/MS/MS method for acrylamide Analysis in Foods. Journal of Food and Drug Analysis, 17, 190–197.
8. Chuang, W. H., Chiu, C. P., & Chen, B. H. (2006). Analysis and formation of acrylamide in French fries and chicken legs during frying. Journal of Food Biochemistry, 30, 497–507.
9. Daniali, G., Jinap, S., Hanifah, N. L., & Hajeb, P. (2013). The effect of maturity stages of banana on the formation of acrylamide in banana fritters. Food Control, 32, 386–391.
10. Ehling, S., Hengel, M., & Shibamoto, T. (2005). Formation of acrylamide from lipids (1st ed.). In M. Friedman & D. Mottram (Eds.), Chemistry and safety of acrylamide in food (pp. 223–233). Springer.
11. Esterbauer, H., Schaur, R. J., & Zollner, H. (1991). Chemistry and biochemistry of 4-hydroxynonenal, malonaldehyde and related aldehydes. Free Radical Biology and Medicine, 11, 81–128.
12. Ewert, A., Granvogl, M., & Schieberle, P. (2014). Isotope-labeling studies on the formation pathway of acrolein during heat processing of oils. Journal of Agriculture and Food Chemistry, 33, 8524–8529.
13. Friedman, M. (2003). Chemistry, biochemistry, and safety of acrylamide. A review. Journal of Agriculture and Food Chemistry, 51, 4504–4526.
14. Hidalgo, F. J., & Zamora, R. (2007). Conversion of phenylalanine into styrene by 2,4-decadienal in model systems. Journal of Agriculture and Food Chemistry, 55, 4902–4906.

15. Lim, P. K., Jinap, S., Sanny, M., Tan, C. P., & Khatib, A. (2013). The influence of deep frying using various vegetable oils on acrylamide formation in sweet potato (Ipomoeabatatas L. Lam) chips. Journal of Food Science, 79, 115–121.
16. Lucentini, L., Ferretti, E., Veschetti, E., Achene, L., Turrio, B. L., Ottaviani, M., & Bogialli, S. (2009). Determination of low level acrylamide in drinking water by liquid chromatography tandem mass spectrometry. Journal of AOAC International, 92, 263–270.
17. Matthaus, B., Haase, N. U., & Vosmann, K. (2004). Factors affecting the concentration of acrylamide during deep-fat frying of potatoes. European Journal of Lipid Science and Technology, 106, 793–801.
18. Matthews, R. F., Scanlan, R. A., & Libbey, L. M. (1971). Autoxidation products of 2,4-decadienal. Journal of the American Oil Chemists Society, 48, 745–747.
19. Mestdagh, M., Castelein, P., Peteghem, C. V., & Meulenaer, B. D. (2008). Importance of oil degradation components in the formation of acrylamide in fried foodstuffs. Journal of Agriculture and Food Chemistry, 56, 6141–6144.
20. Mestdagh, M., Meulenaer, B. D., & Peteghem, C. V. (2007). Influence of oil degradation on the amounts of acrylamide generated in a model system and in French fries. Food Chemistry, 100, 1153–1159.
21. Mestdagh, F. J., Poucke, C. V., Detavernier, C., Cromphou & Peteghem, C. V. (2005). Influence of oil type on the amounts of acrylamide generated in a model system and in French fries. Journal of Agricultural and Food Chemistry, 53, 6170–6174.
22. Mottram, D. S., Wedzicha, B. L., & Dodson, A. T. (2002). Acrylamide is formed in the Maillard reaction. Nature, 419, 448–449.
23. Ou, S., Shi, J., Huang, C., Zhang, G., Teng, J., Jiang, Y., & Yang, B. (2010). Effect of antioxidants on elimination and formation of acrylamide in model reaction systems. Journal of Hazardous Materials, 182, 863–868.
24. Pedreschi, F., Kaack, K., & Granby, K. (2006). Acrylamide content and color development in fried potato strips. Food Research International, 39, 40–46.
25. Schonberg, A., & Moubasher, R. (1952). The Strecker degradation of a-amino acids. Chemical Reviews, 50, 261–277.
26. Selke, E., & Frankel, E. N. (1987). Dynamic headspace capillary gas chromatographic analysis of soybean oil volatiles. Journal of the American Oil Chemists Society, 64, 749–753.
27. Stadler, R. H., Robert, F., Riediker, S., Varga, N., Davidek, T., Devaud, S., ... Blank, I. (2004). In-depth mechanistic study on the formation of acrylamide and other vinylogous compounds by the Maillard reaction. Journal of Agriculture and Food Chemistry, 52, 5550–5558.
28. Stevens, J. F., & Maier, C. S. (2008). Acrolein: Sources, metabolism, and biomolecular interactions relevant to human health and disease. Molecular Nutrition & Food Research, 52, 7–25.
29. Tareke, E., Rydberg, P., Karlsson, P., Eriksson, S., & Törnqvist, M. (2002). Analysis of acrylamide, a carcinogen formed in heated foodstuffs. Journal of Agriculture and Food Chemistry, 50, 4998–5006.
30. Totani, N., Yawata, M., Takada, M., & Moriya, M. (2007). Acrylamide content of commercial frying oil. Journal of Oleo Science, 56, 103–106.
31. Uchida, K., Kanematsu, M., Morimitsu, Y., Osawa, T., Noguchi, N., & Niki, E. (1999). Acrolein Is a Product of Lipid Peroxidation Reaction. Journal of Biological Chemistry, 273, 16058–16066.
32. Umano, K., & Shibamoto, T. (1987). Analysis of acrolein from heated cooking oils and beef fat. Journal of Agricultural and Food Chemistry, 35, 909–912.
33. Yasuhara, A., Tanaka, Y., Hengel, M., & Shibamoto, T. (2003). Gas chromatographic investigation of acrylamide formation in browning model systems. Journal of Agricultural and Food Chemistry, 51, 3999–4003.
34. Yaylayan, V. A., Wnorowski, A., & Perez Locas, C. (2003). Why asparagines needs carbohydrates to generate acrylamide. Journal of Agriculture and Food Chemistry, 51, 1753–1757.
35. Yen, G. C., & Wu, S. C. (2003). Reduction of mutagenicity of the fumes from cooking oil by degumming treatment. Lebensmittel-Wissenschaft and Technologie, 36, 29–35.
36. Zamora, R., & Hidalgo, F. J. (2008). Contribution of lipid oxidation products to acrylamide formation in model systems. Journal of Agriculture and Food Chemistry, 56, 6075–6080.
37. Zamora, R., Gallardo, E., & Hidalgo, F. J. (2007). Strecker degradation initiated by 2,4-decadienal or methyl 13-oxooctadeca-9,11-dienoate in model systems. Journal of Agriculture and Food Chemistry, 55, 1308–1314.
38. Zyzak, D., Sanders, R. A., Stojanovic, M., Tallmadge, D. H., Eberhart, B. L., Ewald, D. K., ... Villagran, M. D. (2003). Acrylamide formation mechanism in heated foods. Journal of Agriculture and Food Chemistry, 51, 4782–4787.