Effect of high temperature cooking on the formation of harmful chemicals (benzopyrene, diisobutyl phthalate, nonaldehyde) in different edible vegetable oils

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Abstract: In this study, the formation laws of harmful chemicals such as benzopyrene, diisobutyl phthalate (DIBP) and nonaldehyde in different edible vegetable oils under high temperature cooking conditions were discussed. Five common edible vegetable oils, soybean oil, rapeseed oil, peanut oil, sunflower oil and corn oil, were heated to different time points (0, 10, 20 and 30 minutes) at three temperature gradients of 160℃, 180℃ and 200℃ respectively, and the samples were analyzed by high performance liquid chromatography and gas chromatography-mass spectrometry. The results showed that the content of benzopyrene was positively correlated with cooking temperature (R^2=0.92, $P < 0.01$), and the content of benzopyrene in peanut oil (18.6μg/kg) exceeded the national standard limit (10μg/kg) at 200℃. The initial content of DIBP may be related to the migration of packaging materials, but high temperature treatment did not significantly increase its content ($p>0.05$). The production of nonanal increased linearly with temperature and time (R^2=0.87). At 200℃, the content of nonanal in peanut oil reached 18.6mg/kg, exceeding the olfactory threshold (5mg/kg), and its production rate was significantly accelerated when the temperature exceeded 195℃. The stability of oil products is related to the content of antioxidant substances and fatty acid unsaturation. Oils with high linoleic acid, such as corn oil and peanut oil, are more likely to generate harmful substances. It is suggested to optimize the oil refining process to reduce the residue of DIBP, and to remind consumers to control the frying temperature and time to reduce the risk of harmful chemicals.

1. Introduction

A variety of harmful chemicals may be produced during high-temperature cooking, which poses a potential threat to people's health. Among them, benzopyrene, diisobutyl phthalate (DIBP) and nonaldehyde are common harmful chemicals in high-temperature cooking [1]. Benzopyrene is a polycyclic aromatic hydrocarbon with strong carcinogenicity, which widely exists in cooking fume and food at high temperature. DIBP is a plasticizer, which may migrate into edible oil through packaging materials and be further released at high temperature [2]; Nonaldehyde is a product in the process of oil oxidation, which has a pungent smell and may have adverse effects on human health.

As an indispensable raw material in high-temperature cooking, the types and quality of edible vegetable oil directly affect the production of harmful chemicals in the cooking process [3-4]. Different kinds of edible vegetable oils show different stability during high-temperature cooking due to their differences in fatty acid composition and antioxidant properties, which further affects the formation of harmful chemicals [5]. Therefore, it is of great significance to study the influence of high-temperature cooking on the formation of harmful chemicals in different edible vegetable oils for ensuring public health and guiding healthy diet.

In this study, the formation of harmful chemicals such as benzopyrene, DIBP and nonaldehyde in different edible vegetable oils under high-temperature cooking conditions was discussed through experiments, and the influence of cooking conditions on the formation of harmful chemicals was analyzed, so as to provide scientific healthy diet suggestions for the public and scientific basis for improving production technology and strengthening quality control for edible oil industry.

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2. Experimental materials and methods

2.1. Experimental materials

Five kinds of edible vegetable oils, including soybean oil, rapeseed oil, peanut oil, sunflower oil and corn oil, were selected in the experiment, and three different brands of first-class refined oil were selected as samples for each oil, totaling 15 samples. All oil samples were sealed and stored in a cold storage environment at 4℃ in the dark before use [6].

Equipped with a precision temperature-controlled electromagnetic heating system, standard-sized stainless steel frying pan, and temperature recorder for basic cooking and monitoring purposes. Additionally, a nitrogen blow concentrator, gas chromatography-mass spectrometer (GC-MS), high-performance liquid chromatograph (HPLC) with a fluorescence detector, and a UV-Visible spectrophotometer were prepared for the in-depth chemical analysis of the samples.

In the experiment, benzopyrene, DIBP, nonaldehyde and other standard substances with purity not less than 99% were selected, as well as auxiliary materials such as chromatographic pure n-hexane, analytical pure anhydrous sodium sulfate, C18 solid phase extraction column and derivatization reagent BSTFA+TMCS.

2.2. Experimental design

Three temperature gradients were designed to simulate different cooking scenes, including a low temperature group of 160℃ (simulating daily frying), a medium temperature group of 180℃ (simulating frying) and a high temperature group of 200℃ (simulating re-frying), and four heating time points (0, 10, 20 and 30 minutes) were set at each temperature.

200mL oil sample was placed in a frying pan and heated to the target temperature at a rate of 10℃/min under the protection of nitrogen to reduce the oxidation reaction [7]. The actual cooking state was simulated by electromagnetic stirring (200rpm) during heating. According to the predetermined time interval (0 minutes as the baseline, and then every 10 minutes until 30 minutes), 10mL oil samples were taken from each group for analysis. Immediately after sampling, the sample was sealed with nitrogen, and stored at -80℃ to keep the sample stable.

2.3. Test method

2.3.1. Benzopyrene detection

The detection of benzopyrene begins with liquid-liquid extraction using a mixture of n-hexane and acetone in a 3:1 ratio, followed by purification with a silica gel column. High-performance liquid chromatography with a fluorescence detector (HPLC-FLD) is used for the final analysis, with an excitation wavelength of 294nm and an emission wavelength of 404nm, utilizing a C18 chromatographic column (dimensions 4.6×250mm, particle size 5μm). The mobile phase consists of acetonitrile and water in an 88:12 ratio, with a flow rate set at 1.0mL/min.

2.3.2. DIBP detection

DIBP was detected by accelerated solvent extraction (ASE), followed by gel permeation chromatography. GC-MS was detected in the mode of electron ionization source (EI source), and the specification of DB-5MS column used was 30m×0.25mm×0.25μm m. The heating program starts from the initial temperature of 80℃, and then it is kept for 1 minute, and then it is raised to 300℃ at the speed of 15℃/min, and kept at this temperature for 5 minutes.

2.3.3. Nonaldehyde detection

The detection of nonanal involves a headspace solid-phase microextraction (HS-SPME) method for sample preparation, using an 85μm CAR/PDMS fiber. The GC-MS operates in selected ion monitoring (SIM) mode, primarily detecting ions with mass-to-charge ratios of m/z 70, 57, and 41. An HP-INNOWax chromatographic column, specified at 60m×0.25mm×0.25μm, is utilized for the analysis.

2.4. Quality control

Ensure the accuracy and reliability of each batch of detection through blank experiments, including reagent and instrument blank; Three concentration levels (0.5μg/kg, 5μg/kg and 50μg/kg) were used to test the recovery rate, and a five-point calibration curve was established for each target to ensure the linear relationship ($r^2 \geq 0.999$). During data collection, three parallel samples were set in each treatment group to ensure the repeatability of the results, and NIST standard oil samples were inserted as quality control samples in each batch analysis. In addition, the instrument is tuned daily to ensure the accuracy and accuracy of the analysis results.

2.5. Statistical analysis

Statistical analysis was conducted using SPSS 26.0, including analysis of variance (ANOVA) to evaluate significant differences under different conditions. A multiple linear regression model $Y=\beta 0+\beta 1T+\beta 2t+\beta 3T \times t+\varepsilon$ (where Y represents target substance content, T represents temperature, and t represents time) was established to quantify the effects of temperature and time on target substance content and their interaction effects. These effects were further visualized through three-dimensional response surface plots. Using Pearson correlation coefficient to explore the relationship between fatty acid composition and harmful substance production.

3. Experimental results and analysis

3.1. Formation of benzopyrene

The content of benzopyrene in all oil samples was positively correlated with cooking temperature ($R^2= 0.92$, $P < 0.01$). At 200℃, the content of benzopyrene in peanut oil (18.6μg/kg) exceeded the national standard limit (10μg/kg). At 180℃, when the heating time was prolonged from 10min to 30min, the amount of benzopyrene production increased by 2.3-3.5 times (for example, soybean oil: 2.5→5.8μg/kg). Peanut oil and corn oil are more prone to produce benzopyrene by lipid peroxidation because of their high content of polyunsaturated fatty acids (linoleic acid accounts for more than 50%) ($p<0.05$). See Table 1 for the specific benzopyrene production at different temperatures.

Table 1 Benzopyrene production at different temperatures (μg/kg)

Oil sample	160℃(30min)	180℃(30min)	200℃(30min)
Soybean oil	2.1±0.3	5.8±0.5	12.4±1.2
rap oil	1.8±0.2	4.3±0.4	9.7±0.9
peanut oil	3.5±0.4	8.2±0.7	18.6±1.8
sunflower seed oil	1.2±0.1	3.6±0.3	7.9±0.8
corn oil	2.9±0.3	6.7±0.6	15.3±1.5

3.2. Generation of DIBP

The difference in the initial content of DIBP may be related to the migration of plastic packaging (peanut oil and corn oil are packed in HDPE, so the migration risk is high). High-temperature treatment did not significantly increase the content of DIBP ($p>0.05$), so it was speculated that its thermal stability was strong (decomposition temperature > 250℃). The initial DIBP content of peanut oil (0.12mg/kg) is close to the migration limit of EU food contact materials (0.15mg/kg). See Table 2.

Table 2 DIBP content test results (mg/kg)

Oil sample	Unheated	200℃(30min)
Soybean oil	0.05±0.01	0.06±0.01
rap oil	0.07±0.02	0.08±0.02
peanut oil	0.12±0.03	0.13±0.03
sunflower seed oil	0.03±0.01	0.04±0.01
corn oil	0.09±0.02	0.10±0.02

3.3. Formation of nonanal

The peak value of nonanal production at 200℃ is shown in Table 3. The nonanal content increases linearly with temperature and time (R^2=0.87), as shown in Figure 1. When the temperature exceeds 195℃, the nonanal production rate increases significantly, especially after the treatment time exceeds 25 minutes. The content of nonanal in peanut oil reached 18.6mg/kg at 30min, which exceeded the olfactory threshold (5mg/kg). Based on the daily intake of 30g oil, the exposure of nonanal is 0.56 mg/kg bw d, which is close to the provisional tolerance of JECFA (0.6 mg/kg bw d). Nonaldehyde has a significant positive correlation with peroxide value (PV) (r=0.79, p<0.01), which can be used as a marker of oxidative deterioration of oils and fats.

Table 3 Peak value of nonanal production at 200℃ (mg/kg)

Oil sample	10min	20min	30min
Soybean oil	4.2	9.7	15.3
rap oil	3.8	8.5	13.9
peanut oil	5.1	11.4	18.6
sunflower seed oil	2.9	6.3	10.1
corn oil	4.6	10.2	16.8

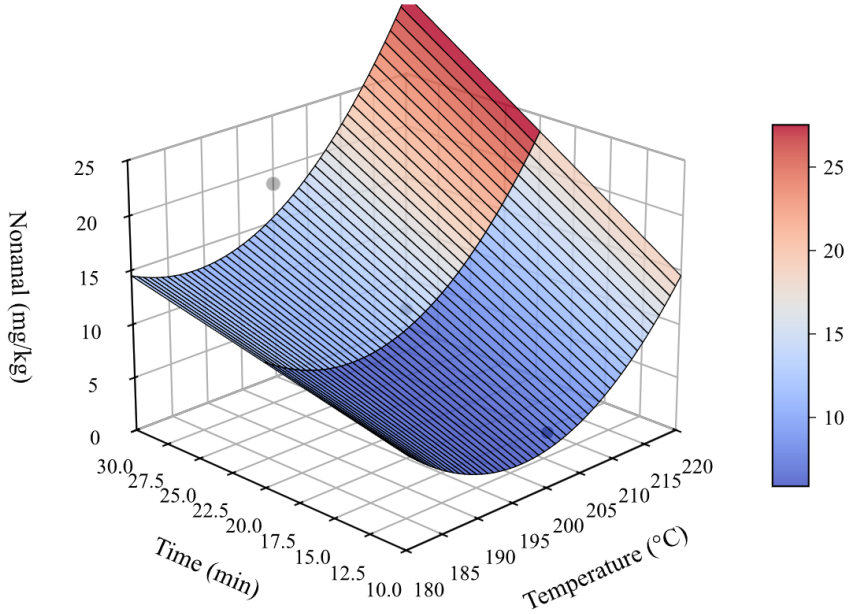

Figure 1 Three-dimensional response surface of nonaldehyde production in peanut oil

3.4. Comprehensive analysis and discussion

The stability of oil products from high to low is sunflower seed oil, rapeseed oil, soybean oil, corn oil and peanut oil, and their order is consistent with the content of antioxidant substances (such as VE and polyphenols) and fatty acid unsaturation in oil. At 200℃, the generation rate of harmful substances increases by 1.8-2.5 times due to the synergistic effect of temperature and time every 10 minutes, which follows the arrhenius formula (activation energy Ea=65-85kJ/mol). Moreover, high linoleic acid oils such as corn oil and peanut oil are more likely to generate nonaldehyde through β-pyrolysis path, and the generation amount of benzopyrene is positively correlated with the conjugated diene content (r=0.82 Based on this, it is suggested to optimize the oil refining process, such as increasing the duration of deodorization process to more than 30 minutes /220℃ to reduce DIBP residue, and remind consumers that frying temperature should not exceed 180℃ and heating time with oil should not exceed 20 minutes at a time.

4. Conclusion

It was found that the content of benzopyrene in all oil samples was positively correlated with

cooking temperature, and the content of benzopyrene in peanut oil exceeded the national standard limit at 200℃. When the heating time is extended to 30 minutes at 180℃, the benzopyrene production increases by 2.3-3.5 times, and peanut oil and corn oil with high polyunsaturated fatty acids are more likely to produce benzopyrene through lipid peroxidation. For DIBP, the difference of its initial content may be related to the migration of plastic packaging, but the high temperature treatment did not significantly increase its content, suggesting that its thermal stability is strong. The initial DIBP content of peanut oil is close to the migration limit of EU food contact materials. The production of nonaldehyde increases linearly with temperature and time. When the temperature exceeds 195℃, the production rate is significantly accelerated, especially after the treatment time exceeds 25 minutes, it shows an exponential growth trend. At 30 minutes, the nonanal content of peanut oil exceeded the olfactory threshold. According to the daily intake of 30g oil, the nonanal exposure was close to the provisional tolerance of JECFA. Comprehensive analysis shows that the stability of oil products from high to low is sunflower seed oil, rapeseed oil, soybean oil, corn oil and peanut oil, which is consistent with the content of antioxidant substances and fatty acid unsaturation in oil. At 200℃, the generation rate of harmful substances increases by 1.8-2.5 times due to the synergistic effect of temperature and time every 10 minutes. Oils with high linoleic acid content, such as corn oil and peanut oil, are more likely to produce nonanal through β -pyrolysis path, and the amount of benzopyrene produced is positively correlated with the conjugated diene content. Based on the above research results, it is suggested to optimize the oil refining process, such as increasing the duration of deodorization process to reduce the residue of DIBP, and remind consumers that the frying temperature should not exceed 180℃ and the heating time of single oil use should not exceed 20 minutes to reduce the generation of harmful chemicals and protect public health.

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