



## NRC Publications Archive Archives des publications du CNRC

### **Application of fourier transform infrared (FTIR) spectroscopy to investigate the degradation of cooking oils during fire suppression** Kanabus-Kaminska, J. M.; Liu, Z. G.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /  
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

**NRC Publications Record / Notice d'Archives des publications de CNRC:**  
<https://nrc-publications.canada.ca/eng/view/object/?id=2342f803-12f5-4014-96ef-fec6bcf7699c>  
<https://publications-cnrc.canada.ca/fra/voir/objet/?id=2342f803-12f5-4014-96ef-fec6bcf7699c>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at  
<https://nrc-publications.canada.ca/eng/copyright>  
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site  
<https://publications-cnrc.canada.ca/fra/droits>  
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at  
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





---

# **NRC - CNRC**

---

## **Application of fourier transform infrared (FTIR) spectroscopy to investigate the degradation of cooking oils during fire suppression**

**Kanabus-Kaminska, J.M.; Liu, Z.G.**

**NRCC-44996**

A version of this paper is published in / Une version de ce document se trouve dans :  
Spring Technical Meeting of the Combustion Institute, Canadian Section, Montreal, May  
13-16, 2001, pp. 1-6

[www.nrc.ca/irc/ircpubs](http://www.nrc.ca/irc/ircpubs)

# **Application of Fourier Transform Infrared (FTIR) Spectroscopy to Investigate the Degradation of Cooking Oils during Fire Suppression**

J. M. Kanabus-Kaminska and Zhigang Liu  
Fire Risk Management Program

National Research Council of Canada, Ottawa, Canada, K1A 0R6

## **Introduction**

Auto-ignition of cooking oils causes a significant proportion of household fires [1,2]. In addition, the majority of the 50% of all accidental fires in hotels, restaurants and fast food outlets that start in kitchens involve liquid cooking oil or fat as the primary ignition source [3,4]. The potential risk of loss of life and property damage due to cooking oils fires is high. Cooking oils and fats have flash points in the broad range of 160 to 335°C, and high auto-ignition temperature varying from 315-445°C. The flash point and auto-ignition temperature values reported in the literature can differ substantially for the same type of oil [2,5]. Cooking oil fires are difficult to extinguish because the temperature of the burning oil can quickly reach 400-600°C, where a substantial pyrolysis to volatile lower molecular weight species occurs, and it is taxing to cool large amount of such hot oil to below its auto-ignition temperature. In addition cooking oil can change its auto-ignition temperature during heating and fire suppression. The new auto-ignition temperature may be as much as 60°C below the original auto-ignition temperature. Such significant lowering of the auto-ignition temperature was noticed during fire suppression tests carried out at the Fire Risk Management Program (FRMP) when a vat of oil that had been overheated to auto-ignition was extinguished with water mist [6]. This observation suggested that thermal stress followed by exposure to water discharge causes deep changes in oil composition that lower the auto-ignition temperature and create fuel more dangerous than fresh oil. This new, low auto-ignition temperature (~300°C), further increases complexity of extinguishing cooking oil fires. To date, however, there is no study or understanding of how this depression of cooking oil's auto-ignition temperature occurs.

During the recent full-scale water-mist suppression tests of cooking oil fires conducted by the Fire Risk Management Program (FRMP) at NRC, Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the degradation of the oil. In this paper the qualitative differences between the IR spectral features of the fresh, heated, and exposed-to-water oil are presented. The breakdown products generated during the oxidative and hydrolytic degradation of the cooking oil are described and the main degradation pathways of the oil are explained. The role of the flash-hydrolysis products in the lowering of the auto-ignition temperature of the oil is also discussed.

## **Testing Facility**

A commercial deep fat fryer with a capacity of 20 L of oil was used in the tests. The fryer was placed approximately 1 m below an overhead hood constructed of stainless steel according to the manufacturers' recommendations. A single water mist nozzle was located at the front of the hood and aimed at the centre point of the cooking area of the fryer. A thermocouple tree with 5 thermocouples was used to measure the temperatures of the fire, the cooking oil, and the fryer metal surface. One thermocouple was located 25.4 mm below the surface of the oil and 80 mm away from the fryer's wall to measure

the cooking oil temperature. Three other thermocouples were located above the oil surface to measure air and flame temperatures and 1 thermocouple was attached to the top of the fryer's metal surface to measure its temperature.

A Bio-Rad FTS 175 FTIR spectrometer was used to characterise the virgin cooking oil and to identify the functional groups of new components formed during the fire tests. The oil was sampled at different temperatures and after auto-ignition and water mist exposure. The oil specimens were analysed by the FTIR in a very short path cell as single beam emission spectra. These were then routinely processed to the absorption spectrum format using a single beam spectrum of ambient air in an "empty" cell as reference.

### **Cooking Oils**

The cooking oil used in fire tests was a commercially available vegetable oil. It was a mix of canola oil and/or soybean oils with BHA and BHT antioxidants and dimethypolysiloxane antifoaming agent added.

### **Test Procedures**

To simulate a restaurant kitchen fire, a deep fat fryer was filled with fresh liquid cooking oil and heated at the energy input assuring the rate of increase of the oil temperature in the range of 8 to 12°C/min. Once the cooking oil auto-ignited, the fire was left for 2 minutes of free burning, while the heat supply to the fryer was maintained. At the end of the free burning period, the heating was shut off and the water mist discharge activated. After the fire was extinguished, the discharge of water mist was maintained to cool the cooking oil and to prevent its re-ignition.

To examine the changes in the cooking oil's composition during heating and fire suppression by water mist, the surface oil was sampled at different oil temperatures. The aliquots were taken at: 100°C, 200°C, 300°C, and 350°C, as well as after the cooking oil fire was extinguished by water mist and the surface cooled to approximately 270°C. The oil samples were then stored in teflon-lined screw-cap vials, stored in a refrigerator and analysed later by the FTIR.

### **FTIR Measurements**

The cooking oil samples were analysed at room temperature in the extended mid-infrared range using a computer controlled FTS175 spectrometer (Bio-Rad) run under Win-IR v.3 software (Bio-Rad/Grams). The instrument was equipped with MIR source, KBr-substrate beam splitter, KBr windows and a standard (Room Temperature) DTGS detector. The instrument was run in Internal Beam configuration at a resolution of 1 cm<sup>-1</sup> at ~2000 cm<sup>-1</sup>, aperture of 1 cm<sup>-1</sup>, gain = 8, the scanning velocity of the mirror of 10kHz and the filter at 5kHz. The spectra were collected in the 4500-400 cm<sup>-1</sup> range as averages of 128 or 256 scans, single scan taking ~2s. Triangular apodization was used for computing of the spectra.

To enhance the subtle spectral changes observed in used oil, a normalised simple absorption spectrum of fresh oil was subtracted from the simple absorption spectrum of the same oil at different stages of heating and from the spectrum of the oil that had undergone auto-ignition and extinguishment. Two low intensity peaks characteristic of the ester bonds of bulk oil at 3475 cm<sup>-1</sup> or at 730 cm<sup>-1</sup> were used for normalisation [7].

The spectra were intended only for qualitative evaluation and identification of newly formed functional groups.

## Results

During continuous heating the cooking oil in the fryer auto-ignited at the sub-surface oil temperature of 365°C. During a subsequent 2-min long free burning period, the fire developed from a small fire attached to the oil surface to a large one reaching the overhead hood. The fire growth rate was accelerated after the first minute of free burning. With a large fire over the oil surface, the oil overheated to 395°C. The cooking oil fire was extinguished by water mist at 8 s after discharge and the water mist supply was continued for 20 s to further cool the oil.

Figures 1 to 3 show the selected diagnostic ranges of differential (computed against the spectrum of fresh oil) and normalized FTIR spectra of the oil specimens exposed to higher temperatures. There was no visible change in the oil's spectra when the oil was heated from room temperature up to 300°C, compared with the fresh oil. This suggests that the induction period, when the antioxidants protect the oil from auto-oxidation, was not completed during the initial heating. However, when the oil was heated near to the auto-ignition temperature (350°C) and after the fire was extinguished by water mist, the functional groups and therefore the oil's composition were notably changed.

**A) Oil heated to 350°C:** Figure 1 shows a strong and broad peak of stretching vibrations of associated O-H groups in the region of 3700 to 3100  $\text{cm}^{-1}$  with a maximum at ~3430  $\text{cm}^{-1}$ . This band indicates that hydroperoxides and some hydroperoxide-degradation products, such as high molecular weight alcohols and shorter acids, were formed in the heated oil. Figure 2 shows a faint shoulder at wave number 1689  $\text{cm}^{-1}$  in the region of 1725  $\text{cm}^{-1}$  to 1600  $\text{cm}^{-1}$ , typical of the carbonyl bond of saturated aldehydes formed during the degradation of hydroperoxides. Figure 3 shows a bimodal band/double peak at 997 and 972  $\text{cm}^{-1}$  in the 1050 to 900  $\text{cm}^{-1}$  region. Peak at lower wavenumber is typical of *trans* double bonds formed also from collapsing hydroperoxides.

**B) Oil auto-ignited and extinguished with water mist:** Figure 1 shows that the hydroperoxide peak collapsed and a low intensity broad band peaking at ~3330  $\text{cm}^{-1}$  was created. This spectral feature can be attributed to hydroxy groups in alcohols, including glycerol and partially hydrolysed triglycerides, and O-H of free fatty acids. Figure 2 shows a well-defined peak at 1712  $\text{cm}^{-1}$  in the carbonyl stretching region typical of unsaturated aldehydes. Figure 3 shows a very well defined strong peak at 968  $\text{cm}^{-1}$  in the *trans* region attesting to extensive *cis-trans* isomerisation of double bonds in unsaturated fatty acids.

## Discussion

Cooking oils of plant origin undergo deterioration during storage and during the thermal stress of frying [7,9]. The main culprit is an auto-oxidation reaction of the double bonds in the fatty acid of triglycerides resulting in the formation of hydroperoxides. The UV light, temperature and metal ion complexes (iron and tin) accelerate this reaction. The hydro-peroxide can form on any of the allylic positions resulting, e.g., for oleic acid, in a mixture of 8-, 9-, 10-, and 11- derivatives. The hydroperoxides are not stable at higher temperature [10] and undergo degradation to lower, medium and some higher molecular weight species following several different pathways.

Cleavage of the C-C bond in  $\alpha$  position to hydroperoxide-bearing carbon (closer to carboxyl group) produces from oleic hydroperoxides aldehydes  $\text{CH}_3-(\text{CH}_2)_x-\text{C}(\text{O})\text{H}$  where  $x = 8, 9, 10, 11$ . Cleavage of the C-C bond  $\beta$  to the hydroperoxide gives C7-C10 alkenes, aldehydes and alcohols. Cleavage of the C-O bond in the hydroperoxide reproduces a double bond of the original acid moiety of triglyceride, mostly in *trans* configuration. It can also lead to formation of dimers or intramolecular cyclization. Cleavage of O-O bond in hydroperoxide can produce hydroxylated parent molecule, peroxy-dimers and epoxies. Dehydration of hydroperoxide gives ketones. Finally, cleavage of the O-H bond of the hydroperoxide leads to intramolecular peroxides.

Most of the new compounds produced from hydroperoxides during overheating and thermal degradation, such as shorter-chain alcohols and aldehydes, have relatively low boiling points and low auto-ignition temperatures, compared with the parent triglycerides [11,12].

Introduction of water to the hot oil causes flash hydrolysis of the triglycerides that produces glycerol, free fatty acids, and mono- and diglycerides. Mono-, di- and triglycerides can undergo further hydrolysis as more water mist is discharged to cool the oil. That leads to accumulation of large amounts of glycerol and mono- and diglycerides in the surface oil due to their relatively high boiling points [11]. When the cooler surface oil starts to sink and to mix with deeper hot oil, the accumulated glycerol can vigorously decompose at its boiling point of  $290^\circ\text{C}$  to acrolein. This compound has a low boiling point and a low auto-ignition point,  $53^\circ\text{C}$  and  $235^\circ\text{C}$ , respectively [12]. As a result, during fire suppression with water mist, the cooking oil has a strong propensity for re-ignition, as it can have higher bulk temperature than the new, lower auto-ignition temperature caused by the changes in its chemical composition.

## Summary

Test results suggest that in our tests the fresh vegetable cooking oil heated to auto-ignition and exposed to water mist can decompose following two different pathways.

During the initial heating an oxidation of the unsaturated bonds of the fatty acids of triglycerides occurs producing hydroperoxides. Hydroperoxides are unstable and decompose to specific aldehydes, alcohols, and other products of smaller molecular weight. The flash points of such degradation products are usually below  $200^\circ\text{C}$  but initially they form slowly and boil out without ignition. The conditions for auto-ignition are produced when the thermal degradation intensifies in the range of  $310\text{--}360^\circ\text{C}$ , depending on the type of unsaturation of the oil. The burning oil overheats to an even higher temperature and starts to decompose to numerous products of deep pyrolysis.

When the water mist is discharged on burning oil and cools the surface it can cause flash hydrolysis of triglycerides to glycerol. The sudden dehydration of glycerol to acrolein at the glycerol's boiling point produces the lower auto-ignition.

Figure 4 illustrates the processes that may take place in the oil during a water mist test:

1. Formation of the hydroperoxides that accelerates above  $300^\circ\text{C}$ , and peaks shortly before auto-ignition at  $\sim 350^\circ\text{C}$ ;
2. Thermal degradation of the hydroperoxides, that accelerates when the oil is heated beyond  $350^\circ\text{C}$  and can generate large amounts of volatile, medium molecular weight alcohols, acids, aldehydes, and ketones that can auto-ignite above the oil's surface.

3. Extensive pyrolysis of the hydrocarbon backbone of the fatty acids and cracking of the ester bond that occurs in the oil overheated to 400-500°C that result in more vigorous burning.
4. Hydrolysis of triglycerides on the surface of the burning oil after the discharge of water mist that produces glycerol, free fatty acids and mono- and diglycerides.
5. Thermal decomposition of accumulated glycerol to acrolein at 290°C during mixing of the cooled oil with the hot oil.
6. Auto-ignition of acrolein vapours at an apparent temperature lower than the initial auto-ignition temperature of the oil.

To further explain and confirm the mechanism proposed above for the lowering of the auto-ignition point of cooking oils exposed to water more data are needed. That includes small scale tests of different oils and fats under various heating and suppression regimes, and analysis of the oil and its volatile degradation products by FTIR equipped with a flow through cuvette and other techniques, such as GC/MS, at the different stages of heating.

## References

1. Wijayasinghe, M. S., and Makey, T. B. "Cooking Oil: A Home Fire Hazard in Alberta, Canada", *FireTechnology*, 33(2), 140-166, 1997.
2. Koseki, H., Natsume, Y., and Iwata, Y., "Combustion of High Flash Point Materials", Proceedings: 7<sup>th</sup> International Fire and Materials Conference, 339-349, San Francisco, January 2001.
3. Edwards, N., "A New Class of Fire," *Fire Prevention*, Vol. 310, p. 8, June 1998.
4. Voelkert, C., "Out of the Frying Pan", *Fire Prevention*, Vol. 314, pp. 24-26, November 1998.
5. National Fire Protection Association, "Fire Protection Guide on Hazardous Materials" 11<sup>th</sup> edition, NFPA, Boston, MA, 1994.
6. Liu, Z. and Kim, A. K., "Fire protection of a restaurant cooking area with water mist suppression systems," Proceedings: Third International Conference on Fire Research and Engineering, Chicago, USA, 1999.
7. Ma, K., van de Voort, F. R., Ismail, A. A., and Sedman, J., "Quantitative Determination of Hydroperoxides by Fourier Transform Infrared Spectroscopy with disposable Infrared Card", *J. Am. Oil Chem. Soc.*, **75**:1095-1101, 1998.
8. Sedman, J., van de Voort, F.R., Ismail, A. A. and Maes, P., "Industrial Validation of Fourier Transform Infrared Trans and Iodine Value Analyses of Fats and Oils", *J. Am. Oil Chem. Soc.*, 75:33-39, 1998.
9. Fritsh, C. W., "Measurements of Frying Fat Deterioration", *J. Am. Oil Chem. Soc.*, **58**:272-274, 1981.
10. Neff, W.E., and Selke, E., "Volatile Compounds from the Triacylglycerol of *cis,cis* 9,15-Linoleic Acid", *J. Am. Oil Chem. Soc.*, **70**: 157-161, 1998.
11. Lide, D. R., Editor in Chief, "CRC Handbook of Chemistry and Physics", 74<sup>th</sup> edition, CRC Press, Boca Raton, FL, 1993-1994.
12. Sax, N. I., "Dangerous Properties of Industrial Materials", 6<sup>th</sup> Edition, Van Nostrand-Reinhold Co., New York, NY, 1984.

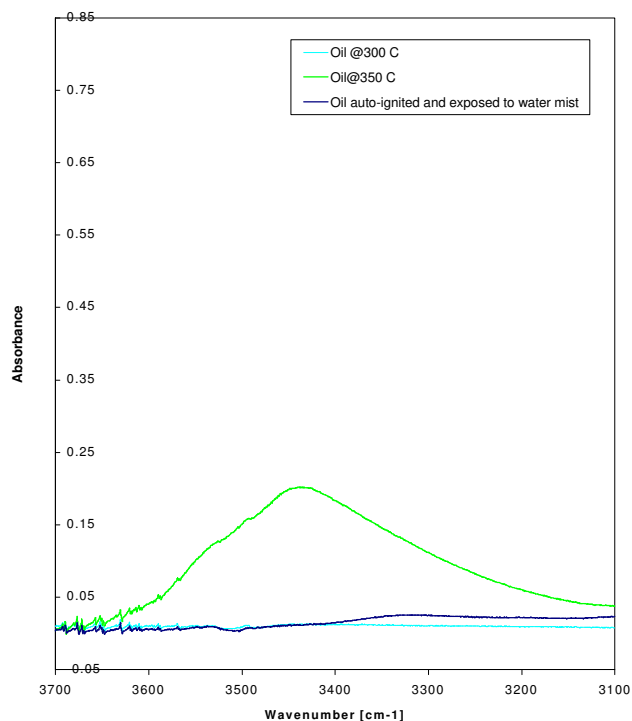


Figure 1: Differential Spectra of Heated Oils in Hydroxyl Region

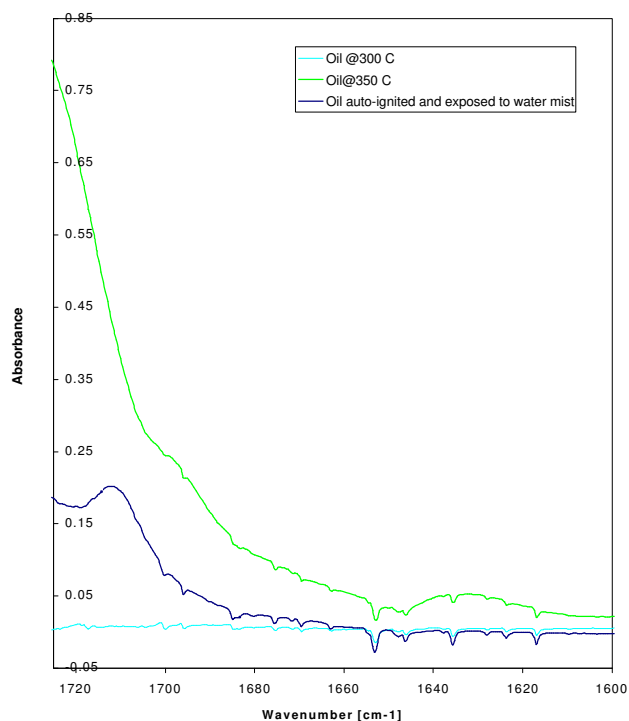


Figure 2: Differential Spectra of Oils in Aldehyde-carbonyl Region

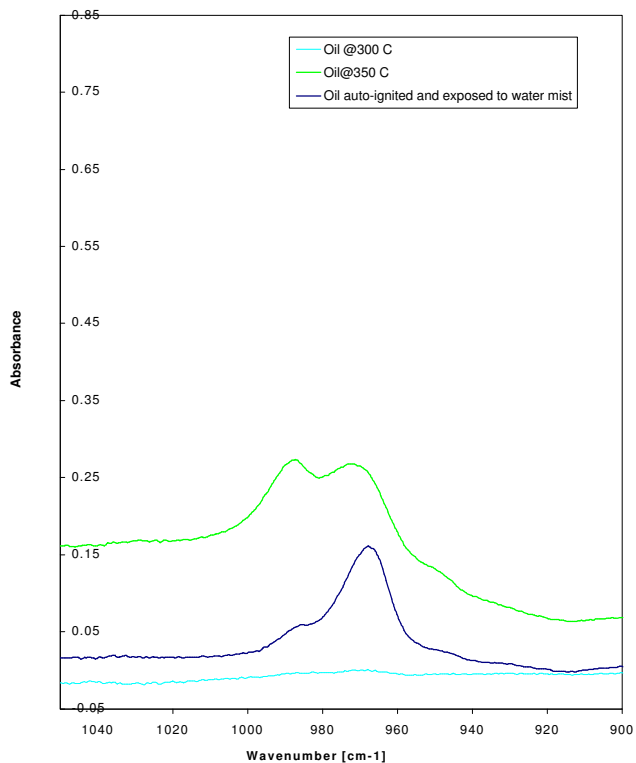


Figure 3: Differential Spectra of Heated Oils in *trans* Region

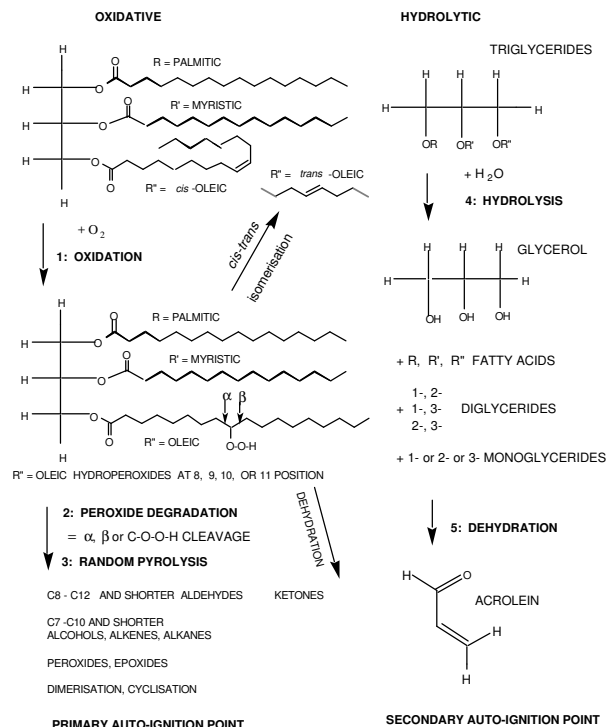


Figure 4: Degradation Pathways of Cooking Oils