Trends in Renewable Energy
OPEN ACCESS ISSN: 2376-2144
Peer-Reviewed Article futureenergysp.com/index.php/tre

Pyrolysis-Gas Chromatography/Mass Spectrometry Analysis of Oils from Different Sources

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Received March 10, 2021; Accepted May 22, 2021; Published May 23, 2021

Regenerated gutter oil (*i.e.*, waste oil) accounts for 10% of the edible oil market, which has caused serious food safety issues. Currently, there is no standard protocol for the identification of the gutter oil. In this study, the pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) method was employed to analyze eleven oil samples including edible vegetable oils (tea oil, corn oil, olive oil, sunflower oil, peanut oil and blend vegetable oil) and waste oils (used frying oil, lard, chicken fat, inferior oil and kitchen waste grease). Three factors of pyrolysis temperature, reaction time and sample volume were investigated to optimize the analytical parameters. The optimal pyrolysis conditions were determined to be 600°C, 1 min and an injection volume of 0.3 μL. Five characteristic components (tetradecane, z,z-9,12-octadecadienoic acid, decanoic acid-2-propenyl ester, 17-octadecenoic acid, and z-9-octadecenoic acid) were found in all oil samples. The existence of C11-C16 olefins in the pyrolytic products of the animal fats and the other low-quality oils could be utilized to distinguish vegetable oils from gutter oils.

Keywords: Pyrolysis; Gutter oil; GC/MS; Waste oil; Olefins

Introduction

In the past ten years, food safety issues related to the reuse of waste oil or grease (*i.e.*, gutter oil) have been frequently exposed [1]. It is estimated that the regenerated waste oil accounts for up to 10% of the cooking oil market, *i.e.*, about 2.5 to 3 million tons of waste oil returns to the dining table every year [2]. As edible oils are a necessity in everyday life, the National Health Department of China began to focus on strengthening the techniques to detect and analyze edible oils.

In addition to the conventional physical and chemical indicators, the current detection/analytical methods of waste oils include various chromatographic methods, spectroscopy, nuclear magnetic resonance, etc. [3-5]. However, due to the complicated sources of waste oil, the complex composition, different processing methods, and different refining degrees, there is no single specific indicator or standard to distinct waste oils from edible oils. Consequently, it is imperative to develop a standard analytical method for the detection of the waste oil.

Because of the high boiling point, food oils are hardly to be analyzed directly. Therefore, the oil or grease is usually methylated and then analyzed by gas chromatography (GC) or gas chromatography coupled with mass spectrometry (GC/MS) [6]. In terms of the pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

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Tr Ren Energy, 2021, Vol.7, No.1, 53-72. doi: 10.17737/tre.2021.7.1.00127

technology, oils can be directly pyrolyzed and the small molecules produced by the pyrolysis process are further identified by GC/MS [7]. The obtained pyrolytic products are a very intuitive reflection of the cracked fragments of the oil, which is equivalent to a series of changes in the simulated oil under pyrolytic temperature conditions [8]. The pyrolysis reactor adopts a vertical micro-furnace structure to measure the temperature of the sample in real time. The pyrolysis results demonstrate good reproducibility and overcome the deficiency of easy loss of high-boiling substances, which is conducive to obtaining more accurate analysis results [9].

In this study, eleven different oil samples were collected. The samples included vegetable oils (tea oil, olive oil, peanut oil, corn oil, sunflower oil, and blend vegetable oil), animal fat/oils (lard and chicken fat), and some low-quality oils (used frying oil, kitchen waste grease, and inferior oil). Py-GC/MS was conducted to analyze the pyrolytic products and characteristic peaks of oils from different sources.

Materials and Methods

Sample Collection and Preservation

The samples of this study mainly included two categories: edible vegetable oils and waste oils (used frying oil, lard, chicken fat, inferior oil and kitchen waste grease). The edible vegetable oils were purchased from the supermarket. The used frying oil and animal oils (chicken fat and lard) were collected from the home kitchen following cooking. The inferior oil with a very low price was purchased from the market. The waste grease was collected from the dining hall of the University. The sample names and the sources are summarized in Table 1. All samples were stored at room temperature.

Table 1. The oil samples from different sources*

Number	Name	**Brand or Source**
1	Sunflower seed oil	Jinlongyu®
2	Corn oil	Jinlongyu®
3	Peanut oil	Hujihua®
4	Olive oil	Geely Tree®
5	Tea oil	Jinggangshan®
6	Blend vegetable oil	Maidelong®
7	Frying oil	Home kitchen after cooking
8	Inferior oil	Market place
9	Waste grease	Dining hall of the University
10	Lard	Home kitchen after cooking
11	Chicken fat	Home kitchen after cooking

*The oil samples of 7 to 11 satisfied with the definition of the gutter oil or the waste oil.

Pretreatment of Oil Samples

The oil samples of 9-11 (*i.e.*, waste grease, lard, and chicken fat) contained a small amount of water. Therefore, a pretreatment was conducted to remove the moisture from these oils. Firstly, an appropriate amount of oil sample was poured into the centrifuge tube, and then an appropriate amount of anhydrous sodium sulfate was added to the centrifuge tube. The centrifuge tube was vortexed and the water absorption of the sodium sulfate can be observed. In case, if there is no floating matter aggregates, it is still necessary to add a small amount of sodium sulfate until granular particles appeared.

Finally, the centrifuge tube was centrifuged at 3000×G for 20 minutes. Then, the supernatant was carefully collected as the pretreated oil sample.

Pyrolysis Coupled with Gas Chromatograph/Mass Spectrometer (Py-GC/MS)

Pyrolysis of oil samples was conducted in a sample cup of Frontier PY-2020iD pyrolyzer (Fukushima, Japan). For each experiment, the pyrolyzer was pre-heated to the desired temperature (300°C, 400°C, 500°C or 600°C), and then purged with ultra-purity helium to remove oxygen. A certain amount of samples (0.1 μL,0.3 μL, or 0.5 μL) was allowed to drop into the pyrolyzer, whereby the sample was pyrolyzed for 30 s, 1 min, 3 min or 5 min. The volatilized products were injected directly into a Shimadzu GCMS-QP2010 gas chromatograph/mass spectrometer (Shimadzu, Japan) equipped with a Frontier Ultra-Allov5 capillary column (Fukushima, Japan).

For GC/MS analysis, the carrier gas of helium (99.999% purity) with a flow rate of 1 $mL \cdot min^{-1}$ and the split ratio of 50:1 were used. The inlet temperature of GC was maintained at 300°C. The temperature of the GC oven was initially set at 35°C and held at 35°C for 2 min, then ramped to 350°C at a rate of 15 $°C \cdot min^{-1}$ and held at 350°C for 10 min. The pyrolytic products were identified by comparison with the NIST mass spectral library (National Institute of Standards and Technology, USA). The distribution of compounds was calculated as the peak area percentage.

Results and Discussions

This study attempted to optimize the detection method of the waste oils, mainly from the three influencing factors of pyrolysis temperature, the sample amount, and the pyrolysis residence time. The pyrolysis temperature refers to the temperature whose sample is pyrolyzed in the pyrolysis furnace, *i.e.*, the temperature before entering the GC column.

Determination of Pyrolysis Reaction Conditions

Impact of Pyrolysis Temperature

The direct pyrolysis of the waste oils without methyl esterification was performed by Py-GC/MS and the parameters were optimized accordingly. Firstly, the effect of the pyrolysis temperature was studied. Because the smoke point of edible oils starts at 170°C, a lower pyrolysis temperature of 150-200°C was first studied. However, it was found that the pyrolysis at the low temperature was difficult to obtain the volatile effluent, and almost no pyrolytic products appeared. Therefore, the pyrolysis temperature was further increased to 300°C, 400°C, 500°C and 600°C. Taking sunflower oil as an example, the experiments were carried out under the conditions of the sample volume of 1 μL and the pyrolysis time of 1 min. The total ion current (TIC) chromatograms are shown in Figures 1 and 2.

Comparison of Figure 1 with Figure 2 shows that as the pyrolysis temperature rose from 300°C to 600°C, the number of pyrolytic products gradually increased, resulting in more peaks on the TIC chromatogram. The resolution was higher at 600°C which is determined as the optimal pyrolysis temperature in this study.

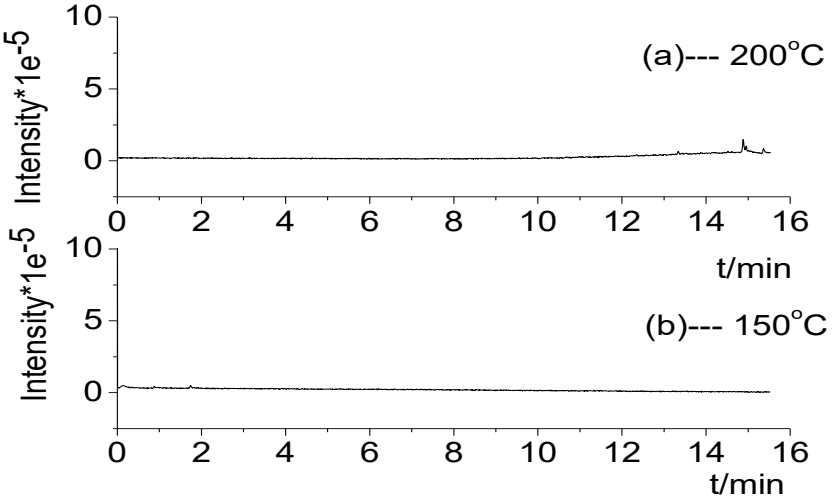

Figure 1. The pyrolysis TIC chromatogram of sunflower oil at (a) 200°C, (b) 150°C

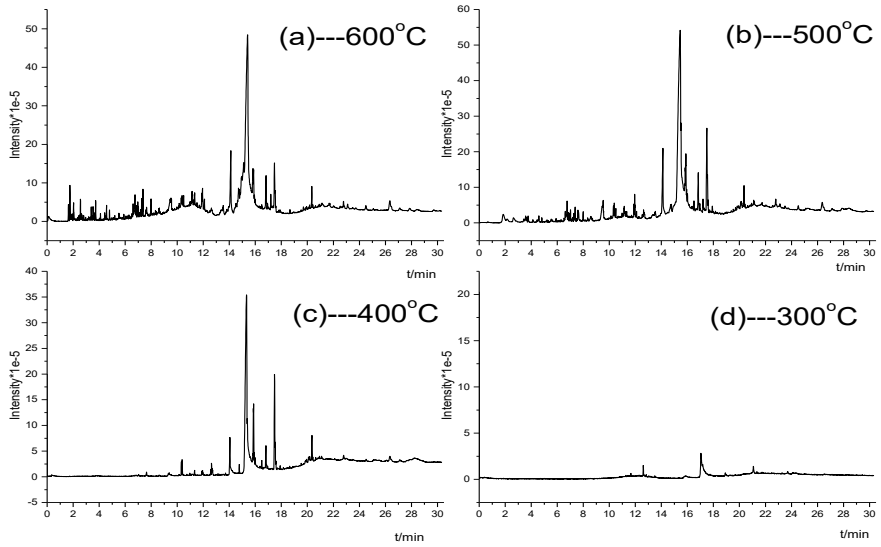

Figure 2. The pyrolysis TIC chromatogram of sunflower oil at (a) 600°C, (b) 500°C, (c) 400°C and (d) 300°C

Optimization of Sample Volume

To optimize the sample volume of pyrolysis, the oil samples of 0.1 μL, 0.3 μL and 0.5 μL were injected into the Py-GC/MS. After each pyrolysis, a blank experiment was performed under the same reaction conditions to check the residue remaining in the GC column. Taking the peanut oil as an example, all experiments were conducted at the pyrolysis temperature of 600°C for 1 min. The TIC chromatogram results are shown in Figures 3-5.

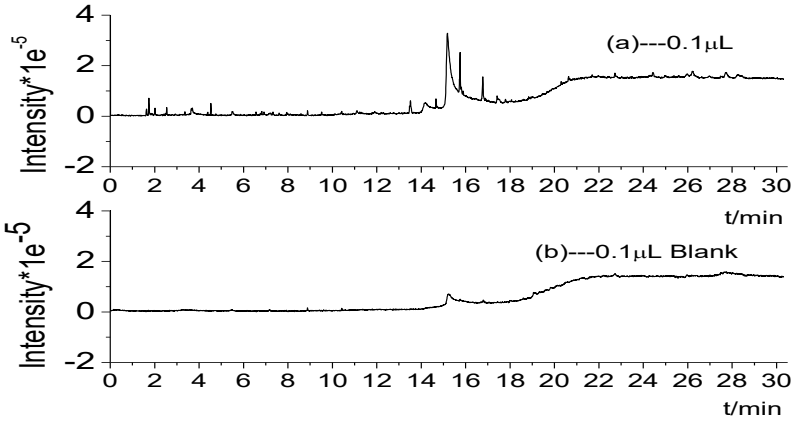

Figure 3. The pyrolysis TIC chromatogram of 0.1 μL peanut oil and the blank analysis after pyrolysis

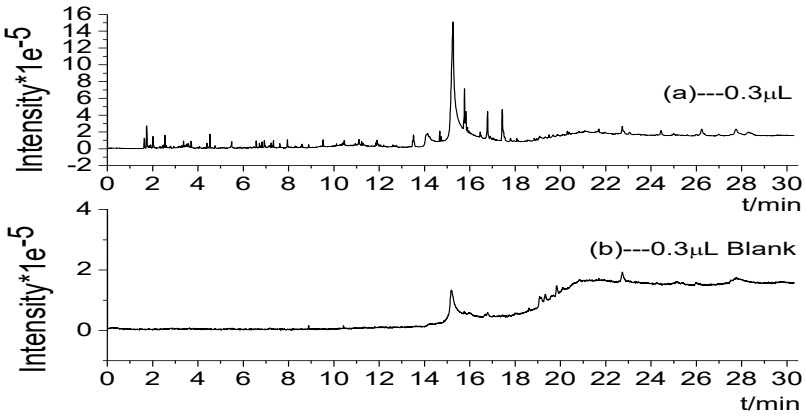

Figure 4. The pyrolysis TIC chromatogram of 0.3 μL peanut oil and the blank analysis after pyrolysis

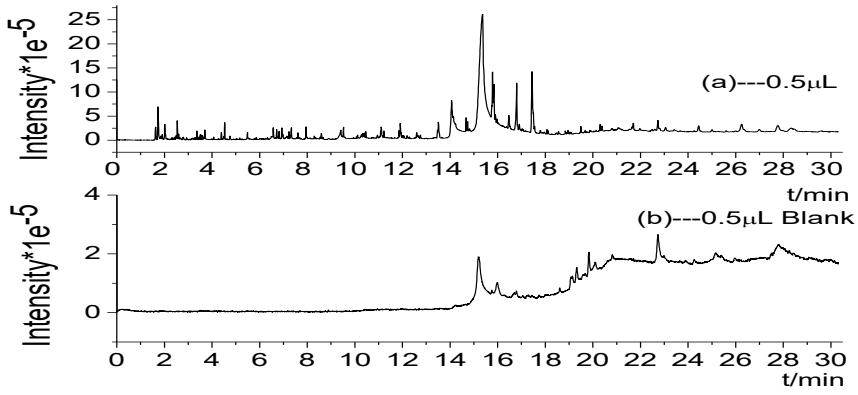

Figure 5. Pyrolysis TIC chromatogram of 0.5 μL peanut oil and the blank analysis after pyrolysis

The comparison with the blank chromatogram after pyrolysis shows that when the injection volume was 0.1 μL and 0.3 μL, the amount of residue in the GC column was

relative negligible. When the injection volume increased to 0.5 μL, the amount of residue in the column was more evident. This may affect the analytic results of the following samples. Additionally, the peaks of the TIC chromatogram were not clear for the sample injection of 0.1 μL. Therefore, the optimal injection volume was determined as 0.3 μL in this study.

Optimization of Pyrolysis Reaction Time

Pyrolysis time was investigated at the pyrolysis temperature of 600°C and an injection volume of 0.3 μL. Times studied were 30 s, 1 min, 3 min, and 5 min. The TIC chromatogram in Figure 6 shows very similar results under the reaction time of 0.5 to 5 min. However, when the pyrolysis time was greater than 1 min, the peak intensities of the total ion current were more evident than those of 0.5 min. Accordingly, the optimal pyrolysis time was determined as 1 min.

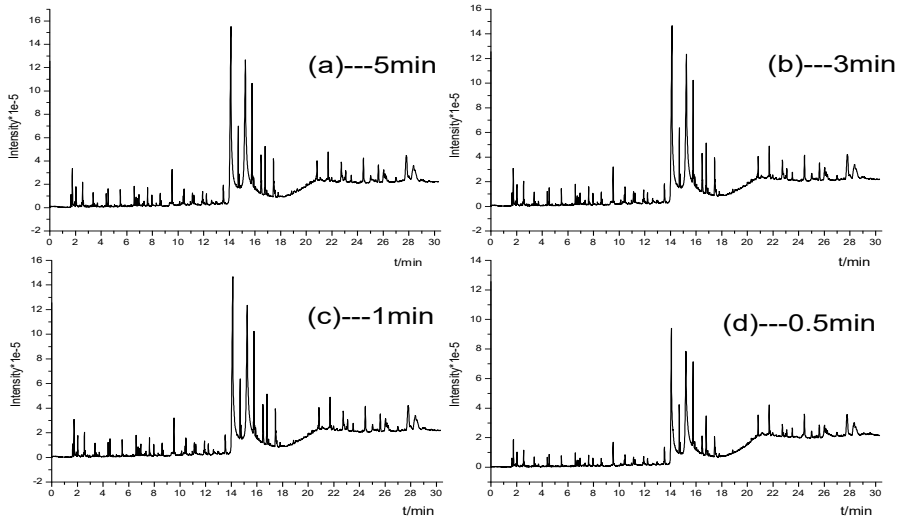

Figure 6. The pyrolysis TIC chromatogram of the inferior oil for (a) 5 min, (b) 3 min, (c) 1 min, (d) 0.5 min

Pyrolysis of Oils from Different Sources

The oil samples including tea oil, olive oil, peanut oil, corn oil, sunflower oil, vegetable blend oil, used frying oil, lard, chicken fat, inferior oil and kitchen waste grease were pyrolyzed at 600°C and a volume of 0.3 μL for 1 min. The TIC results are shown in Figures 7-17.

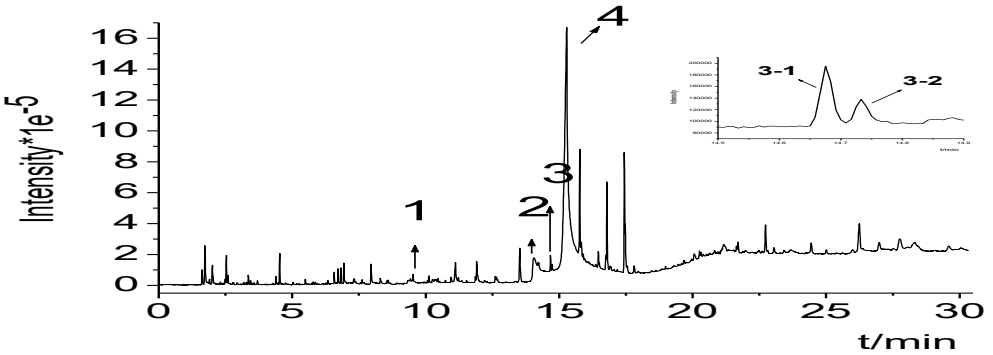

Figure 7. The pyrolysis TIC chromatogram of the tea oil

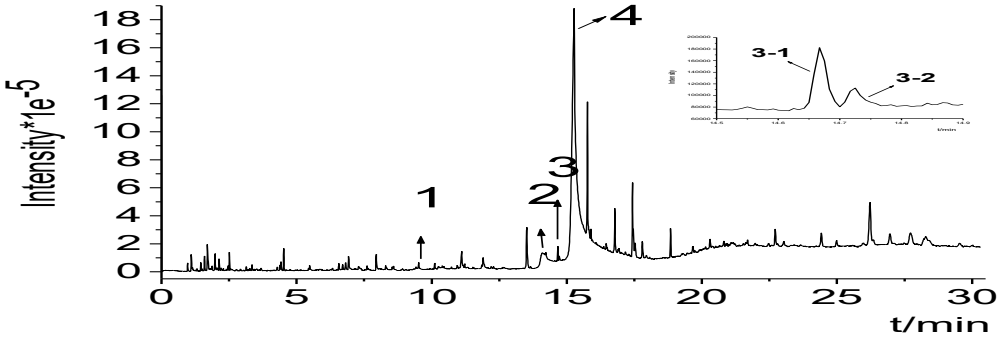

Figure 8. The TIC chromatogram of pyrolysis of the olive oil

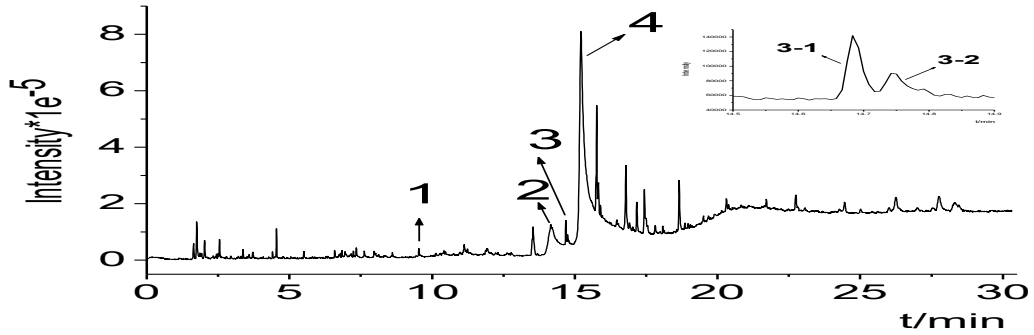

Figure 9. The pyrolysis TIC chromatogram of the peanut oil

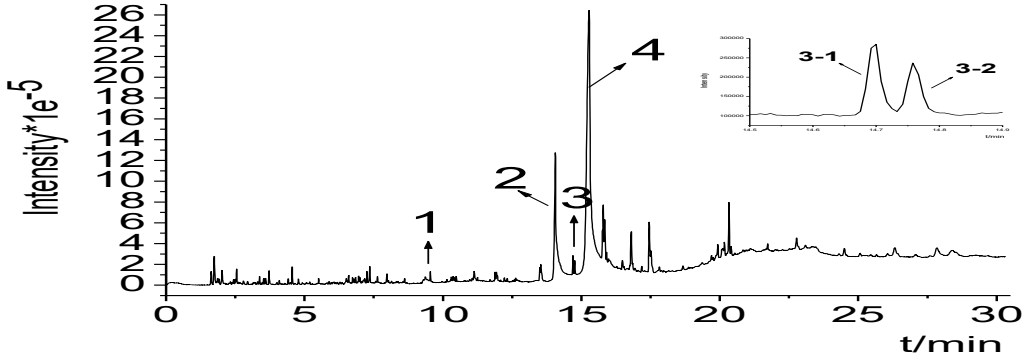

Figure 10. The pyrolysis TIC chromatogram of the corn oil

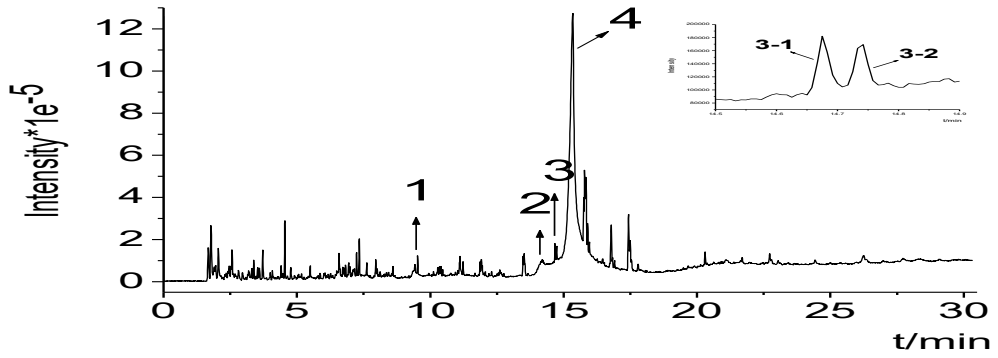

Figure 11. The pyrolysis TIC chromatogram of the sunflower oil

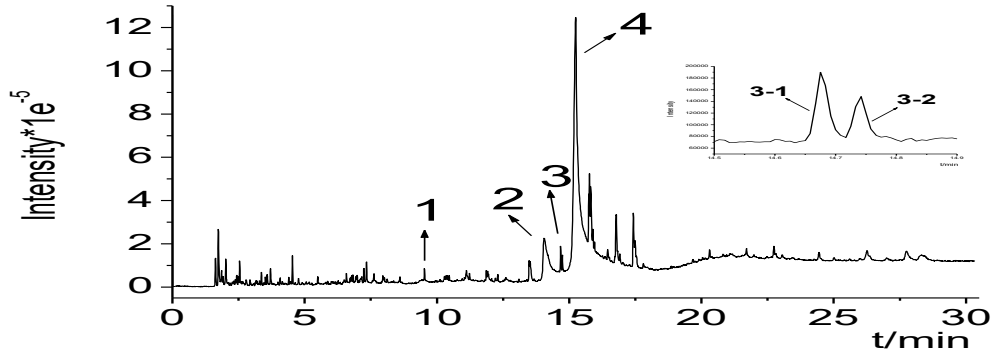

Figure 12. The TIC chromatogram results of pyrolysis of the blend vegetable oil

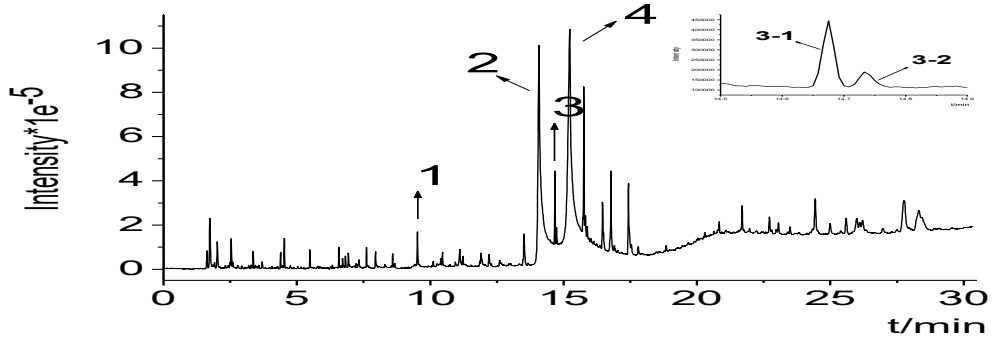

Figure 13. The pyrolysis TIC chromatogram of the used frying oil

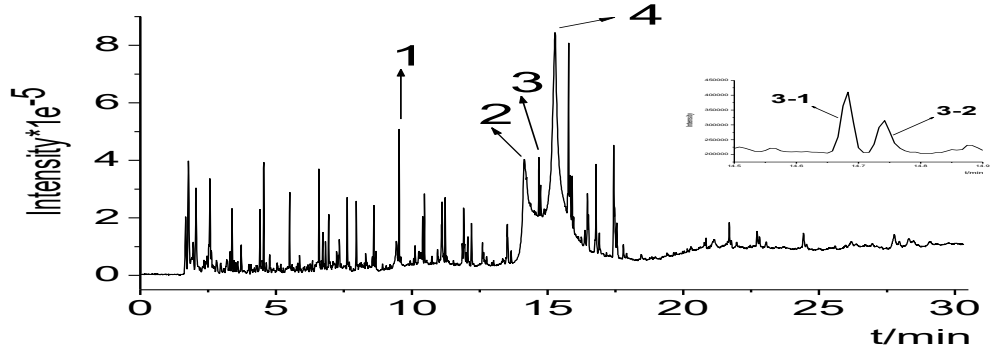

Figure 14. The pyrolysis TIC chromatogram of the lard

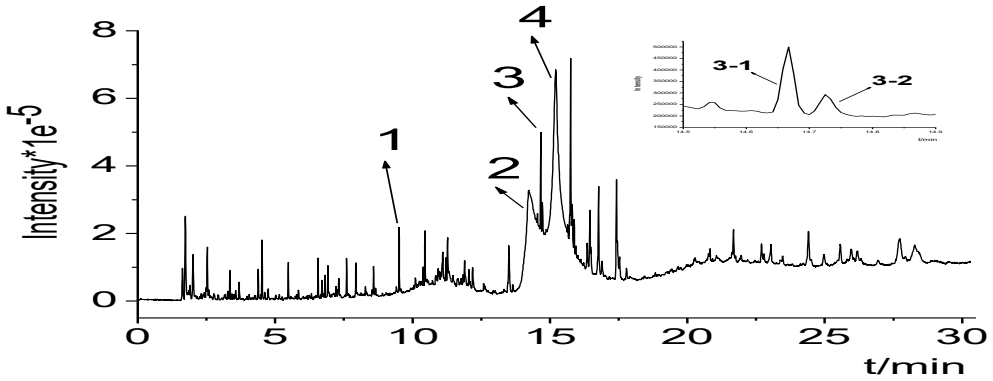

Figure 15. The pyrolysis TIC chromatogram of the chicken fat

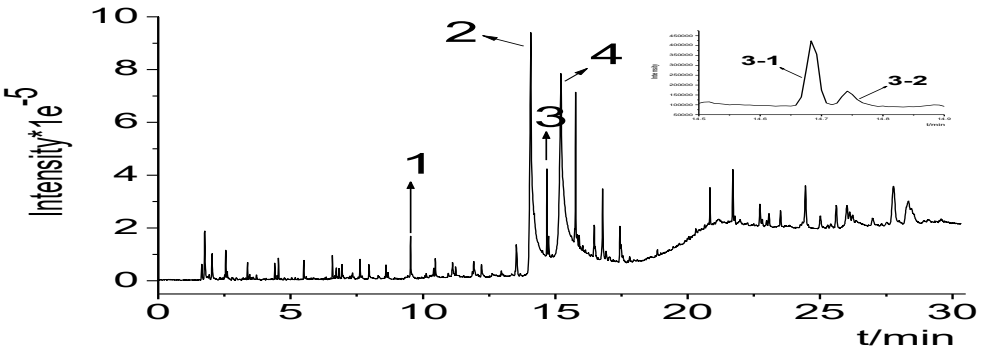

Figure 16. The pyrolysis TIC chromatogram of the inferior oil

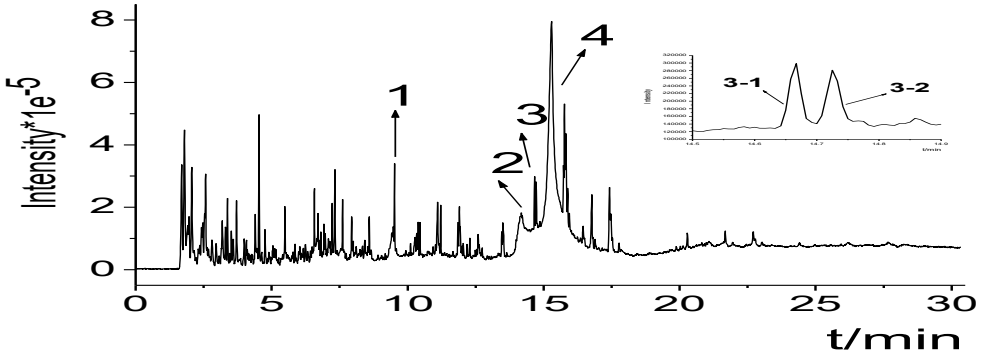

Figure 17. The pyrolysis TIC chromatogram of the kitchen waste grease

The TICs of all oil samples were quite complicated in terms of the number of peaks and the peak shape. Because vegetable oils or animal oils are essentially fatty acid glycerides, the resulting TICs after pyrolysis were very similar. Nevertheless, the TICs of oil samples from different sources could be distinguished by either the retention time for different compounds or the peak height/area for the same compound.

A specific peak, named as Peak 1 was observed at the retention time of 9.5 min. This peak was identified as tetradecane by searching through the NIST library. The comparison of Peak 1 of different oil samples is listed in Table 5.

Table 5. Comparison of Peak 1 of different samples

Sample	Retention time (min)	Peak area	Peak height	Similarity
Tea oil	9.524	6.74E+04	7.30E+04	92%
Olive oil	9.518	4.94E+04	6.69E+04	92%
Peanut oil	9.535	3.50E+04	4.17E+04	90%
Corn oil	9.545	1.14E+05	1.32E+05	92%
Sunflower oil	9.527	1.11E+05	1.24E+05	92%
Blend vegetable oil	9.529	8.60E+04	8.58E+04	92%
Used frying oil	9.519	2.31E+05	1.71E+05	96%
Chicken fat	9.51	2.52E+05	5.10E+05	97%
Lard	9.532	5.65E+05	2.21E+05	96%
Inferior oil	9.532	2.10E+05	1.70E+05	96%
Kitchen waste grease	9.517	3.38E+05	3.42E+05	95%

The area of Peak 1 of all edible vegetable oils was less than 2.0E+05, and the peak height was less than 1.50E+05. And the similarity of all edible vegetable oils in this peak was less than 92%, while the results of animal oils, used frying oil, inferior oil, and kitchen waste grease showed opposite trends. This feature may be employed as an evaluation indicator to distinguish vegetable oils from lard, chicken fat, kitchen waste grease, and inferior oil.

Two other distinct peaks appeared between 14 and 16 minutes were marked as Peak 2 and 4, respectively. These two peaks showed obvious higher peak intensities. A smaller peak between Peak 2 and 4 was marked as Peak 3. To be more specific, Peak 3 could be distinguished into two very close small peaks, labeled as Peaks 3-1 and 3-2. The height of these peaks of various oil samples is summarized in Table 6.

Table 6. The height of Peak 2, 3 and 4 of various oils and fats

Sample	H#2	H#3-1	H#3-2	H#4	Ratio of H#4/H#2
Tea oil	1.79E+05	1.95E+05	1.37E+05	1.67E+06	9.33
Olive oil	1.36E+05	1.82E+05	1.13E+05	1.89E+06	13.90
Peanut oil	1.28E+05	1.42E+05	9.47E+04	8.16E+05	6.38
Corn oil	1.27E+06	2.84E+05	2.43E+05	2.65E+06	2.09
Sunflower oil	1.06E+05	1.84E+05	1.69E+05	1.27E+06	11.98
Blend vegetable oil	2.27E+05	1.89E+05	1.48E+05	1.25E+06	5.51
Used frying oil	1.01E+06	4.50E+05	1.91E+05	1.09E+06	1.08
Chicken fat	4.04E+05	4.12E+05	3.18E+05	8.46E+05	2.09
Lard	3.33E+05	5.00E+05	2.92E+05	6.84E+05	2.05
Inferior oil	9.48E+05	4.25E+05	1.70E+05	1.86E+05	0.20
Kitchen waste grease	1.87E+05	3.04E+05	2.86E+05	7.95E+05	4.25

H: the peak height; #: the peak number

For most vegetable oils, the height of Peak 2 was shorter, but the height of Peak 4 was higher. In terms of the peak height ratio of these two peaks, the ratio of H#4/H#2 was the largest for vegetable oils. For animal oils and other low-quality oils, this ratio was small. For example, the height of Peak 2 of the inferior oil was slightly higher than that of Peak 4 with a ratio of 0.20. However, corn oil and kitchen waste oil did not

conform to the above rules. This ratio (2.09) for corn oil was not as large as other vegetable oils, while kitchen waste grease had a sufficient height difference with a ratio of 4.25. The height of Peak 3-2 of all oils and fats peaks was relatively close. But the height of Peak 3-1 was obviously different, *i.e.*, the peak heights of all edible vegetable oils were less than 3.00E +05 and others were greater than 3.00E+05. Therefore, edible vegetable oils can be distinguished from other fats.

Analysis of Pyrolytic Products of Oils from Different Sources

Because the structure of the pyrolytic products following Peak 4 was relatively complex and the similarities of the corresponding chemicals were low, this study specifically analyzed the pyrolytic products prior to Peak 4 and compared the similarity of various oils. The main ingredients (about 90%) are listed in the following Tables 7-17.

Table 7. Analysis of the pyrolytic products of tea oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	96%	56	C_3H_4O	1.725
2	Cyclopentene	92%	68	C_5H_8	1.9
3	Hexene	97%	84	C_6H_{12}	2.009
4	Cyclohexene	94%	82	C_6H_{10}	2.492
5	Heptene	98%	98	C_7H_{14}	2.533
6	Octene	95%	112	C_8H_{16}	3.358
7	E-1,4-octadiene	90%	110	C_8H_{14}	3.7
8	Nonene	95%	126	C_9H_{18}	4.392
9	Cyclooctene	98%	110	C_8H_{14}	4.534
10	Decene	93%	140	$C_{10}H_{20}$	5.492
11	1-Undecene	95%	154	$C_{11}H_{22}$	6.575
12	2-Undecene	95%	154	$C_{11}H_{22}$	6.717
13	1,4-Undecene	91%	152	$C_{11}H_{20}$	6.933
14	E-1,8-Dodecadiene	91%	166	$C_{12}H_{22}$	7.949
15	Tetradecene #1	92%	196	$C_{14}H_{28}$	9.524
16	8-heptadecene	97%	238	$C_{17}H_{34}$	11.908
17	Cis-9-hexadecenal	96%	238	$C_{16}H_{30}O$	13.525
18	Z,Z-9,12-octadecadienoic acid#2	87%	282	$C_{18}H_{34}O_2$	14.042
19	Decanoic acid-2-propenyl ester#3-1	85%	212	$C_{13}H_{24}O_2$	14.2
20	17-octadecenoic acid #3-2	86%	282	$C_{18}H_{34}O_2$	14.233
21	Z-9-octadecenoic acid #4	96%	282	$C_{18}H_{34}O_2$	15.284

#1---Peak 1; #2---Peak 2; #3-1---Peak 3-1; #3-2---Peak 3-2; #4---Peak 4

Table 8. Analysis of the pyrolytic products of olive oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	94%	56	C_3H_4O	1.7
2	Hexene	96%	84	C_6H_{12}	1.982
3	Heptene	97%	98	C_7H_{14}	2.515
4	Octene	93%	112	C_8H_{16}	3.35
5	Nonene	93%	126	C_9H_{18}	4.382
6	Cyclooctene	97%	110	C_8H_{14}	4.524
7	Decene	88%	140	$C_{10}H_{20}$	5.483
8	Undecene	93%	154	$C_{11}H_{22}$	6.566
9	2-Undecene	93%	154	$C_{11}H_{22}$	6.699
10	E-1,4-Undecadiene	91%	152	$C_{11}H_{20}$	6.926
11	E-1,8-Dodecadiene	90%	166	$C_{12}H_{22}$	7.951
12	2E,4Z-Dodecadiene	93%	166	$C_{12}H_{22}$	8.291
13	E-7-tetradecene	90%	196	$C_{14}H_{28}$	8.591
14	Tetradecene #1	92%	196	$C_{14}H_{28}$	9.517
15	8-heptadecene	94%	238	$C_{17}H_{34}$	11.899
16	Cis-9-hexadecenal	96%	238	$C_{16}H_{30}O$	13.518
17	Z,Z-9,12-octadecadienoic acid#2	90%	280	$C_{18}H_{32}O_2$	14.092
18	Decanoic acid-2-propenyl ester#3-1	86%	212	$C_{13}H_{24}O_2$	14.666
19	17-octadecenoic acid #3-2	87%	282	$C_{18}H_{34}O_2$	14.725
20	Z-9-octadecenoic acid #4	92%	282	$C_{18}H_{34}O_2$	15.274

Table 9. Analysis of the pyrolytic products of peanut oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-propenaldehyde	93%	56	C_3H_4O	1.75
2	Hexene	95%	84	C_6H_{12}	2.025
3	Heptene	96%	98	C_7H_{14}	2.55
4	Octene	93%	112	C_8H_{16}	3.375
5	Nonene	90%	126	C_9H_{18}	4.409
6	Cyclooctene	96%	110	C_8H_{14}	4.542
7	Decene	90%	140	$C_{10}H_{20}$	5.5
8	Undecene	91%	154	$C_{11}H_{22}$	6.591
9	6-Butyl-1,4-cycloheptadiene	89%	150	$C_{11}H_{18}$	7.342
10	Dodecene	88%	168	$C_{12}H_{24}$	7.626
11	Cetyl Alcohol	91%	242	$C_{16}H_{34}O$	9.533
12	Tetradecene #1	90%	196	$C_{14}H_{28}$	9.535
13	Cis-9-hexadecenal	92%	238	$C_{16}H_{30}O$	13.533
14	Z,Z-9,12-octadecadienoic acid#2	87%	280	$C_{18}H_{32}O_2$	14.158
15	Decanoic acid-2-propenyl ester#3-1	83%	212	$C_{13}H_{24}O_2$	14.683
16	17-octadecenoic acid #3-2	86%	280	$C_{18}H_{32}O_2$	14.742
17	Z-9-octadecenoic acid #4	88%	280	$C_{18}H_{32}O_2$	15.209

Table 10. Analysis of the pyrolytic products of corn oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	94%	56	C_3H_4O	1.733
2	Cyclopentene	92%	68	C_5H_8	1.917
3	Hexene	97%	84	C_6H_{12}	2.016
4	Cyclohexene	93%	82	C_6H_{10}	2.508
5	Heptene	96%	98	C_7H_{14}	2.55
6	3-methyl-cyclohexene	92%	96	C_7H_{12}	2.942
7	Octene	93%	112	C_8H_{16}	3.375
8	2-octene	94%	112	C_8H_{16}	3.525
9	1,3-octadiene	94%	110	C_8H_{14}	3.717
10	Nonene	91%	126	C_9H_{18}	4.408
11	Cyclooctene	96%	110	C_8H_{14}	4.55
12	1,3-nonadiene	90%	124	C_9H_{16}	4.783
13	Decene	92%	140	$C_{10}H_{20}$	5.508
14	Undecene	90%	154	$C_{11}H_{22}$	6.6
15	6-Butyl-1,4-cycloheptene	92%	150	$C_{11}H_{18}$	7.358
16	Dodecene	90%	168	$C_{12}H_{24}$	7.633
17	Tridecene	91%	182	$C_{13}H_{26}$	8.617
18	Tetradecene #1	92%	196	$C_{14}H_{28}$	9.545
19	Cetyl Alcohol	92%	242	$C_{16}H_{34}O$	9.542
20	Z,Z-9,17-octadecadienal	93%	264	$C_{18}H_{32}O$	13.501
21	Cis-9-hexadecenal	92%	238	$C_{16}H_{30}O$	13.534
22	Z,Z-9,12-octadecadienoic acid#2	86%	284	$C_{18}H_{36}O_2$	14.058
23	Decanoic acid-2-propenyl ester#3-1	86%	212	$C_{13}H_{24}O_2$	14.7
24	17-octadecenoic acid #3-2	87%	254	$C_{16}H_{30}O_2$	14.758
25	Z-9-octadecenoic acid #4	91%	280	$C_{18}H_{32}O_2$	15.284

Table 11. Analysis of the pyrolytic products of sunflower oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	93%	56	C_3H_4O	1.775
2	Cyclopentene	93%	66	C_5H_8	1.95
3	Hexene	96%	84	C_6H_{12}	2.059
4	Cyclohexene	95%	82	C_6H_{10}	2.525
5	Heptene	97%	98	C_7H_{14}	2.567
6	Octene	93%	112	C_8H_{16}	3.383
7	2-octene	94%	112	C_8H_{16}	3.525
8	1,3-octadiene	95%	110	C_8H_{14}	3.717
9	Nonene	93%	126	C_9H_{18}	4.408
10	Cyclooctene	98%	110	C_8H_{14}	4.55
11	E-1,3-nonadiene	91%	124	C_9H_{16}	4.767
12	Decene	93%	140	$C_{10}H_{20}$	5.5
13	6-Butyl-1,4-cycloheptadiene	93%	150	$C_{11}H_{18}$	7.342
14	3-dodecene	91%	166	$C_{12}H_{24}$	7.616

15	Tridecene	91%	182	$C_{13}H_{26}$	8.6
16	Tetradecene #1	92%	196	$C_{14}H_{28}$	9.527
17	Z-6-pentadecenal	91%	226	$C_{15}H_{30}O$	10.35
18	Hexadecene	91%	224	$C_{16}H_{32}$	11.225
19	9,17-octadecadienal	93%	264	$C_{18}H_{32}O$	13.475
20	Cis-9-hexadecenal	94%	238	$C_{16}H_{30}O$	13.516
21	Z,Z-9,12-octadecadienoic acid#2	88%	280	$C_{18}H_{32}O_2$	14.2
22	Decanoic acid-2-propenyl ester#3-1	82%	212	$C_{13}H_{24}O_2$	14.675
23	17-octadecenoic acid #3-2	87%	282	$C_{18}H_{34}O_2$	14.741
24	Z-9-octadecenoic acid #4	89%	280	$C_{18}H_{32}O_2$	15.335

Table 12. Analysis of the pyrolytic products of the blend vegetable oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	95%	56	C_3H_4O	1.733
2	Hexene	97%	84	C_6H_{12}	2.016
3	Heptene	97%	98	C_7H_{14}	2.542
4	Octene	92%	112	C_8H_{16}	3.367
5	2-octene	93%	112	C_8H_{16}	3.509
6	1,3-octadiene	94%	110	C_8H_{14}	3.708
7	Nonene	92%	126	C_9H_{18}	4.4
8	Cyclooctene	97%	110	C_8H_{14}	4.542
9	Decene	91%	140	$C_{10}H_{20}$	5.492
10	6-Butyl-1,4-cycloheptene	92%	150	$C_{11}H_{18}$	7.342
11	n-hexadecene	92%	224	$C_{16}H_{32}$	9.525
12	Tetradecene #1	92%	196	$C_{14}H_{28}$	9.529
13	Z-9,17-octadecadienal	94%	264	$C_{18}H_{32}O$	13.484
14	Z,Z-9,12-octadecadienoic acid#2	91%	280	$C_{18}H_{32}O_2$	14.050
15	Decanoic acid-2-propenyl ester#3-1	86%	212	$C_{13}H_{24}O_2$	14.675
16	17-octadecenoic acid #3-2	86%	282	$C_{18}H_{34}O_2$	14.741
17	Z-9-octadecenoic acid #4	93%	280	$C_{18}H_{32}O_2$	15.241

Table 13. Analysis of the pyrolytic products of used frying oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	95%	56	C_3H_4O	1.733
2	Hexene	98%	84	C_6H_{12}	2.016
3	Heptene	97%	98	C_7H_{14}	2.542
4	Octene	95%	112	C_8H_{16}	3.358
5	Nonene	96%	126	C_9H_{18}	4.391
6	Cyclooctene	98%	110	C_8H_{14}	4.525
7	Decene	95%	140	$C_{10}H_{20}$	5.483
8	Undecene	96%	154	$C_{11}H_{22}$	6.567
9	2-Undecene	93%	154	$C_{11}H_{22}$	6.709
10	1,4-Undecadiene	90%	152	$C_{11}H_{20}$	6.926
11	6-Butyl-1,4-cycloheptene	88%	150	$C_{11}H_{18}$	7.326

12	Dodecene	96%	168	$C_{12}H_{24}$	7.608
13	E-1,8-Dodecadiene	90%	166	$C_{12}H_{22}$	7.95
14	Tridecene	95%	182	$C_{13}H_{26}$	8.592
15	Tetradecene #1	96%	196	$C_{14}H_{28}$	9.517
16	Pentadecene	92%	210	$C_{15}H_{30}$	10.392
17	Pentadecane	93%	212	$C_{15}H_{32}$	10.458
18	6-pentadecenol	94%	226	$C_{15}H_{30}O$	11.108
19	n-hexadecene	94%	224	$C_{16}H_{32}$	11.226
20	8-heptadecene	94%	238	$C_{17}H_{34}$	11.908
21	Cis-9-hexadecenal	96%	238	$C_{16}H_{30}O$	13.516
22	Z,Z-9,12-octadecadienoic acid#2	84%	284	$C_{18}H_{36}O_2$	14.075
23	Decanoic acid-2-propenyl ester#3-1	87%	212	$C_{13}H_{24}O_2$	14.675
24	17-octadecenoic acid #3-2	87%	282	$C_{18}H_{34}O_2$	14.733
25	Z-9-octadecenoic acid #4	93%	282	$C_{18}H_{34}O_2$	15.233

Table 14. Analysis of the pyrolytic products of chicken fat

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	94%	56	C_3H_4O	1.733
2	Hexene	97%	84	C_6H_{12}	2.009
3	Heptene	97%	98	C_7H_{14}	2.534
4	Octene	96%	112	C_8H_{16}	3.35
5	1,3-octadiene	94%	110	C_8H_{14}	3.691
6	Nonene	97%	126	C_9H_{18}	4.384
7	Cyclooctene	98%	110	C_8H_{14}	4.525
8	Decene	96%	140	$C_{10}H_{20}$	5.476
9	Undecene	96%	154	$C_{11}H_{22}$	6.559
10	2-Undecene	94%	154	$C_{11}H_{22}$	6.7
11	1,4-Undecadiene	91%	152	$C_{11}H_{20}$	6.916
12	6-Butyl-1,4-cycloheptadiene	90%	152	$C_{11}H_{18}$	7.316
13	Dodecene	96%	168	$C_{12}H_{24}$	7.6
14	E-1,8-Dodecadiene	90%	166	$C_{12}H_{22}$	7.942
15	2E,4Z-Dodecadiene	90%	166	$C_{12}H_{22}$	8.283
16	Tridecene	96%	182	$C_{13}H_{26}$	8.584
17	Tetradecene #1	97%	196	$C_{14}H_{28}$	9.509
18	Pentadecene	93%	210	$C_{15}H_{30}$	10.383
19	Pentadecane	95%	212	$C_{15}H_{32}$	10.449
20	6-pentadecenal	91%	226	$C_{15}H_{30}O$	11.101
21	Hexadecene	92%	224	$C_{16}H_{32}$	11.217
22	8-heptadecene	93%	238	$C_{17}H_{34}$	11.9
23	Octadecenal	94%	266	$C_{18}H_{36}O$	12.183
24	Cis-9-hexadecenal	96%	238	$C_{16}H_{30}O$	13.501
25	Z,Z-9,12-octadecadienoic acid#2	91%	282	$C_{18}H_{34}O_2$	14.225
26	Decanoic acid-2-propenyl ester#3-1	86%	212	$C_{13}H_{24}O_2$	14.667
27	17-octadecenoic acid #3-2	93%	282	$C_{18}H_{34}O_2$	14.725
28	Z-9-octadecenoic acid #4	89%	282	$C_{18}H_{34}O_2$	15.208

Table 15. Analysis of the pyrolytic products of lard

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	91%	56	C_3H_4O	1.775
2	Cyclopentene	95%	66	C_5H_8	1.95
3	Hexene	97%	84	C_6H_{12}	2.05
4	Heptene	97%	98	C_7H_{14}	2.567
5	Octene	96%	112	C_8H_{16}	3.384
6	2-octene	90%	112	C_8H_{16}	3.517
7	1,3-octadiene	93%	110	C_8H_{14}	3.717
8	Nonene	97%	126	C_9H_{18}	4.408
9	Cyclooctene	98%	110	C_8H_{14}	4.55
10	1,3-nonadiene	91%	124	C_9H_{16}	4.767
11	Decene	96%	140	$C_{10}H_{20}$	5.5
12	Undecene	93%	154	$C_{11}H_{22}$	6.583
13	2-Undecene	94%	154	$C_{11}H_{22}$	6.724
14	1,4-Undecadiene	91%	152	$C_{11}H_{20}$	6.942
15	6-Butyl-1,4-cycloheptene	89%	150	$C_{11}H_{18}$	7.333
16	Dodecene	96%	168	$C_{12}H_{24}$	7.616
17	E-1,8-Dodecadiene	91%	166	$C_{12}H_{22}$	7.958
18	Tridecene	96%	182	$C_{13}H_{26}$	8.6
19	Tridecane	92%	184	$C_{13}H_{28}$	8.675
20	Tetradecene #1	96%	196	$C_{14}H_{28}$	9.533
21	Pentadecene	95%	210	$C_{15}H_{30}$	10.4
22	Pentadecane	96%	212	$C_{15}H_{32}$	10.467
23	6-pentadecenol	93%	226	$C_{15}H_{30}O$	11.116
24	Hexadecene	96%	224	$C_{16}H_{32}$	11.233
25	8-heptadecene	96%	238	$C_{17}H_{34}$	11.908
26	Octadecenal	95%	266	$C_{18}H_{36}O_2$	12.2
27	Cis-9-hexadecenal	95%	238	$C_{16}H_{30}O$	13.516
28	Z,Z-9,12-octadecadienoic acid#2	87%	282	$C_{18}H_{34}O_2$	14.141
29	Decanoic acid-2-propenyl ester#3-1	82%	212	$C_{13}H_{24}O_2$	14.683
30	17-octadecenoic acid #3-2	88%	282	$C_{18}H_{34}O_2$	14.742
31	Z-9-octadecenoic acid #4	84%	282	$C_{18}H_{34}O_2$	15.275

Table 16. Analysis of the pyrolytic products of inferior oil

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	94%	56	C_3H_4O	1.758
2	Hexene	97%	84	C_6H_{12}	2.034
3	Heptene	97%	98	C_7H_{14}	2.55
4	Octene	96%	112	C_8H_{16}	3.375
5	1,3-octadiene	87%	110	C_8H_{14}	3.708
6	Nonene	96%	126	C_9H_{18}	4.4
7	Cyclooctene	97%	110	C_8H_{14}	4.542
8	Decene	96%	140	$C_{10}H_{20}$	5.5

9	Undecene	95%	154	$C_{11}H_{22}$	6.583
10	2-Undecene	93%	154	$C_{11}H_{22}$	6.725
11	1,4-Undecadiene	91%	152	$C_{11}H_{20}$	6.942
12	6-Butyl-1,4-cycloheptene	86%	150	$C_{11}H_{18}$	7.342
13	Dodecene	96%	168	$C_{12}H_{24}$	7.624
14	Tridecene	95%	182	$C_{13}H_{26}$	8.6
15	Tetradecene #1	96%	196	$C_{14}H_{28}$	9.534
16	Pentadecene	93%	210	$C_{15}H_{30}$	10.408
17	Pentadecane	95%	212	$C_{15}H_{32}$	10.467
18	6-pentadecenol	93%	226	$C_{15}H_{30}O$	11.116
19	n-hexadecene	92%	224	$C_{16}H_{32}$	11.234
20	8-heptadecene	95%	238	$C_{17}H_{34}$	11.917
21	Tetradecenal	95%	212	$C_{14}H_{28}O$	12.208
22	Cis-9-hexadecenal	96%	238	$C_{16}H_{30}O$	13.524
23	Z,Z-9,12-octadecadienoic acid#2	88%	284	$C_{18}H_{36}O_2$	14.075
24	Decanoic acid-2-propenyl ester#3-1	86%	212	$C_{13}H_{24}O_2$	14.683
25	17-octadecenoic acid #3-2	84%	282	$C_{18}H_{34}O_2$	14.742
26	Z-9-octadecenoic acid #4	91%	282	$C_{18}H_{34}O_2$	15.209

Table 17. Analysis of the pyrolytic products of kitchen waste grease

No.	Possible chemical	Similarity	Molecular Weight	Formula	Retention time
1	2-Acrylic aldehyde	90%	56	C_3H_4O	1.784
2	Cyclopentene	96%	68	C_5H_8	1.966
3	Hexene	96%	84	C_6H_{12}	2.067
4	Heptene	98%	98	C_7H_{14}	2.575
5	Octene	93%	112	C_8H_{16}	3.375
6	2-octene	93%	112	C_8H_{16}	3.517
7	1,3-octadiene	96%	110	C_8H_{14}	3.708
8	Nonene	94%	126	C_9H_{18}	4.4
9	Cyclooctene	97%	110	C_8H_{14}	4.542
10	E-1,3-nonadiene	92%	124	C_9H_{16}	4.758
11	Decene	93%	140	$C_{10}H_{20}$	5.483
12	Undecene	89%	154	$C_{11}H_{22}$	6.576
13	1,4-Undecadiene	89%	152	$C_{11}H_{20}$	6.925
14	6-Butyl-1,4-cycloheptene	90%	150	$C_{11}H_{18}$	7.325
15	Dodecene	93%	166	$C_{12}H_{24}$	7.608
16	Tridecene	92%	182	$C_{13}H_{26}$	8.592
17	Tetradecene #1	95%	196	$C_{14}H_{28}$	9.517
18	Pentadecene	91%	210	$C_{15}H_{30}$	10.392
19	Pentadecane	91%	212	$C_{15}H_{32}$	10.45
20	Hexadecene	93%	224	$C_{16}H_{32}$	11.217
21	E,8-Heptadecene	90%	238	$C_{17}H_{34}$	11.9
22	Cis-9-hexadecenal	93%	238	$C_{16}H_{30}O$	13.5
23	Z,Z-9,12-octadecadienoic acid#2	88%	280	$C_{18}H_{32}O_2$	14.174
24	Decanoic acid-2-propenyl ester#3-1	82%	212	$C_{13}H_{24}O_2$	14.667

25	17-octadecenoic acid #3-2	87%	282	$C_{18}H_{34}O_2$	14.725
26	Z-9-octadecenoic acid #4	90%	280	$C_{18}H_{32}O_2$	15.375

According to these results, during the first 6.5 minutes, the pyrolytic products of all oil samples were quite similar, most of which were small-molecule chemicals such as 2-acrolein, hexene, heptane, aldehydes, and olefins. Moreover, these substances had a higher similarity, mostly over 90%.

For animal fat/oils, inferior oil, and kitchen waste grease, pentadecane (C15) was observed at the retention time of 10.4 min, and the similarity was higher than 90%. Other vegetable oils did not show pentadecane in the pyrolytic products.

Peak 2 was identified as z,z-9,12-octadecadienoic acid, while Peak 3-1 was identified as decanoic acid-2-propenyl ester. Due to its low strength, Peak 3-2 was identified as 17-octadecenoic acid, but the potential was low. For the used frying oil, animal fat/oils, and inferior oil, Peak 4 was mainly z-9-octadecenoic acid. But Peak 4 of vegetable oils could also be a mixture of z-9-octadecenoic acid and z,z-9,12-octadecadienoic acid.

As shown in the mass spectrum, not all olefins having a carbon number higher than 11 (undecane) were present in the pyrolytic products of vegetable oils. For example, dodecane, tridecane, and pentadecene were absent from the products of tea oil, olive oil, and peanut oil. But the products from animal fats, used frying oil, and inferior oil contained all kinds of C11-16 olefins (Table 18). The possible reason is that these oils have been used and recovered, wherein the C16-C18 fatty acids were degraded to a certain degree. So, the pyrolytic products of these low-quality oils contained all kinds of olefins. This can be used as a key indicator to distinguish inferior oils and animal fats from vegetable oils.

Table 18. Olefin present in the products

Oil	Undecene C11	Dodecone C12	Tridecene C13	Tetradecene C14	Pentadecene C15	Hexadecone C16
Tea oil	√			√		√
Olive oil	√			√		
Peanut oil	√	√		√		
Corn oil	√	√	√	√		
Sunflower oil			√	√		√
Blend vegetable oil				√		√
Used frying oil	√	√	√	√	√	√
Chicken fat	√	√	√	√	√	√
Lard	√	√	√	√	√	√
Inferior oil	√	√	√	√	√	√
Kitchen waste grease	√	√	√	√	√	√

CONCLUSIONS

The pyrolysis conditions of oil samples were optimized as the pyrolysis temperature of 600°C, the sample volume of 0.3 μL, and the reaction time of 1 min. According to the TIC of Py-GC/MS, when the retention time was less than or equal to 6.5

min, the pyrolytic products of all oil samples were similar. But at the retention time of 9.5 min, the area of Peak 1 (tetradecene) of the vegetable oils was less than 2.00E+05 and the peak high was lower than 1.50E 05. Dodecane, tridecane, and pentadecene were absent from the products of tea oil, olive oil, and peanut oil. The pyrolytic products from animal oils, used frying oil, inferior oil and kitchen waste grease contained C11-C16 olefins. Therefore, the Py-GC/MS technology could be used to distinguish vegetable oils from animal fat/oil, inferior oil, and kitchen waste grease.

ACKNOWLEDGMENTS

This work was partially supported by Natural Science Foundation of Guangdong Province (2017A030310133) and the College of Chemistry and Environmental Engineering at Shenzhen University.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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