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Atmospheric Chemistry of Stir-Frying Emissions

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Atmospheric Chemistry of Stir-Frying Emissions

A Thesis submitted in partial satisfaction
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in

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by

Yuehua Gu

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ABSTRACT OF THE THESIS

Atmospheric Chemistry of Stir-Frying Emissions

by

Yuehua Gu

Master of Science Degree, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, September 2018
Dr. David Cocker, Chairperson

Cooking is widely recognized as an element source of volatile organic compounds(VOCs) and particulate matter(PM) which do harm to human health. In addition, cooking processes were recognized as major contributors to $PM_{2.5}$ pollution besides industrial pollution and vehicle emissions in urban areas. Many studies have characterized PM emissions from cooking in terms of different cooking oils. However, the chemical composition, characteristics and oxidation behaviors of cooking oil emissions are poorly understood.

Both the physical and the chemical characteristics of cooking oils are greatly influenced by the kind and proportion of the fatty acids. The predominant fatty acids present in vegetable oils are saturated fatty acid and unsaturated fatty acid with straight aliphatic chains. Oleic acid ($C_{18}H_{34}O_2$) is the most widely distributed and abundant unsaturated fatty acid in cooking oil. It is widely concerned as a model system used to study atmospheric oxidation of fatty acid, not only because it is a major component of cooking oil, but also because it contains both single bond and double bond. Many studies have observed the mechanism of heterogeneous oxidation of oleic acid with OH radicals or ozone, but the real application of oleic acid has not been completely understood yet. Under realistic conditions, oleic acid is not the only component of cooking oils, a key challenge remains in how cooking oils oxidant in the atmosphere.

In this study, canola oil, peanut oil and corn oil were used to react with O_3 or OH radicals in a flow tube reactor or a potential aerosol mass(PAM) oxidation flow reactor. A scanning mobility particle sizer (SMPS) and an Aerosol Particle Mass Analyzer(APM) were used to identify the particle density, mass concentration and size distribution. A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) is used to characterize the chemical composition of aerosols and how the oxidation occurred.

The results showed secondary organic aerosols(SOA) formation in this situation is less important, and instead of that, the loss of oil is dominated. The oxidation reaction occurred at the particle surface and the cooking oil that contains more double bonds is more likely to oxidized and get saturated by the addition of OH or O_3 groups.

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Acronyms and Abbreviations

POAs	Primary Organic Aerosols
SOAs	Secondary Organic Aerosols
PM	particulate matter
PM2.5	ultra-fine particulate matter less than 2.5 µm (certification gravimetric reference method)
VOCs	Volatile Organic Compounds
O_3	Ozone
OH	Hydroxide
AMS	Aerosol Mass Spectrometer
SMPS	Scanning Mobility Particle Sizer
APM	Aerosol Particle Mass Analyzer
PAM	Potential Aerosol Mass
LPM	Liter Per Minuet
HO_2	Hydroperoxyl
HEPA filter	High-Efficiency Particulate Air filter
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DBE	Double Bond Equivalent
UCR	University of California at Riverside

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1. Introduction

Airborne particles are one of the most important and certainly the most visible aspects of air pollution. Aerosols are small particles that are suspended in the atmosphere which can be in the solid or liquid phase. Organic aerosols comprise a significant fraction of fine aerosol particle mass in the atmosphere [1] and thus do harm to climate change, visibility and human health. Organic aerosols can be classified into two classes, primary organic aerosols (POAs) and secondary organic aerosols (SOAs). The chemical composition of both directly emitted, primary organic particles and those formed by secondary processes is transformed continuously in the atmosphere [2]. POAs are directly emitted into atmosphere and constitute the emissions from both natural and anthropogenic sources, such as from emissions by vegetation, volcanic eruptions, biomass burning (forest fire) and combustion of fossil fuels. SOAs are air pollutants formed in the atmosphere by gas-particle conversion processes such as nucleation, condensation and heterogeneous and multiphase chemical reactions [3]. SOAs are a major component of fine particle pollution (also known as $PM_{2.5}$), which has been found to be associated with lung and heart problems and other health effects. According to American Cancer Society (ACS) cohort study and National Mortality and Morbidity Air Pollution Study (NMMAPS), Fann et al. estimated that there were 130,000 premature deaths per year of exposure that are resulted from $PM_{2.5}$ levels [4].

As we all know, cooking can produce very high concentrations of volatile organic compounds (VOCs) and particulate matter (PM) which do harm to human health [5]. Cooking emissions which were generated by oil, fat and carbohydrates after a series of complex chemical reactions were regarded as one of the main sources of the indoor and outdoor air pollution [6]. In addition, cooking processes were recognized as major contributors to $PM_{2.5}$ pollution besides industrial pollution and vehicle emissions in urban areas [7]. Prolonged exposure to these pollutants can lead to heart and respiratory problems. In the case of indoor air pollution in doing the household cooking, young children, as well as their mothers have a higher risk of morbidity and mortality from acute respiratory infections [8] and increased rates of cardiovascular disease [9].

Many studies have characterized PM emissions from cooking in terms of different cooking oils [10], ingredients [11] and cooking processes. Particle emissions occur when cooking oils emit semi-volatile compounds that condense and form a liquid aerosol phase [12]. However, the physical and chemical characteristics and oxidation behaviors of cooking oils are poorly understood.

Both the physical and the chemical characteristics of cooking oils are greatly influenced by the kind and proportion of the fatty acids. The predominant fatty acids present in vegetable oils are saturated and unsaturated compounds with straight aliphatic chains. Oleic acid ($C_{18}H_{34}O_2$) is the most widely distributed and abundant unsaturated fatty acid that occurs naturally in various animal and vegetable fat and oils. Approximately 60%-70% of the fatty acids in vegetable oil come from oleic acid, a monounsaturated fatty acid. Oleic acid is widely concerned as a model system used to study atmospheric oxidation of fatty acid, not only because it is a major component of cooking oil, but also because it contains both single bond and double bond (shown in Fig.1).

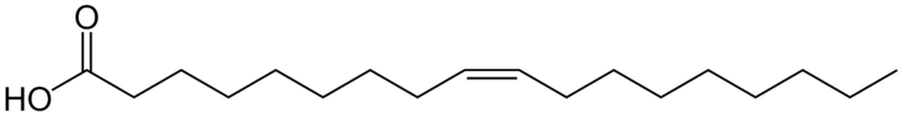


Fig.1 Oleic Acid Formula

Linoleic acid ($C_{18}H_{32}O_2$) is a doubly unsaturated fatty acid, which is necessary for human health and cannot be produced within the human body. It must be acquired through diet and used in cell membranes. Linoleic acid is wildly found in seeds, nuts, and many common vegetable oils. In terms of its structure, it is an 18-carbon chain with two double-bonds (shown in Fig.2).

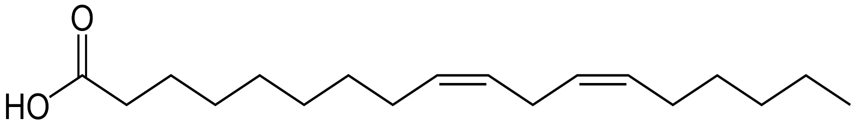


Fig.2 Linoleic Acid Formula.

Saturated fatty acid ($C_{18}H_{36}O_2$) is a type of fat in which the fatty acid chains have all or predominantly single bonds (shown in Fig.3) and is typically solid at room temperature. In general, a higher degree of unsaturation of fatty acids in vegetable oils indicates a higher susceptibility oxidative deterioration. Therefore, it is necessary to know the composition of fatty acids in the cooking oil, to identify their characteristics.

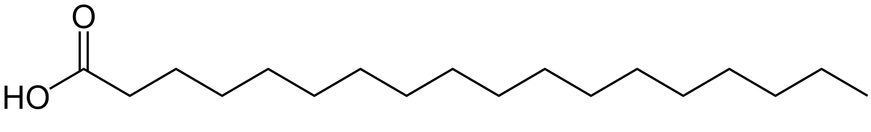


Fig.3 Saturated fatty acid Formula.

OH radical is an abundant oxidant in the atmosphere, thus, it plays an important role in chemical aging of organic aerosols. Recently, many studies have concentrated on the heterogeneous reactions of oleic acid with OH radical. Nah and Kessler suggested OH addition to the C=C double bond is not the sole reaction and there are secondary reactions that consume the oleic acid without increasing the particulate oxygen content [13].

Several studies have focused on the kinetics study of heterogeneous reactions of O_3 with oleic acid. He et al. observed that the overall kinetics are dominated by surface reaction, and the effect of surface adsorption plays an important role during the reaction [14]. Morris et al. present a first-time study of aerosol kinetics using a novel aerosol mass spectrometric technique [15].

The oxidation reaction of oleic acid with OH radicals or ozone has been well studied, but the real application of oleic acid has not been completely understood yet. Under realistic conditions, oleic acid is not the only component of cooking oils, the oxidation of cooking oils in the atmosphere is worth studying.

So, the main goal of this study is to understand the reactions of canola oil, peanut oil and corn oil with OH and O_3 separately, and it is expected that the products contain more PM and form a great number of SOA. Oxidation occurs in a flow tube reactor/ potential aerosol mass oxidation flow reactor (PAM) that using high radical concentrations could simulate the photo-oxidation in the atmosphere in a short residence time. An Aerosol Particle Mass Analyzer (APM) and Scanning Mobility Particle Sizer (SMPS) are used to determine the particle density, mass concentration and size distribution. Real-time characterization of aerosol and gas phase composition of oxidation reaction of cooking oil with OH / O_3 was performed using a high-resolution time-of-flight aerosol mass spectrometer (AMS).

2. Experimental procedures

In this study, canola oil, peanut oil (Brand A and Brand B), and corn oil were investigated to determine the composition and chemical characteristics of cooking emissions. Each oil has an oxidation reaction with both O_3 or OH radical separately in a flow tube reactor of a PAM reactor except canola oil. The flow tube reactor was only available for the reaction of canola oil with O_3. The rest of the experiments all took place in the PAM reactor.

The first aerosol flow tube reaction experiment is regarded as a preliminary work to determine whether the PM can be formed successfully during the reaction. When it successes, a new PAM reactor has been built for the same reactions. This is the first application of the PAM reactor in our lab.

$$\text{Cooking oil} + \text{OH} \xrightarrow{\text{UV}} \text{Products}$$

$$\text{Cooking oil} + O_3 \longrightarrow \text{Products}$$

The cooking oil particles were atomized to the aerosol size distribution, mass concentration and density were obtained by using a Scanning Mobility Particle Sizer and an Aerosol Particle Mass Analyzer. A high-resolution time-of-flight aerosol mass spectrometer was used to characterize the produced aerosols.

2.1 Instruments

Flow Tube

Laboratory studies of heterogeneous organic aerosol oxidation have mostly been investigated in flow tube reactors, which use high radical concentrations and short reaction times to mimic low radical concentrations and long reaction time in the real atmosphere. In this study, the flow tube reactor was only available for the first reaction of canola oil with O_3, and was regarded as a preliminary work to determine whether the aerosols could form successfully during the reaction. When it success, the PAM reactor was built and was used for the same reactions.

PAM

Potential Aerosol Mass is the maximum aerosol mass that the oxidation of precursor gases produces. Same as the flow tube reactor, the PAM reactor is a highly oxidizing environment that simulates oxidation processes on timescales of days in the atmosphere in minutes in real time. It is not only being developed for measuring potential aerosol mass in the atmosphere but also using for observing SOA formation process in the laboratory.

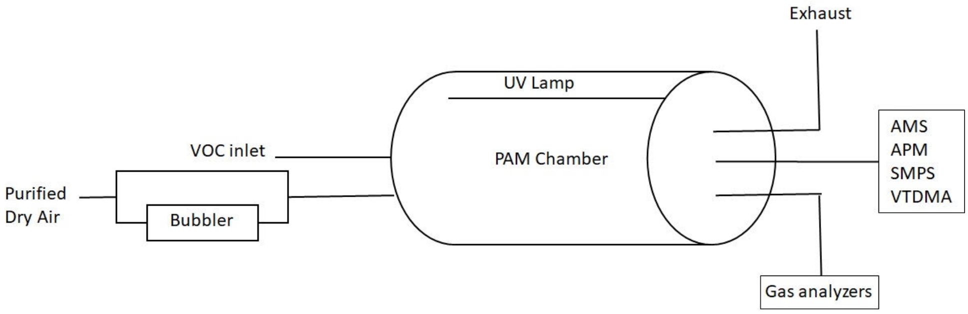


Fig.4 Schematic diagram of the PAM reactor setup

During the measurement, all precursor gases are rapidly oxidized with extreme amounts of oxidants like ozone (O_3), hydroxyl (OH), and hydroperoxyl (HO_2) to low volatility compounds, resulting in the aerosol formation. This method could simulate the photo-oxidation in the atmosphere—all of the processes, including oxidation of precursor gas, and gas and particle partitioning, should occur as they do in the atmosphere. In addition, instead of taking hours, the processes only take a few minutes to complete [16].

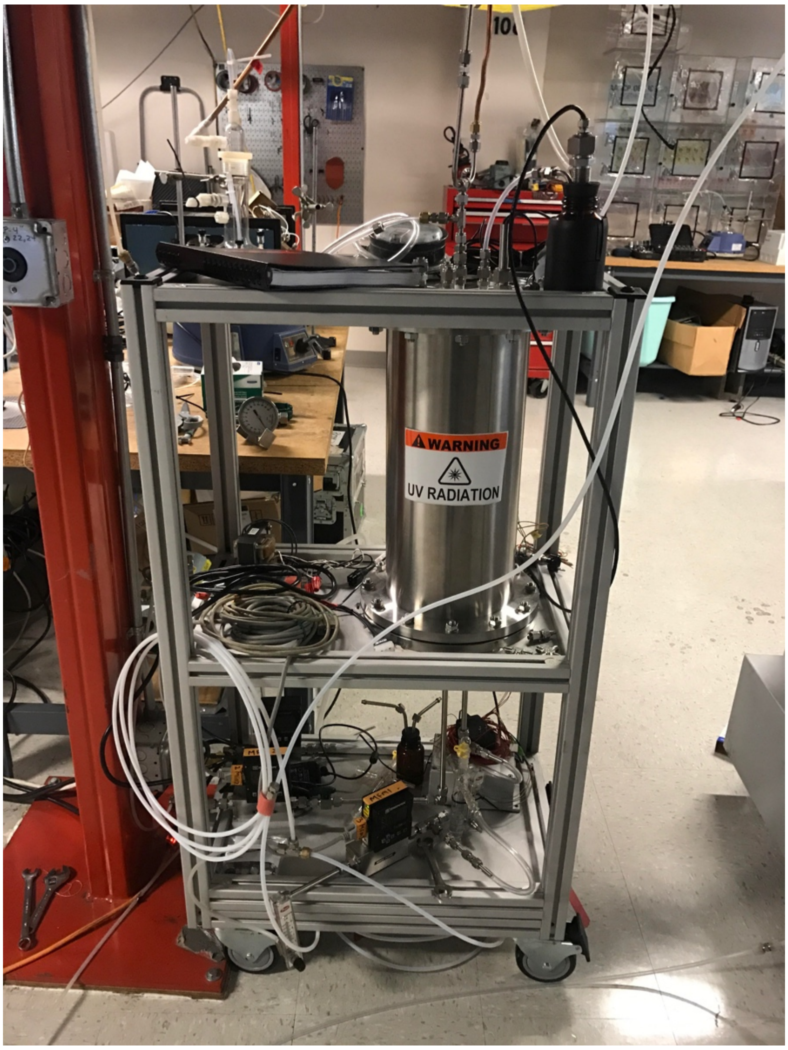


Fig.5 The PAM reactor setup in laboratory

Fig.4 shows the laboratory setup of the PAM reactor. The compressed air was humidified by passing it through a glass bubbler containing deionized water. The relative humidity was controlled by varying the fraction of the total flow rate that passes through the bubbler. In this study, the clean flow rate is 3LPM and the relative humidity is fixed at 50%-70% in the PAM chamber. A HEPA filter, placed downstream of the bubbler, removes any contaminant particles. The sample air was continuously added to the PAM reactor and released out through an exhaust tube at a constant flow rate of 2

LPM. Oxidation occurs in a small, flow-through chamber that has a short residence time and is irradiated with ultraviolet light. The amount of the oxidants can be measured directly and literally, can be controlled by varying the UV light and the relative humidity. However, in this situation, the relative humidity is sensitive and hard to control, it can`t be used as a standard for changing the oxidants concentration. So, in PAM experiments, the oxidants concentration can`t be controlled but the amount of the oxidants could be measured; we collected the data 30 mins before and after the reaction occurred. Humidity and temperature are monitored by a humidity and a temperature sensor.

APM

Aerosol Particle Mass Analyzer(APM) is widely used to classify particles by mass based on the balance between centrifugal force and electrostatic force. The aerosol densities of fresh oil and aging oil were assumed to be 0.9 g/ cm^3 and 1.14 g/ cm^3.

SMPS

Scanning Mobility Particle Sizer (SMPS) is widely used to measure particle number concentrations and size distributions. The column was ramped from -40 to -7000 V to monitor particle diameters from 28-730 nm. Combining the data from SMPS and APM, the aerosol mass concentrations can be calculated by multiplying the aerosol densities and total volume concentrations.

AMS

The organic aerosol composition was characterized using a high-resolution time-of-flight aerosol mass spectrometer (AMS). It can operate alternated between the high sensitivity V-mode and the high-resolution W-mode every minute. The V-mode data were analyzed using a fragmentation table to separate sulfate, ammonium, and organic spectra and to time-trace specific mass-to-charge ratios [17]. W-mode data were analyzed using a separate high-resolution spectra toolbox known as PIKA to determine the chemical formulas contributing to distinct mass-to-charge (m/z) ratios [18]. The ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C) were regarded as a standard to determine the aging of produced aerosols [19].

2.2 Aerosol Flow Tube Reaction Experiments

The cooking oils were purchased locally and stored in the laboratory at the room temperature. Figure 6 shows the scheme of the reaction of canola oil with O_3 in a flow tube reactor. A solution of 9 drops of canola oil in 400 mL methanol (analytical reagent grade, Fisher) was prepared for use in a constant-output atomizer. The atomizer was filled with clean air and exit flow rate of 10 L/min. The aerosol stream was then passed through a heater in order to evaporate methanol. Two charcoal denuders were used to remove methanol from the particles.

A series of steady state reactions of canola oil and ozone were carried out in the flow tube reactor (1.4 m long, 5.8 cm inner diameter, quartz tube). The flow tube was supplied with a constant wet air of 1 $L \cdot min^{-1}$ so that the humidity was not zero throughout the experiments. The total flow through the flow tube was fixed at 2.0

L·min−1, corresponding to a residence time of ~110 s. The relative humidity was fixed at 30% in the flow tube reactor. O_3 (150−2700 ppb) was generated by an O_3 generator (Ozone Solution Inc., HG-1500) at a constant flow rate at first, then increased the concentration of O_3, and concentration was measured by an O_3 monitor (2B Technologies, Inc.). The aerosol size distribution was monitored using a Scanning Mobility Particle Sizer (SMPS, TSI model 3936) which has been modified to achieve higher transmission of particles and improved sampling frequency. A high-resolution Time- to Flight aerosol mass spectrometer was used to characterize the produced aerosols. The density revolution of aerosols can be obtained by using an Aerosol Particle Mass Analyzer. Experiments were performed in an air-conditioned laboratory at 25°C.

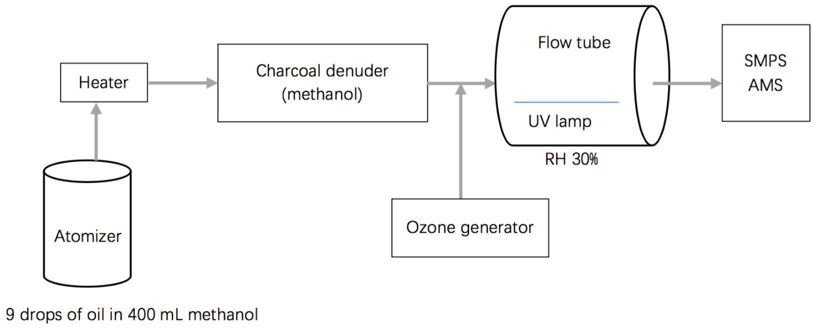


Fig.6 Schematic diagram of laboratory setup for the reaction of canola oil with O_3 in the flow tube reactor.

2.3 Potential Aerosol Mass(PAM) Experiments

The experimental scheme of a PAM reactor is similar to the scheme of a flow tube reactor (shown in Fig.7). A solution of 9 drops of peanut oil/ corn oil in 400 mL methanol (analytical reagent grade, Fisher) was prepared for use in a constant-output atomizer. The atomizer was filled with clean air and exit flow rate of 10 L/min. The aerosol stream was then passed through a heater in order to evaporate methanol. One charcoal denuder was used to remove methanol from the particles.

A series of steady state reactions of cooking oil and OH radical were carried out in PAM reactor (46 cm long, 20 cm diameter). The PAM chamber can provide a continuous flow at 2 LPM with a long enough residence time (~170s) that the fresh oil gases will be fully oxidized to aerosol particles. The relative humidity was fixed at 50%-70% in the PAM reactor. O_3 was generated by an O_3 generator (Ozone Solution Inc., HG-1500) at a constant flow rate of 1.7 LPM and the exit O_3 concentration is about 58ppm. The 8-hour average O3 concentration in the atmosphere is only about 45ppb, the O3 oxidation reaction occurs in the PAM reactor is hundreds of times faster than O3 oxidation in the atmosphere.

The OH radicals were formed in the PAM chamber from the reaction of water vapor with $O(^1D)$, produced from ozone photolysis by mercury lamps (λ = 254 nm, UVP, LLC). The OH concentration in the PAM cannot be adjusted since the O3 concentration cannot be controlled. The OH exposure ranged from zero to 1.33E12 molecules$\cdot$cm$^{-3}\cdot$s, equivalent to ten days` oxidation in the troposphere assuming a 24-h average OH concentration of 1.5E6 molecules$\cdot$cm^{-3}.

$$O_3 \xrightarrow{UV} O_2 + O(^1D)$$

$$H_2O + O(^1D) \longrightarrow OH$$

Equivalent time:

$$\text{OH:} \qquad \frac{1.33E12 mole/cm3*s}{1.5E6\frac{mole}{cm3}*3600s/h*24h} = 10\ days$$

For the first reaction of canola oil with OH radical, the flow through the PAM changed from 1 LPM to 2.5 LPM, but the aerosol particle mass concentration, size distribution and chemical composition didn`t change too much, and this indicates that the way by varying the flow rate through the PAM cannot change the concentration of OH radical. So in the rest experiments, the PAM flow rate is controlled, and the aerosol samples were collected for 30 min at a flow rate of 2 LPM. The aerosol mass concentration and size distribution was monitored using an APM and a SMPS, respectively. Oxidation product analysis by an AMS mass spectrometry. Experiments were performed in an air-conditioned laboratory at 25°C.

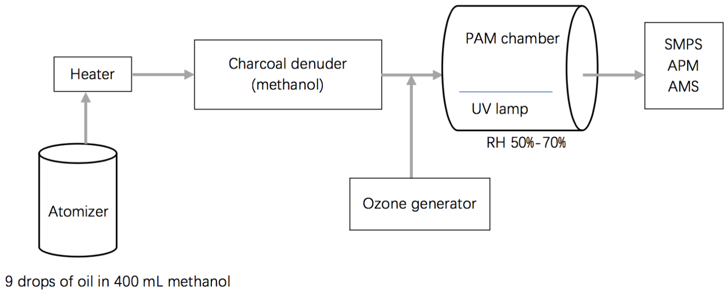


Fig.7 Schematic diagram of laboratory setup the reaction of cooking oil with O_3/OH radicals in PAM Reactor.

3. Results and Discussion

This study provides the measurements of aerosol density, potential aerosol mass, mass spectra of aerosols and O/C and H/C ratios determines the composition of the produced aerosols, and discusses how these aerosols are formed in oxidation reactions.

As Table 1 shows, the constituents of common cooking oil are quite different. Corn oil contains about 60% linoleic acid and 30% oleic acid, but in contrast to corn oil, in canola oil, there are only 30% linoleic acid and 64% oleic acid.

Table 1 Composition of common cooking oil [20]

Fat	Canola oil	Peanut(A) oil	Peanut(B) oil	Corn oil
profile	As weight percentage (%) of total fat			
Saturated fat	8	17	17	13
Oleic acid	64	51	51	28
Linoleic acid	28	32	32	59

Of the saturated fatty acid, 80% are palmitic acid (C16:0), 14% stearic acid (C18:0), and 3% arachnidan acid (C20:0)

Double bond equivalent is a method to determine the degree of unsaturation, and it can be calculated using this equation:

$$DBE = C + 1 - \frac{H}{2} - \frac{X}{2} + \frac{N}{2}$$

Where: C: Number of carbon atoms present

H: Number of Hydrogen atoms present

X: Number of Halogen atoms present

N: Number of Nitrogen atoms present

Table 2 Double bond equivalent of common cooking oil

Cooking oil	Canola oil	Peanut(A) oil	Peanut(B) oil	Corn oil
DBE	2.2	2.15	2.15	2.46

For Oleic acid, the DBE is 2, which means it has to abstract 2 pairs of hydrogens to get to the corresponding alkane. The DBE of linoleic acid is 3, the DBE of saturated fatty acid is 1, then the DBE of different cooking oil can be calculated (Table 2). The corn oil has a larger DBE comparing with that of peanut oil and canola oil, and this suggests that the corn oil contains more C=C double bonds and will abstract more pairs of hydrogens to get saturated. Therefore, these different levels of double bonds will cause differences in oxidation levels.

3.1 Density of Fresh oil and Aged oil

The normalized APM aerosol density obtained from canola oil, peanut oil and corn oil reactions with O_3 or OH separately is shown in Table 3. Since in the flow tube reactions the APM wasn`t hooked up to the system, the density of canola oil aerosols during reaction with O_3 could not be detected.

In a previous study, the density of cooking oil varies with type and temperature, and typically the range is from 0.91 to 0.93 g/cm^3[21]. In this study, the room temperature is 25°C, regardless of what kind of oil was heating, the density of unreacted oil particles was stable around 0.94+0.01 g/cm^3 and the density of aerosol particles that were obtained by the reaction was 1.07+0.7 g/cm^3. The density of methanol is 0.792g/cm^3, and if there was any methanol mixed in the aerosol flow, the density of aerosols should be lower than 0.93 g/cm^3. However, the density of each fresh oil is still big, which indicates that the oil that introduced into the PAM reactor is pure and methanol has been totally removed from particles. Therefore, the data collected from these instruments are reliable and the chemical compositions of aerosols can be measured.

In addition, the densities of aerosols have changed before and after these reactions, indicating the chemical composition is changing and there was reaction going on. In the O_3 oxidation experiments, the level of density variation of corn oil and peanut oil are similar, it`s about 0.13+0.01g/cm$^3$. In the OH oxidation experiments, the density of canola oil aerosols changed most comparing with that of corn oil and peanut oil, however, the density of canola oil aerosols in $O_3$ oxidation experiments has not been detected, it`s hard to confirm that the canola oil has a better oxidation ability.

Table 3 Density of fresh oil and aged oil

Density(g/cm3)	Canola oil	Peanut(A) oil	Peanut(B) oil	Corn oil
O_3 No reaction		0.94	0.94	0.95
O_3 reaction		1.07	1.07	1.09
OH No reaction	0.94	0.94	0.94	0.94
OH reaction	1.14	1.08	1.09	1.11

Fig.8 Density of fresh oil and aged oil

In conclusion, from the level of density variation of fresh oils and aged oils, it`s difficult to write a conclusion that which cooking oil has a good oxidation ability, but it is obvious that there was a reaction going on and the chemical compositions of aerosols were changed in the PAM reactor.

3.2 Potential Aerosol Mass of aerosols

Figures 9 and 10 show the particle mass from peanut oil and corn oil that in reaction with O_3 or OH radicals in the PAM reactor. The thin columns are represented for the actual mass concentration and the shadow parts are the average mass concentration. Since the particle density has changed from 0.94 g/cm^3 for fresh oil particles to 1.07+0.07 g/cm^3 for the aging aerosol particles, the total volume data cannot be used to represent the actual particle mass. Combining the density and volume data from APM and SMPS, the particle mass concentration can be calculated and summarized below.

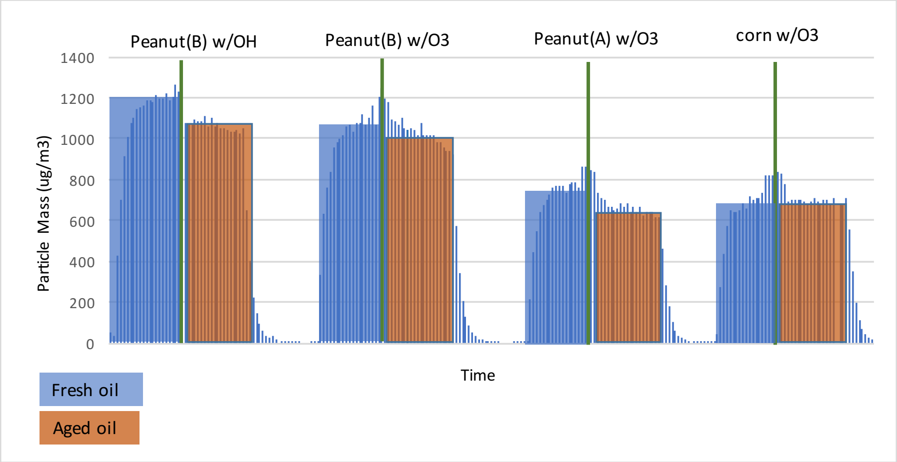


Fig.9 Particle mass of aerosols from Peanut oil (A), Peanut oil (B) and corn oil in O_3/ OH reaction

When the ultraviolet lamp of the O_3 generator was turned on, initiating injection of O_3 into the PAM. Concomitantly, the measured OA mass includes both the gas-phase oxidation products of the cooking oil that condense onto particles (SOA) and products of particle-phase heterogeneous chemistry which reside in the aerosol. The SOA was expected to produce as much as ten times by increases in the organic particle mass loading. Interestingly, there is a huge observation in this case, the particle mass decreased both in O_3 reaction and OH reaction, which stresses the SOA formation in this situation is less important. Conversely, the decreases in particle mass are dominated by the loss of oil. And the only reason for losing oil is the oxidation reaction occurred at particle surface or near-surface region.

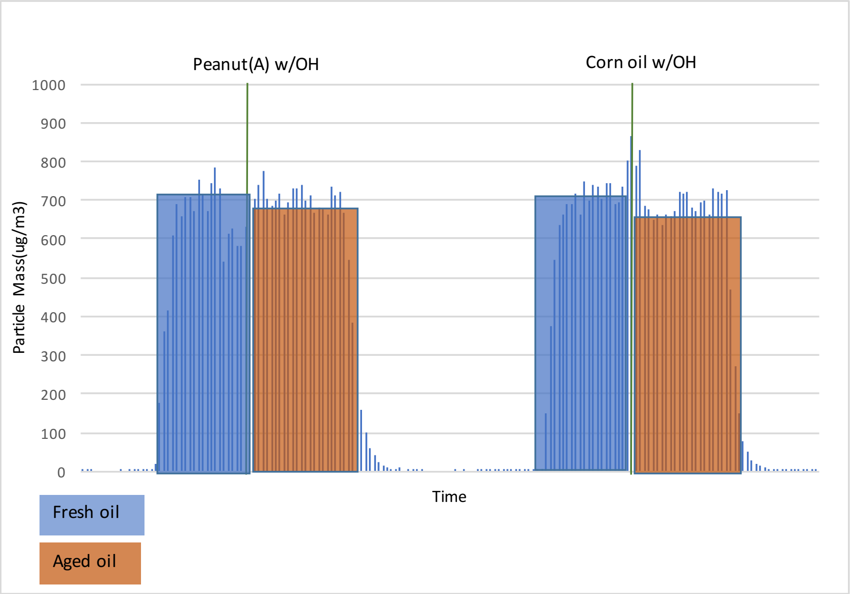


Fig.10 Particle mass of aerosols from peanut oil(A) and corn oil in reaction with OH in the PAM reactor.

3.3 Particles Size Distribution

Typically, the size of an oil droplet in the atmosphere depends on the temperature. In this case, all reactions occurred at the room temperature, so, the only reason for particle size shifts is the oxidation reaction. Fig 11 shows examples of the aerosol particle size distribution before and after the reactions with O_3 in the PAM reactor. When the reaction comes to equivalent, the size distribution shift left a little bit, which indicates the particle which participates in the reaction actually shrinks in size as the reaction progresses.

The particle shrinks in size in O_3 oxidation reactions agreed well with particle mass decreased when the O_3 initiating injection in the PAM. The agreement between size distribution shifts left and particle mass decreases, is evidence both that the particle which participates in the reaction react at the particle surface.

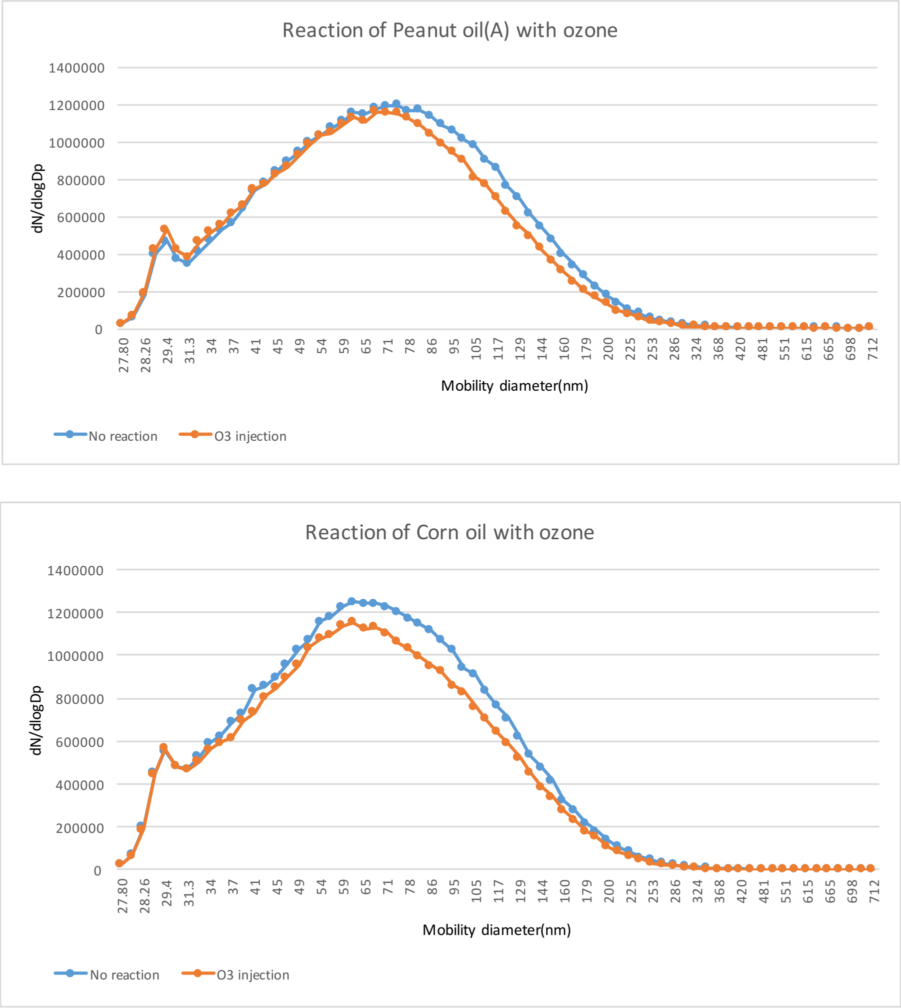


Fig.11 Examples of particle size distribution: (a) peanut oil reaction with ozone and (b) corn oil reaction with ozone.

When the particle size is around 30 nm, there is a small peak. The reason may be because of an artifact of the algorithm (data inversion) in the program matrix caused by the wide distribution when the raw counts were under processed. Typically, this small inversion is less than 1%, so there is no need to focus on that.

3.4 Comparisons of Aerosol Mass Spectrums

So far, we can confirm that there was a reaction in the PAM reactor. In contrast to other oxidations in the atmosphere where SOA formation is expected to be the most important reaction, the loss of oil droplets is the dominant process regardless of the cooking oils. But which ion responds for this loss of oil is not clear. A high-resolution time-of-flight aerosol mass spectrometer is used to characterize the chemical composition of aerosols in more detail.

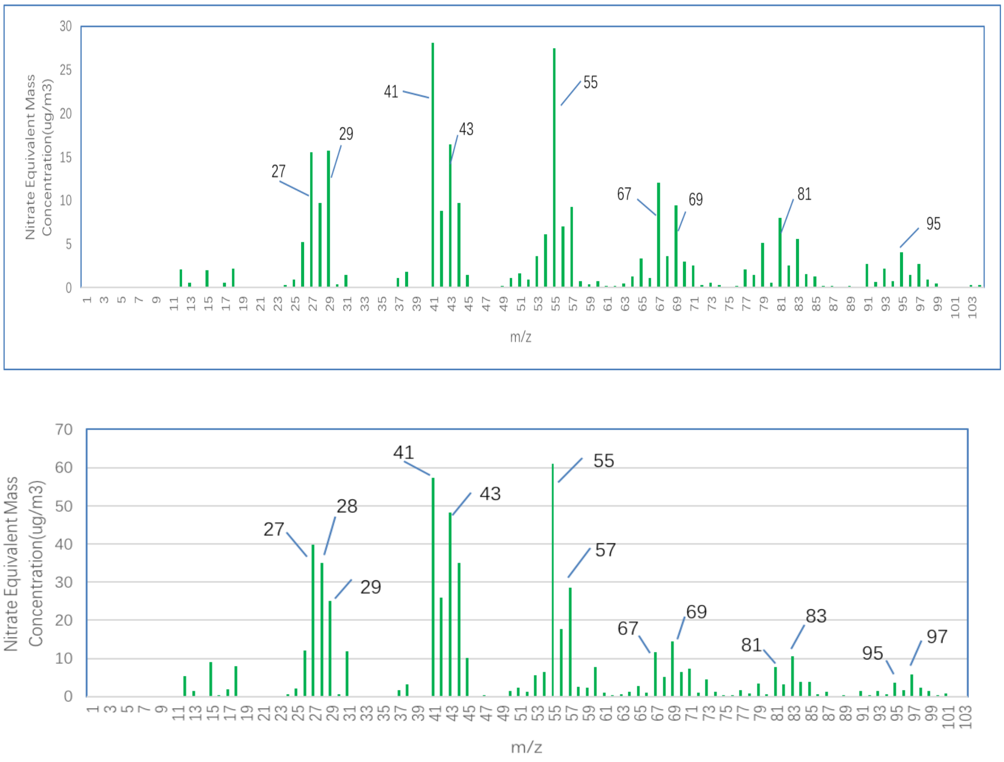


Fig.12 Representative examples of mass spectra, showing the main ion fragments: (a) canola oil, (b) peanut oil

Fig 12 shows the background average mass spectra of fresh oil: canola oil and peanut oil. Emissions from canola oil were abundant in components with m/z = 27, 29, 41, 43, 55, 67, 69, 81 and 95. While the emissions from corn oil were abundant at m/z=27, 28, 29, 41, 43, 55, 57, 67, 69, 81, 83, 95 and 97.

To compare the differences between the mass spectra of different type of cooking oil and understand more about how these mass spectra vary before and after in each reaction, a spectral-contrast-angle (θ) method is used to compare the similar structural isomers` mass spectra between fresh oil and aged oil [22].

This method represents collisionally active dissociation (CAD) spectra as vectors in space. Mass spectra of different isomers are represented as different vectors, having characteristic lengths and direction. The derived spectral angle, which is a measure of the angle between two vectors corresponding to two closely related spectra, is a measure of whether the mass spectra are the same or significantly different. A 90º angle indicates a maximal spectral differentiation.

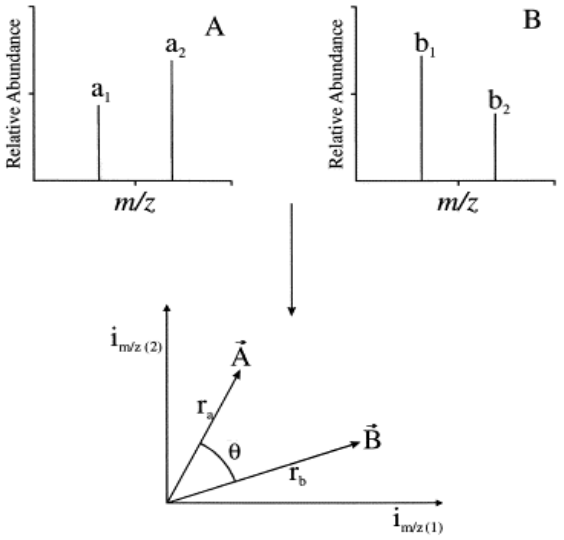


Fig.13 Schematic vector representations of the Spectra A and B

Figure 13 illustrates the representation for two isomeric compounds (A and B) if their production spectra are presented as vectors. It shows only two peaks in the scheme for simplicity, but the whole *m/z* range in the production spectra can be used in the vector representation. An *N*-dimensional vector is then constructed when *N* different *m/z* values are used.

The length and direction in space of the vector is determined by the peak *m/z* and intensities. The lengths (*r*) of vectors A and B (Figure 12) are determined by these two equations and are proportional to the compounds' concentrations.

$$r_a=\sqrt{\sum_i a_i^2}$$

$$r_b=\sqrt{\sum_i b_i^2}$$

Mass spectra can be quantitatively compared by the derived spectral contrast angle (θ). The angle, θ, is defined as:

$$cos\theta=\frac{\sum_i a_i^2 b_i^2}{\sqrt{\sum_i a_i^2 \sum_i b_i^2}}$$

where a_i and b_i are the relative intensities of production peaks at *m/z* value *i* for isomers A and B. An angle of zero degrees means there are no discernible spectral differences. Spectra that resemble each other have vectors that point in the same direction in the space. A 90° angle indicates a maximal spectral differentiation.

Table 4 Spectral contrast angle of fresh oil vs aged oil

Cooking oil	Canola oil	Peanut(A) oil	Peanut(B) oil	Corn oil
Angle in O3	22.83	24.07	19.97	29.78
Angle in OH	24.14	20.87	21.22	26.53

Table 4 shows spectral contrast angle of different types of cooking oil in reactions with O_3 or OH radicals. As shown in Table 4, no matter in O_3 or OH oxidation reactions, corn oil has the largest angle of about 30°, which is larger than canola oil around 23° and peanut oil around 20°. The differences between these angles indicate that the changing level of these mass spectra are different. The angle of corn oil is largest because it contains more double bonds.

On the other hand, an angle of 20° means the two similar mass spectrums are different, the composition of fresh oil has changed after the oxidation, but we don`t know which ion should response for the change. Therefore, we need to use a high resolution AMS data of more specific ions to identify these differences.

3.5 Specific Ion Mass Spectra

Table 5 Table of common fragment Ions (%)

m/z	Compounds	Canola oil	Peanut oil	Corn oil
27	C_2H_3	6.67	5.34	5.17
29	C_2H_5, CHO	2.22	5.45	5.05
41	C_3H_5,	13.69	12.50	11.56
43	C_3H_7, CH_3CO	7.99	9.61	7.96
55	C_4H_7	15.89	15.56	14.11
57	C_4H_9, C_2H_5CO	4.24	6.45	5.20
67	C_5H_7	8.16	7.83	10.28
69	C_5H_9	6.08	7.51	6.71
81	C_6H_9	5.51	5.38	6.85

The observed m/z values are assigned to the most likely compounds as shown in Table 5. The compounds that relative intensity larger than 5% are summarized in this table. Comparing the common fragment ions in canola oil, peanut oil and corn oil, the emissions from peanut oil and corn oil were both abundant in components with m/z=27, 41, 43, 55, 57, 67, 69, 81. The reason why the emissions from canola oil were not abundant in components with m/z=29 is worth to explore in the future work.

The ion signal at m/z= 29, 43 and 57 are typically regarded as a standard to indicate the reason for increases of O/C ratios. The mass concentration of CHO, C2H3O, and C3H5O increased significantly when the reaction began, which suggests the oxygen atom added into the double bond and caused increases of O/C ratios.

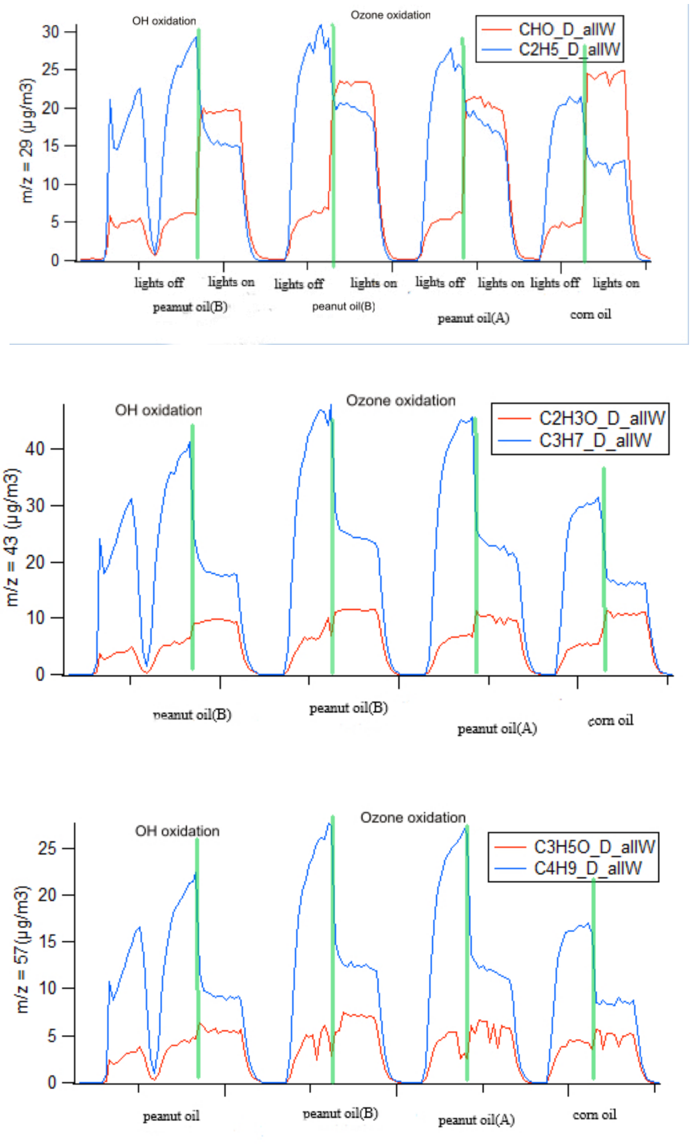


Fig.14 Special mass spectra at m/z=29, 43, 57 of peanut oil and corn oil after oxidation.

3.5 O/C and H/C Ratios

Oxygen to Carbon (O/C) Ratio ratios characterize the oxidation state of organic aerosol (OA), and O/C from ambient urban OA ranges from 0.2 to 0.8 with a diurnal cycle that decreases with primary emissions and increases because of photochemical processing and secondary organic aerosol (SOA) production.

Fig.15 shows the H/C and O/C ratios of canola oil in reaction with O_3 in Flow tube reactor. The concentration of O_3 kept increasing during the reaction, O_3 exposure can be calculated in this equation

$$O_3\ \text{exposure}=[O_3]\cdot T$$

Where:

$[O_3]$ is the concentration of O_3 (ppm)

T is the exposure time (min)

The exposure time is the average time that the sample air is exposed to the O_3 in the chamber. The H/C ratio of Canola oil aerosols were expected to decrease when oxidation reaction happened, because more oxygen atoms added on the particle, more hydrogen atoms subtracted. But in this case, all the H/C ratios increased a little bit.

The OH radicals have two ways to react with C=C double bond, one is abstract the hydrogen atom, the other one is adding the hydrogen atom on the particle. In this situation, the OH radicals are more likely to add hydrogen atoms on the particle, which makes the C=C double bond get saturated to form single bond.

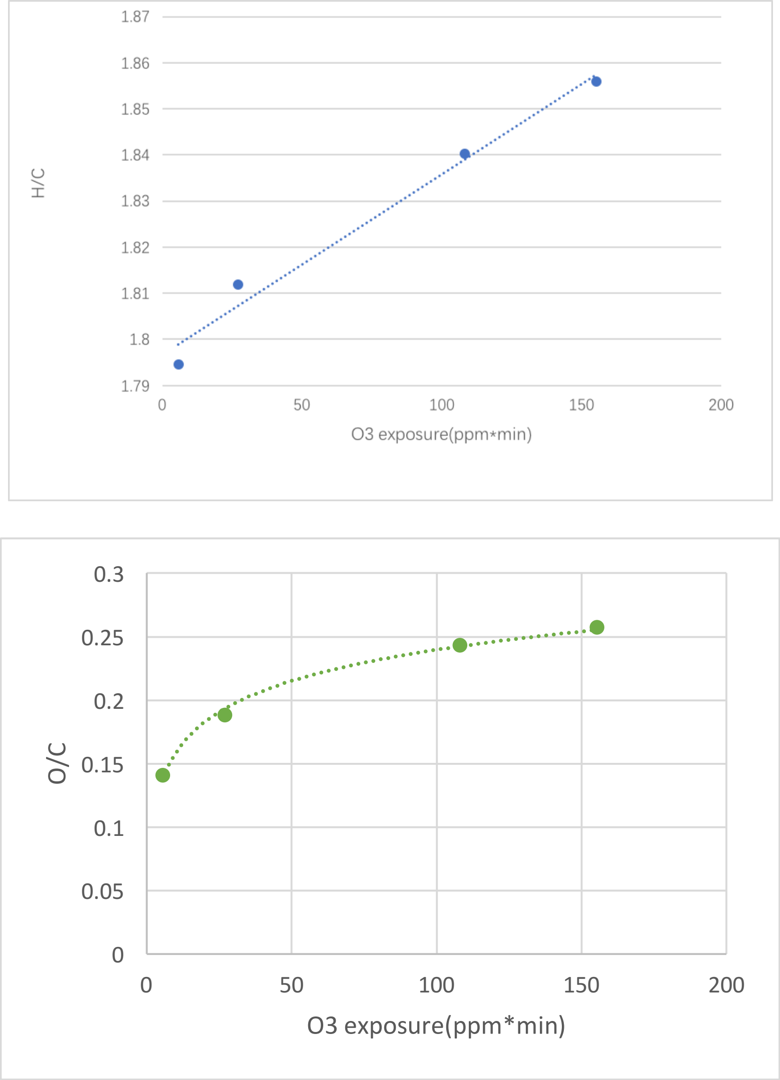
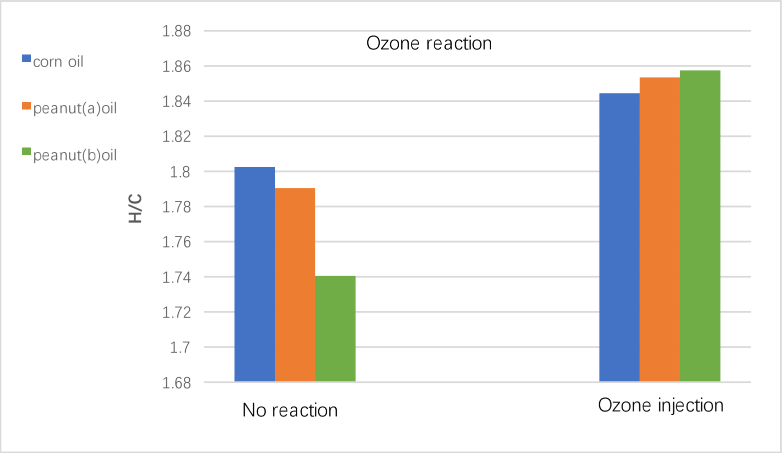


Fig.15 H/C and O/C ratios of Canola oil in reaction with O_3 in the flow tube reactor

The O/C ratio of canola oil is a function of O_3 exposure, it increased rapidly when the O_3 exposure is smaller than 50 ppm*min, when the O_3 exposure larger than 100 ppm*min, the O/C ratio increased smoothly. The plateau is caused by the mass transfer limitation, which plays an important role in the rate of reaction. Estimating the transformation rate of oxidation is a good aspect for future work.



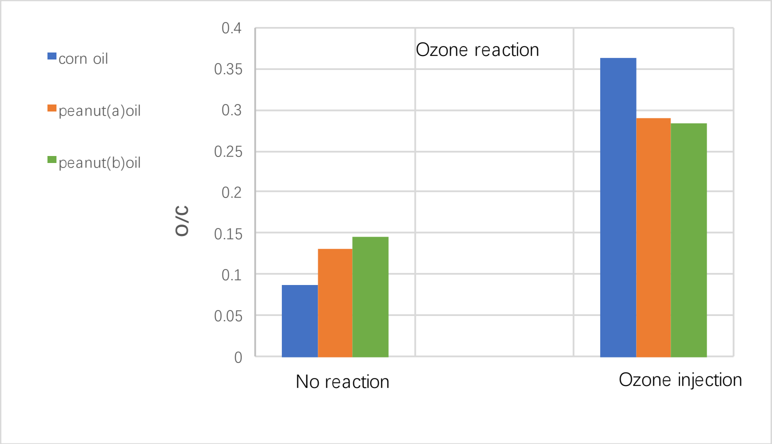


Fig.16 H/C and O/C ratios of Corn oil and Peanut oil in reaction with O_3 in the PAM reactor

Fig.16 shows the H/C and O/C ratios of corn oil, peanut oil in reaction with O_3 in the PAM chamber, the reason for the increases of H/C ratios is the same as that of canola oil, the C=C double bonds lost and formed single bonds to get saturated.

In O_3 oxidation reactions, O_3 selectively reacts with unsaturated C=C double bond but behaves inertly toward saturated hydrocarbons. As Fig.16 shown, the O/C ratios of corn oil and peanut oil increase significantly when the O_3 injected into the PAM as expected based on increased oxidation, the background average O/C value further indicates this trend of increasing O/C with increased processing time or “age”.

From the DBE data, the corn oil has a larger DBE comparing with that of peanut oil and canola oil, it suggests the corn oil contains more C=C double bonds. The O/C ratio of corn oil increased significantly compared with that of peanut oil, which agreed well with the corn oil has a larger DBE. In other words, the corn oil contains more double bonds, makes it easier to oxidant in the reaction.

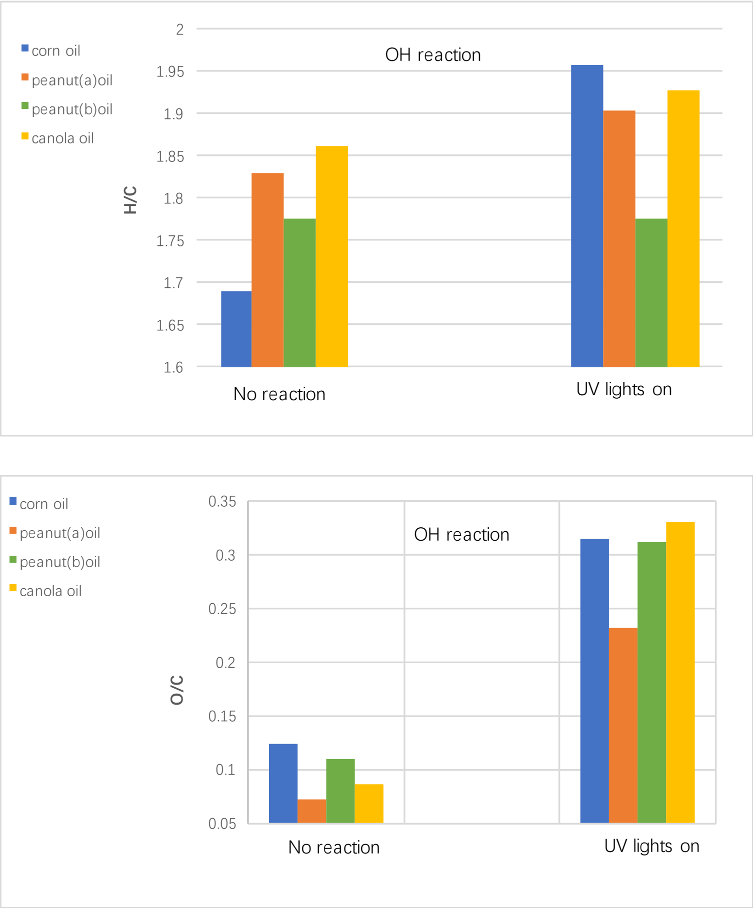


Fig.17 H/C and O/C ratios of corn oil, peanut oil and canola oil in reaction with OH in the PAM chamber

In OH oxidation reactions, OH could both react with saturated hydrocarbons to form water or add itself on the unsaturated hydrocarbons. In Fig 17, we report the H/C ratios of different cooking oils, in agreement with the observations by other authors such as Kroll et al. [23], Chowdhury et al. [24], it is interesting to observe the initial increase in H/C ratios with oxidation, possibly due to the addition of OH groups to the multiple C=C double bonds in the molecule. The increasing O/C ratio verifies the oxidation happened. However, the O/C ratio is complicated by the competition of functionalization and fragmentation. The constant increases of O/C ratios in different oils is not a giant observation.

4. Conclusion

Cooking processes were recognized as major contributors to $PM_{2.5}$ pollution besides industrial pollution and vehicle emissions in some cities. The chemical compositions and oxidation behaviors of cooking oils are well understood in this study.

Canola oil, peanut oil and corn oil were used to react with O_3 or OH radicals in a flow tube reactor or a PAM reactor. The scanning mobility particle sizer and an aerosol particle mass analyzer were combined to identify the particle density, mass concentration and size distribution. A high-resolution time-of-flight aerosol mass spectrometer is used to characterize the chemical composition of aerosols and speculate how cooking oils oxidant in the atmosphere.

The results and conclusions can be summarized as below:

1. Corn oil contains about 60% linoleic acid and 30% oleic acid, while canola oil and peanut oil contain about 30% linoleic acid and 60% oleic acid. The proportion of fatty acids is different making the DBE is different. Corn oil has a larger DBE. These different levels of double bonds in cooking oil will cause differences in oxidation behaviors.

2. The density of cooking oil was typically ranged from 0.91 to 0.93 g/cm^3, and the density of methanol is 0.792 g/cm^3, if there was any methanol mixed in the aerosol flow, the density of aerosols should be lower than 0.93 g/cm^3. However, the densities of different types of fresh oils are higher than 0.94 g/cm^3, which indicates the oil that introduced into the PAM reactor is pure, and the methanol has been totally removed from particles. The density of cooking oils varied before and after the reaction, indicates there was a reaction going on and the chemical compositions of aerosols were changed in the PAM reactor.
3. The SOA was expected to produce as much as ten times by increases in the organic particle mass loading because of the gas-phase oxidation products of the cooking oil that condensed on particles. However, the particle mass decreased both in O_3 reaction and OH reaction, which stresses the SOA formation in this situation is less important. Conversely, the decreases in particle mass are dominated by the loss of oil. And the only reason for losing oil is the oxidation particle-phase heterogeneous chemistry reaction occurred at particle surface or near-surface region.
4. The left shift of size distribution can verify the mass decay in the oxidation reactions. The loss of oil dominated the reaction and the reaction occurred at particle surface or near-surface region.
5. A high-resolution time-of-flight aerosol mass spectrometer is used to characterize the chemical composition of aerosols. The background average mass spectra of different types of cooking oils are quite similar. A spectral-contrast-angle (θ) is the method used to compare the similarity mass spectra of fresh oil and aged oil. Corn oil has the largest angle about 30°, which is larger

than canola oil around 23° and peanut oil around 20°. The differences between these angles indicate that the changing level of these mass spectra are different. The corn oil has a larger DBE makes its mass spectra changed most. The higher number of double bonds gives the more opportunities for oxidation.

6. When the ozone exposure high enough will cause a plateau in O/C ratio because of the mass transfer limitations. The O/C ratio increased after the reaction, verifying there was an oxidation happened. However, the O/C ratio is complicated by the competition of functionalization and fragmentation. It`s normal to see the increases of O/C ratios in different oils are constant.
7. The increase in H/C ratios in this study, possibly due to the addition of oxidant groups to the multiple C=C double bonds in the molecule, the loss of double bonds makes particle become more saturated.

Although we have observed a special pathway in which cooking oil may oxidized in atmosphere, there are still some results can`t be explained clearly and worth for further research in the future.

1. We have detected the oxidation reaction of cooking oil occurred on the particle surface, but the mechanism heterogeneous oxidation and in-particle reactions of cooking oil in atmosphere is not clear.
2. The relative humilities in the flow tube and the PAM chamber are different, how this difference effect the oxidation process is worth discussing.
3. The common compounds fraction of corn oil and peanut oil are similar, while canola oil miss some specific ions, what caused this difference?

4. When the ozone exposure is high enough, the O/C ratio increased slowly. Because the mass transformation limits the further reactions in particles, so, what`s the mass transformation rate of oxidation?

5. References

1. Murphy, Brandi; Lyle, Mitchell W; Olivarez Lyle, Annette (2006): (Table T1) Carbon composition and biogenic silica of ODP Hole 199-1221C sediments. PANGAEA.

2. Ziemann PJ, Atkinson R. (2012) Kinetics, products, and mechanisms of secondary organic aerosol formation. Chem Soc Rev. 2012 Oct 7;41(19):6582-605. doi: 10.1039/c2cs35122f. Epub 2012 Aug 31.

3. Abdullahi, K.L., Delgado-Saborit, J.M., Harrison, R.M., 2013. Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: a review. Atmos. Environ. 71, 260–294.

4. Fann N, Lamson AD, Anenberg SC, Wesson K, Risley D, Hubbell BJ. (2012). Estimating the national public health burden associated with exposure to ambient $PM_{2.5}$ and ozone. Risk Analysis. 2012;32(1):81–95.

5. Kearney, J., Wallace, L., MacNeill, M., Xu, X., VanRyswyk, K., You, H., Kulka, R. and Wheeler, A.J. (2011). Residential Indoor and Outdoor Ultrafine Particles in Windsor, Ontario. Atmos. Environ. 45: 7583–7593.

6. He, L.Y., Hu, M., Huang, X.F., Yu, B.D., Zhang, Y.H., and Liu, D.Q. (2004). Measurement of Emissions of Fine Particulate Organic Matter from Chinese Cooking. Atmos. Environ. 38: 6557–6564.

7. Amouei Torkmahalleh, M., Goldasteh, I., Zhao, Y., Udochu, N.M., Rossner, A., Hopke, P.K., Ferro, A.R., 2012. PM2.5 and ultrafine particles emitted during heating of commercial cooking oils. Indoor Air 22, 483–491.

8. Smith KR, Samet JM, Romieu I, Bruce N. Indoor air pollution in developing countries and acute lower respiratory infections in children. Thorax. 2000;55(6):518–32. doi: 10.1136/thorax.55.6.518.

9. Smith KR. National burden of disease in India from indoor air pollution. Proc Natl Acad Sci. 2000;97(24):13286–93. doi: 10.1073/pnas.97.24.13286.

10. Amouei Torkmahalleh, M., Zhao, Y., Hopke, P.K., Rossner, A., Ferro, A.R., 2013. Additive impacts on particle emissions from heating low emitting cooking oils. Atmos. Environ. 74, 194–198.

11. Kansal Sources and reactivity of NMHCs and VOCs in the atmosphere: a review J. Hazard. Mater, 166 (2009), pp. 17-26

12. Buonanno, G., Johnson, G., Morawska, L. and Stabile, L. (2011) Volatility characterization of cooking-generated aerosol particles, Aerosol Sci. Technol., 45, 1069– 1077.

13. Theodora Nah, Sean H. Kessler (2013) OH-initiated oxidation of sub-micron unsaturated fatty acid particles. Phys.Chem,2013,15,18649.

14. Xiang He, Chunbo Leng, Shufeng Pang and Yunhong Zhang, 2017.Kinetics study of heterogeneous reactions of ozone with unsaturated fatty acid single droplets using micro-FTIR spectroscopy. RSC Advances, 2017, 7, 3204.

15. J. W. Morris and P. Davidovits, J. T. Jayne, J. L. Jimenez, Q. Shi, C. E. Kolb, and D. R. Worsnop, 2002. Kinetics of submicron oleic acid aerosols with ozone: A novel aerosol mass spectrometric technique. Geophysical Research Letters, VOL. 29, NO. 9, 1357, 10. 1029/2002GL014692, 2002.

16. E. Kang, M. J. Root, D. W. Toohey, and W. H. Brune (2007) Introducing the concept of Potential Aerosol Mass (PAM). Atmos. Chem. Phys., 7, 5727–5744, 2007

17. Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnopf, D. R.: A generalised method for the extraction of chemically resolved mass spectra from aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909–922, doi:10.1016/j. jaerosci.2004.02.007, 2004.

18. DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Fielddeployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–8289, doi:10.1021/Ac061249n, 2006.

19. Canagaratna, M.R., Jimenez, J.L., Kroll, J.H., Chen, Q., Kessler, S.H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L.R., Wilson, K.R., Surratt, J.D., Donahue, N.M., Jayne, J.T., Worsnop, D.R., 2015. Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications. Atmos. Chem. Phys. 15, 253–272.

20. "Corn oil, industrial and retail, all-purpose salad or cooking, fat composition, 100 g". US National Nutrient Database, Release 28, United States Department of Agriculture. May 2016. Retrieved 6 September 2017.

21. Shreya N. Sahasrabudhe, Veronica Rodriguez-Martinez, Meghan. O'Meara & Brian E. Farkas, 2017.Density, viscosity, and surface tension of five vegetable oils at elevated temperatures: Measurement and modeling. International Journal of Food Properties.1965-1981, 29 Dec 2017

22. Katty X. Wan, IIan Vidavsky, and Michael L. Gross. Jan 2002.Comparing Similar Spectra: From Similarity Index to Spectral Contrast Angle. Journal of the American Society for Mass Spectrometry. January 2002, Volume 13, Issue1, pp 85-88.

23. Jesse H. Kroll, Christopher Y. Lim, Sean H. Kessler, and Kevin R. Wilson, 2015. Heterogeneous Oxidation of atmospheric Organic Aerosol: Kinetics of Changes to the Amount and Oxidation state of Particle-Phase organic carbon. J. Phys. Chem. A 2015, 119, 10767-10783.

24. Pratiti Home Chowdhury, Quanfu He, Tatyana Lasitza Male, William H. Brune, Yinon Rudich, and Michal Pardo, 2018. Exposure of Lung Epithelial Cells to Photochemically Aged Secondary Organic Aerosol Shows Increased Toxic Effects. Environ. Sci. Technol. Lett. 2018, 5, 424–430.