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

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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)
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.

| 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-Allo5 capillary column (Fukushima, Japan).

For GC/MS analysis, the carrier gas of helium (99.999% purity) with a flow rate of 1 mL·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·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.

![Pyrolysis TIC Chromatogram](image)

**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
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   | 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+05 | 2.09            |
| Sunflower oil     | 1.06E+05 | 1.84E+05 | 1.69E+05 | 1.27E+06 | 11.98           |
| Blend vegetable   | 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               | C₃H₄O       | 1.725          |
| 2   | Cyclopentene                   | 92%        | 68               | C₅H₈        | 1.9            |
| 3   | Hexene                         | 97%        | 84               | C₆H₁₂       | 2.009          |
| 4   | Cyclohexene                    | 94%        | 82               | C₆H₁₀       | 2.492          |
| 5   | Heptene                        | 98%        | 98               | C₇H₁₄       | 2.533          |
| 6   | Octene                         | 95%        | 112              | C₈H₁₆       | 3.358          |
| 7   | E-1,4-octadiene                | 90%        | 110              | C₈H₁₄       | 3.7            |
| 8   | Nonene                         | 95%        | 126              | C₉H₁₈       | 4.392          |
| 9   | Cyclooctene                    | 98%        | 110              | C₈H₁₄       | 4.534          |
| 10  | Decene                         | 93%        | 140              | C₁₀H₂₀      | 5.492          |
| 11  | 1-Undecene                     | 95%        | 154              | C₁₁H₂₂      | 6.575          |
| 12  | 2-Undecene                     | 95%        | 154              | C₁₁H₂₂      | 6.717          |
| 13  | 1,4-Undecene                   | 91%        | 152              | C₁₁H₂₀      | 6.933          |
| 14  | E-1,8-Dodecadiene              | 91%        | 166              | C₁₂H₂₂      | 7.949          |
| 15  | Tetradecene #1                 | 92%        | 196              | C₁₄H₂₈      | 9.524          |
| 16  | 8-heptadecene                  | 97%        | 238              | C₁₇H₃₄      | 11.908         |
| 17  | cis-9-hexadecenal              | 96%        | 238              | C₁₆H₃₂O     | 13.525         |
| 18  | Z,Z-9,12-octadecadienoic acid #2| 87%      | 282              | C₁₈H₃₆O₂     | 14.042         |
| 19  | Decanoic acid-2-propenyl ester#3-1 | 85%    | 212              | C₁₃H₂₄O₂    | 14.2           |
| 20  | 17-octadecenoic acid #3-2      | 86%        | 282              | C₁₈H₃₄O₂     | 14.233         |
| 21  | Z-9-octadecenoic acid #4       | 96%        | 282              | C₁₈H₃₄O₂     | 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-Acryl aldehyde                  | 94%        | 56               | C₃H₄O    | 1.7            |
| 2   | Hexene                            | 96%        | 84               | C₆H₁₂     | 1.982          |
| 3   | Heptene                           | 97%        | 98               | C₇H₁₄     | 2.515          |
| 4   | Octene                            | 93%        | 112              | C₈H₁₆     | 3.35           |
| 5   | Nonene                            | 93%        | 126              | C₉H₁₈     | 4.382          |
| 6   | Cyclooctene                       | 97%        | 110              | C₈H₁₄     | 4.524          |
| 7   | Decene                            | 88%        | 140              | C₁₀H₂₀    | 5.483          |
| 8   | Undecene                          | 93%        | 154              | C₁₁H₂₂    | 6.566          |
| 9   | 2-Undecene                        | 93%        | 154              | C₁₁H₂₂    | 6.699          |
| 10  | E-1,4-Undecadiene                 | 91%        | 152              | C₁₁H₃₀    | 6.926          |
| 11  | E-1,8-Undecadiene                 | 90%        | 166              | C₁₂H₂₂    | 7.951          |
| 12  | 2E,4Z-Dodecadiene                 | 93%        | 166              | C₁₂H₂₂    | 8.291          |
| 13  | E-7-tetradecene                   | 90%        | 196              | C₁₄H₂₈    | 8.591          |
| 14  | Tetradecene #1                    | 92%        | 196              | C₁₄H₂₈    | 9.517          |
| 15  | 8-heptadecene                     | 94%        | 238              | C₁₇H₃₄    | 11.899         |
| 16  | Cis-9-hexadecenal                 | 96%        | 238              | C₁₈H₃₀O   | 13.518         |
| 17  | Z,Z-9,12-octadecadienoic acid#2   | 90%        | 280              | C₁₈H₃₂O₂  | 14.092         |
| 18  | Decanoic acid-2-propenyl ester#3-1| 86%        | 212              | C₁₃H₂₄O₂  | 14.666         |
| 19  | 17-octadecenoic acid #3-2         | 87%        | 282              | C₁₈H₃₄O₂  | 14.725         |
| 20  | Z-9-octadecenoic acid #4          | 92%        | 282              | C₁₈H₃₄O₂  | 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               | C₃H₄O    | 1.75           |
| 2   | Hexene                            | 95%        | 84               | C₆H₁₂     | 2.025          |
| 3   | Heptene                           | 96%        | 98               | C₇H₁₄     | 2.55           |
| 4   | Octene                            | 93%        | 112              | C₈H₁₆     | 3.375          |
| 5   | Nonene                            | 90%        | 126              | C₉H₁₈     | 4.409          |
| 6   | Cyclooctene                       | 96%        | 110              | C₈H₁₄     | 4.542          |
| 7   | Decene                            | 90%        | 140              | C₁₀H₂₀    | 5.5            |
| 8   | Undecene                          | 91%        | 154              | C₁₁H₂₂    | 6.591          |
| 9   | 6-Butyl-1,4-cycloheptadiene       | 89%        | 150              | C₁₁H₁₈    | 7.342          |
| 10  | Dodecene                          | 88%        | 168              | C₁₂H₃₄    | 7.626          |
| 11  | Cetyl Alcohol                     | 91%        | 242              | C₁₆H₃₄O   | 9.533          |
| 12  | Tetradecene #1                    | 90%        | 196              | C₁₄H₂₈    | 9.535          |
| 13  | Cis-9-hexadecenal                 | 92%        | 238              | C₁₈H₃₀O   | 13.533         |
| 14  | Z,Z-9,12-octadecadienoic acid#2   | 87%        | 280              | C₁₈H₃₂O₂  | 14.158         |
| 15  | Decanoic acid-2-propenyl ester#3-1| 83%        | 212              | C₁₃H₂₄O₂  | 14.683         |
| 16  | 17-octadecenoic acid #3-2         | 86%        | 280              | C₁₈H₃₂O₂  | 14.742         |
| 17  | Z-9-octadecenoic acid #4          | 88%        | 280              | C₁₈H₃₂O₂  | 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               | C₃H₄O      | 1.733          |
| 2   | Cyclopentene                      | 92%        | 68               | C₅H₁₀       | 1.917          |
| 3   | Hexene                            | 97%        | 84               | C₆H₁₂       | 2.016          |
| 4   | Cyclohexene                       | 93%        | 82               | C₆H₁₀       | 2.508          |
| 5   | Heptene                           | 96%        | 98               | C₇H₁₄       | 2.55           |
| 6   | 3-methyl-cyclohexene              | 92%        | 96               | C₇H₁₂       | 2.942          |
| 7   | Octene                            | 93%        | 112              | C₈H₁₆       | 3.375          |
| 8   | 2-octene                          | 94%        | 112              | C₈H₁₆       | 3.525          |
| 9   | 1,3-octadiene                     | 94%        | 110              | C₈H₁₄       | 3.717          |
| 10  | Nonene                            | 91%        | 126              | C₈H₁₈       | 4.408          |
| 11  | Cyclooctene                       | 96%        | 110              | C₉H₁₄       | 4.55           |
| 12  | 1,3-nonadiene                     | 90%        | 124              | C₉H₁₈       | 4.783          |
| 13  | Decene                            | 92%        | 140              | C₁₀H₂₀      | 5.508          |
| 14  | Undecene                          | 90%        | 154              | C₁₁H₂₂      | 6.6            |
| 15  | 6-Butyl-1,4-cycloheptene          | 92%        | 150              | C₁₁H₁₈      | 7.358          |
| 16  | Dodecene                          | 90%        | 168              | C₁₂H₂₄      | 7.633          |
| 17  | Tridecene                         | 91%        | 182              | C₁₃H₂₆      | 8.617          |
| 18  | Tetradecene #1                    | 92%        | 196              | C₁₄H₂₈      | 9.545          |
| 19  | Cetyl Alcohol                     | 92%        | 242              | C₁₆H₃₄O     | 9.542          |
| 20  | Z,Z-9,17-octadecadienal           | 93%        | 264              | C₁₈H₃₂O     | 13.501         |
| 21  | Cis-9-hexadecenal                 | 92%        | 238              | C₁₆H₃₀O     | 13.534         |
| 22  | Z,Z-9,12-octadecadienoic acid #2  | 86%        | 284              | C₁₈H₃₆O₂    | 14.058         |
| 23  | Decanoic acid-2-propenyl ester #3-1| 86%       | 212              | C₁₃H₂₄O₂    | 14.7           |
| 24  | 17-octadecenoic acid #3-2         | 87%        | 254              | C₁₆H₃₀O₂    | 14.758         |
| 25  | Z-9-octadecenoic acid #4          | 91%        | 280              | C₁₈H₃₂O₂    | 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               | C₃H₄O      | 1.775          |
| 2   | Cyclopentene                      | 93%        | 66               | C₅H₁₀       | 1.95           |
| 3   | Hexene                            | 96%        | 84               | C₆H₁₂       | 2.059          |
| 4   | Cyclohexene                       | 95%        | 82               | C₆H₁₀       | 2.525          |
| 5   | Heptene                           | 97%        | 98               | C₇H₁₄       | 2.567          |
| 6   | Octene                            | 93%        | 112              | C₈H₁₆       | 3.383          |
| 7   | 2-octene                          | 94%        | 112              | C₈H₁₆       | 3.525          |
| 8   | 1,3-octadiene                     | 95%        | 110              | C₈H₁₄       | 3.717          |
| 9   | Nonene                            | 93%        | 126              | C₈H₁₈       | 4.408          |
| 10  | Cyclooctene                       | 98%        | 110              | C₉H₁₄       | 4.55           |
| 11  | E-1,3-nonadiene                   | 91%        | 124              | C₉H₁₆       | 4.767          |
| 12  | Decene                            | 93%        | 140              | C₁₀H₂₀      | 5.5            |
| 13  | 6-Butyl-1,4-cycloheptadiene       | 93%        | 150              | C₁₁H₁₈      | 7.342          |
| 14  | 3-dodecene                        | 91%        | 166              | C₁₂H₂₄      | 7.616          |
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               | C₂H₄O       | 1.733          |
| 2   | Hexene                                | 97%        | 84               | C₆H₁₂       | 2.016          |
| 3   | Heptene                               | 97%        | 98               | C₇H₁₄       | 2.542          |
| 4   | Octene                                | 92%        | 112              | C₈H₁₆       | 3.367          |
| 5   | 2-octene                              | 93%        | 112              | C₈H₁₆       | 3.509          |
| 6   | 1,3-octadiene                         | 94%        | 110              | C₈H₁₄       | 3.708          |
| 7   | Nonene                                | 92%        | 126              | C₈H₁₈       | 4.4            |
| 8   | Cyclooctene                           | 97%        | 110              | C₈H₁₄       | 4.542          |
| 9   | Decene                                | 91%        | 140              | C₁₀H₂₀      | 5.492          |
| 10  | 6-Butyl-1,4-cycloheptene              | 92%        | 150              | C₁₁H₁₈      | 7.342          |
| 11  | n-hexadecene                          | 92%        | 224              | C₁₆H₃₂      | 9.525          |
| 12  | Tetradecene #1                       | 92%        | 196              | C₁₄H₂₈      | 9.529          |
| 13  | Z-9,17-octadecadienal                | 94%        | 264              | C₁₃H₃₂O     | 13.484         |
| 14  | Z,Z-9,12-octadecadienoic acid #2     | 91%        | 280              | C₁₈H₃₂O₂    | 14.050         |
| 15  | Decanoic acid-2-propenyl ester #3-1  | 86%        | 212              | C₁₃H₂₈O₂    | 14.675         |
| 16  | 17-octadecenoic acid #3-2            | 86%        | 282              | C₁₈H₃₂O₂    | 14.741         |
| 17  | Z-9-octadecenoic acid #4             | 89%        | 280              | C₁₈H₃₂O₂    | 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               | C₂H₄O       | 1.733          |
| 2   | Hexene                                | 98%        | 84               | C₆H₁₂       | 2.016          |
| 3   | Heptene                               | 97%        | 98               | C₇H₁₄       | 2.542          |
| 4   | Octene                                | 95%        | 112              | C₈H₁₆       | 3.358          |
| 5   | Nonene                                | 96%        | 126              | C₈H₁₈       | 4.391          |
| 6   | Cyclooctene                           | 98%        | 110              | C₈H₁₈       | 4.525          |
| 7   | Decene                                | 95%        | 140              | C₁₀H₂₀      | 5.483          |
| 8   | Undecene                              | 96%        | 154              | C₁₁H₂₂      | 6.567          |
| 9   | 2-Undecene                           | 93%        | 154              | C₁₁H₂₂      | 6.709          |
| 10  | 1,4-Undecadiene                      | 90%        | 152              | C₁₁H₂₀      | 6.926          |
| 11  | 6-Butyl-1,4-cycloheptene             | 88%        | 150              | C₁₁H₁₈      | 7.326          |
Table 14. Analysis of the pyrolytic products of chicken fat

| No. | Possible chemical                        | Similarity | Molecular Weight | Formula       | Retention time |
|-----|------------------------------------------|------------|------------------|---------------|----------------|
| 1   | 2-Acrylaldehyde                          | 94%        | 56               | C₄H₇O         | 1.733          |
| 2   | Hexene                                   | 97%        | 84               | C₆H₁₂         | 2.009          |
| 3   | Heptene                                  | 97%        | 98               | C₇H₁₄         | 2.534          |
| 4   | Octene                                   | 96%        | 112              | C₈H₁₆         | 3.35           |
| 5   | 1,3-octadiene                            | 94%        | 110              | C₈H₁₄         | 3.691          |
| 6   | Nonene                                   | 97%        | 126              | C₉H₁₈         | 4.384          |
| 7   | Cyclooctane                              | 98%        | 110              | C₈H₁₄         | 4.525          |
| 8   | Decene                                   | 96%        | 140              | C₁₀H₂₀        | 5.476          |
| 9   | Undecene                                 | 96%        | 154              | C₁₁H₂₂        | 6.559          |
| 10  | 2-Undecene                               | 94%        | 154              | C₁₁H₂₂        | 6.7            |
| 11  | 1,4-Undecadiene                          | 91%        | 152              | C₁₁H₂₀        | 6.916          |
| 12  | 6-Butyl-1,4-cycloheptadiene              | 90%        | 152              | C₁₁H₁₈        | 7.316          |
| 13  | Dodecene                                 | 96%        | 168              | C₁₂H₂₄        | 7.6            |
| 14  | E-1,8-Dodecadiene                        | 90%        | 166              | C₁₂H₂₂        | 7.942          |
| 15  | 2E,4Z-Dodecadiene                        | 90%        | 166              | C₁₂H₂₂        | 8.283          |
| 16  | Tridecene                                | 96%        | 182              | C₁₃H₃₆        | 8.584          |
| 17  | Tetradecene #1                           | 97%        | 196              | C₁₄H₂₈        | 9.509          |
| 18  | Pentadecene                              | 93%        | 210              | C₁₅H₃₀        | 10.383         |
| 19  | Pentadecane                              | 95%        | 212              | C₁₅H₃₂        | 10.449         |
| 20  | 6-pentadecenal                           | 91%        | 226              | C₁₅H₃₀O       | 11.101         |
| 21  | Hexadecene                               | 92%        | 224              | C₁₆H₃₂        | 11.217         |
| 22  | 8-heptadecene                            | 93%        | 238              | C₁₇H₃₄        | 11.9           |
| 23  | Octadecenal                              | 94%        | 266              | C₁₈H₃₆O       | 12.183         |
| 24  | Cis-9-hexadecenal                        | 96%        | 238              | C₁₈H₃₆O       | 13.501         |
| 25  | Z,Z-9,12-octadecadienoic acid #2        | 91%        | 282              | C₁₉H₃₄O       | 14.225         |
| 26  | Decanoic acid-2-propenyl ester #3-1      | 86%        | 212              | C₁₃H₂₄O₂      | 14.667         |
| 27  | 17-octadecenoic acid #3-2               | 93%        | 282              | C₁₈H₃₆O₂      | 14.725         |
| 28  | Z-9-octadecenoic acid #4                 | 89%        | 282              | C₁₈H₃₆O₂      | 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               | C₅H₈O     | 1.775          |
| 2   | Cyclopentene                               | 95%        | 66               | C₅H₈      | 1.95           |
| 3   | Hexene                                    | 97%        | 84               | C₆H₁₂     | 2.05           |
| 4   | Heptene                                    | 97%        | 98               | C₇H₁₄     | 2.567          |
| 5   | Octene                                    | 96%        | 112              | C₈H₁₆     | 3.384          |
| 6   | 2-octene                                  | 90%        | 112              | C₈H₁₆     | 3.517          |
| 7   | 1,3-octadiene                             | 93%        | 110              | C₉H₁₄     | 3.717          |
| 8   | Nonene                                    | 97%        | 126              | C₉H₁₈     | 4.408          |
| 9   | Cyclooctene                                | 98%        | 110              | C₉H₁₄     | 4.55           |
| 10  | 1,3-nonadiene                             | 91%        | 124              | C₁₀H₁₆    | 4.767          |
| 11  | Decene                                    | 96%        | 140              | C₁₀H₂₀    | 5.5            |
| 12  | Undecene                                  | 93%        | 154              | C₁₁H₂₂    | 6.583          |
| 13  | 2-Undecene                                | 94%        | 154              | C₁₁H₂₂    | 6.724          |
| 14  | 1,4-Undecadiene                           | 91%        | 152              | C₁₁H₂₀    | 6.942          |
| 15  | 6-Butyl-1,4-cycloheptene                  | 89%        | 150              | C₁₁H₁₈    | 7.333          |
| 16  | Dodecene                                  | 96%        | 168              | C₁₂H₂₄    | 7.616          |
| 17  | E-1,8-Dodecadiene                         | 91%        | 166              | C₁₂H₂₂    | 7.958          |
| 18  | Tridecane                                 | 96%        | 182              | C₁₃H₂₆    | 8.6            |
| 19  | Tridecan                                  | 92%        | 184              | C₁₃H₂₈    | 8.675          |
| 20  | Tetradecene #1                            | 96%        | 196              | C₁₄H₃₂    | 9.533          |
| 21  | Pentadecene                               | 95%        | 210              | C₁₅H₃₀    | 10.4           |
| 22  | Pentadecane                               | 96%        | 212              | C₁₅H₃₂    | 10.467         |
| 23  | 6-pentadecenol                            | 93%        | 226              | C₁₅H₄₀O   | 11.116         |
| 24  | Hexadecene                                | 96%        | 224              | C₁₆H₃₂    | 11.233         |
| 25  | 8-heptadecene                             | 96%        | 238              | C₁₇H₃₄    | 11.908         |
| 26  | Octadecenal                               | 95%        | 266              | C₁₈H₃₂O₂  | 12.2           |
| 27  | Cis-9-hexadecenal                         | 95%        | 238              | C₁₆H₆₀O   | 13.516         |
| 28  | Z,Z-9,12-octadecadienoic acid #2          | 87%        | 282              | C₁₈H₃₂O₂  | 14.141         |
| 29  | Decanoic acid-2-propenyl ester #3-1       | 82%        | 212              | C₁₃H₂₅O₂  | 14.683         |
| 30  | 17-octadecenoic acid #3-2                 | 88%        | 282              | C₁₈H₃₂O₂  | 14.742         |
| 31  | Z-9-octadecenoic acid #4                  | 84%        | 282              | C₁₈H₃₂O₂  | 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               | C₅H₈O     | 1.758          |
| 2   | Hexene                                    | 97%        | 84               | C₆H₁₂     | 2.034          |
| 3   | Heptene                                   | 97%        | 98               | C₇H₁₄     | 2.55           |
| 4   | Octene                                    | 96%        | 112              | C₈H₁₆     | 3.375          |
| 5   | 1,3-octadiene                             | 87%        | 110              | C₉H₁₄     | 3.708          |
| 6   | Nonene                                    | 96%        | 126              | C₉H₁₈     | 4.4            |
| 7   | Cyclooctene                               | 97%        | 110              | C₉H₁₄     | 4.542          |
| 8   | Decene                                    | 96%        | 140              | C₁₀H₂₀    | 5.5            |
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               | C3H6O   | 1.784          |
| 2   | Cyclopentene      | 96%       | 68               | C5H8    | 1.966          |
| 3   | Hexene            | 96%       | 84               | C6H12   | 2.067          |
| 4   | Heptene           | 98%       | 98               | C7H16   | 2.575          |
| 5   | Octene            | 93%       | 112              | C8H16   | 3.375          |
| 6   | 2-octene          | 93%       | 112              | C8H16   | 3.517          |
| 7   | 1,3-octadiene     | 96%       | 110              | C9H18   | 3.708          |
| 8   | Nonene            | 94%       | 126              | C9H18   | 4.4            |
| 9   | Cyclooctene       | 97%       | 110              | C8H14   | 4.542          |
| 10  | E-1,3-nonadiene   | 92%       | 124              | C9H16   | 4.758          |
| 11  | Decene            | 93%       | 140              | C10H20  | 5.483          |
| 12  | Undecene          | 89%       | 154              | C11H22  | 6.576          |
| 13  | 1,4-Undecadiene   | 89%       | 152              | C11H20  | 6.925          |
| 14  | 6-Butyl-1,4-cycloheptene | 90% | 150 | C11H18 | 7.325 |
| 15  | Dodecene          | 93%       | 166              | C12H24  | 7.608          |
| 16  | Tridecene         | 92%       | 182              | C13H26  | 8.592          |
| 17  | Tetradecene #1    | 95%       | 196              | C14H28  | 9.517          |
| 18  | Pentadecene       | 91%       | 210              | C15H30  | 10.392         |
| 19  | Pentadecane       | 91%       | 212              | C15H32  | 10.45          |
| 20  | Hexadecene        | 93%       | 224              | C16H32  | 11.217         |
| 21  | E,8-Heptadecene   | 90%       | 238              | C17H34  | 11.9           |
| 22  | Cis-9-hexadecenal | 93%       | 238              | C18H30  | 13.5           |
| 23  | Z,Z-9,12-octadecadienoic acid#2 | 88% | 280 | C18H32O2 | 14.174 |
| 24  | Decanoic acid-2-propenyl ester#3-1 | 82% | 212 | C13H24O2 | 14.667 |

Similarity values range from 82% to 98%.
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 pentadecane 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 | Dodecane C12 | Tridecane C13 | Tetradecene C14 | Pentadecane C15 | Hexadecane 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.

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CONFLICTS OF INTEREST

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

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