

A Proposed Alternative Suggestion for the Disposal of Used Cooking Oil

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Abstract: The control of over-used cooking oil presents a number of problems. Not only are there health issues to consider, the assessment of the degree of degradation also requires tedious and laborious chemical analysis procedures. Once the degree of degradation is established, the disposal or recycling of the used cooking oil presents another huge dilemma. This research note proposes a fast and relatively easy infrared spectroscopic method to measure the amount of waste products formed in the cooking oil as a result of degradation during its use and re-use. It also offers an economic and environmentally sound proposal for its disposal, which can be applied universally all over the world.

Key words: Waste cooking oil, FT-IR, degradation, disposal, analytical measurement, biofuel

INTRODUCTION

Fried food is very popular in South Africa with 87% of food frying establishments in the Pretoria Metropole using sunflower oil for the preparation of the food^[1]. Because of its high percentage of polyunsaturated fatty acids, in particular linoleic acid (C18:2), it is well known that when heated for an extended time, sunflower oil forms oxidation products. Many of these oxidation products such as aldehydes (especially malonaldehyde), hydroperoxides, epoxides and polymeric substances have shown adverse health/biological effects such as growth retardation, increase in liver and kidney size as well as cellular damage to different organs when fed to laboratory animals^[2].

Legislation in South Africa was introduced in 1996 to control the over-use of cooking oil. To be suitable for human consumption, the law requires adherence to certain limits of selective compounds, among them polar components (PC's) and polymerized triglycerides (PTG's). It states that the level of PC's should not be more than 25%, while the limit for PTG's is 16%. A survey done in 1997 by the Department of Biotechnology and Food Technology in the Pretoria Metropole showed severe abuse of cooking oil in some fast food outlets with the

worst sample drawn having 63% PC's and 56% PTG's^[1]. These results are much higher than those found in similar surveys conducted in other countries such as Australia and Saudi Arabia, with their highest PC's recorded in oil being 29 and 33% respectively. In addition, it was found that 54% of the used oil was given/sold to staff and 20% was disposed of in the municipal drainage system^[1].

Besides the health effects of these over-used oils, their disposal could have a huge environmental implication, because of high COD (chemical oxygen demand) levels. This is of particular concern, as an estimated 162 000 tonnes of used oil is discarded annually in South Africa. Thus, these over-used oils constitute a high volume, high value, zero cost waste product which has enormous potential for other uses. One of these is a biotechnological approach, where microorganisms are used to bioconvert this waste product into high value products, also known as biotransformation. Another alternative is a chemical route, whereby these oils are utilised as biofuels.

The use of waste materials as a source of alternative fuel is a practice of increasing popularity in the cement industry worldwide^[3-7]. Since fuel cost is one of the major factors influencing the manufactured price of cement, it is only natural that cement producers would be favourably

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inclined to consider the use of alternative fuel sources. Furthermore, the configuration and operating conditions in cement kilns are most favourable to completely oxidize and destroy most types of organic materials. It is therefore fairly logical that, apart from possible bio-transformations of used cooking oil, one should consider such wastes as a possible alternative fuel source for cement kilns. Waste cooking oil has the advantage that it can be easily transported, handled, pumped and used in current burners in cement kilns. It also has virtually no sulphur or heavy metal element contamination. If this type of waste has a reasonable energy content per unit mass, it could be quite an attractive alternative to coal usage in cement kilns.

An investigation was therefore launched to determine the calorific value of cooking oil samples degraded/abused to various degrees to measure their potentially energy content. The aim was to determine whether there was any correlation between the degree of chemical degradation and the potential energy value of the waste cooking oil. During the course of the investigation it became necessary to find a rapid tool to identify potential spoiled oils and predict the nature of degradation for health purposes. A very useful tool to observe chemical changes, is Fourier Transform Infrared (FTIR) spectroscopy. FTIR was therefore employed to investigate possible changes in the functional groups of the carbon atoms and the structural changes that take place in sunflower oil when it is repeatedly used. With this investigation we hope to stimulate interest for further studies into the quality and chemical structure of used cooking oil and potential beneficial uses of this vast source of waste material.

MATERIALS AND METHODS

PC and PTG determinations: The PC^[8] and PTG^[9] contents of each sample of used cooking oil were determined according to the standard methods.

Caloric value measurements (CV): Calorific value determinations were done on a standard bomb calorimeter, using benzoic acid as a standard reference material.

FTIR analysis: FTIR spectra were obtained using a NICOLET 20SXL FTIR spectrometer equipped with a 486 ACER personal computer, OMNIC FTIR software and a Deuterium Triglycine Sulphate Detector (DTGS) detector. The oil samples were prepared between KBr discs with a 0.5 mm spacer. A blank analysis was performed to obtain an infrared absorption spectrum of the background from 4000 to 500 cm⁻¹. The background absorption was then subtracted from the absorption spectra of the oil samples. The spectral resolution was 0.5 cm⁻¹.

RESULTS AND DISCUSSION

The results in Table 1 indicate that there is no direct relationship between the amount of PC's and PTG's present in each of the samples. It seems as though the contents of these respective types of compounds are related to the environments from which they originate and the particular uses the cooking oil were employed for.

From the values represented in Table 2, no obvious relationship could be deduced between the CV values and the respective PC and PTG contents of the samples. If these latter two parameters are considered a measure of the degree of degradation of the cooking oil, it seems that the degree of abuse of the material has no influence on its ultimate energy value. This is rather surprising, as it can be expected that different chemical compounds would possess different energy values when oxidised to carbon dioxide and water as products. An approximately constant value was obtained for the caloric values of all the cooking oil samples evaluated. However, the most significant observation from these measurements was that the calorific values of the oil, even in their abused state, was still approximately one and a half times higher than that of coal normally employed in burning processes. This confirms the potential of used cooking oil as a viable energy source for the cement and even lime industries. In the latter case it could contribute significantly to the reduction of build-up problems normally experienced with coal usage^[10]. From the point of view of its caloric value, easy handling and transportation as well as decreased pollution potential, used cooking oil seems eminently suitable as a potential alternative fuel source for the cement industry.

Table 1: Polar (PC) and Polymerised-triglycerides (PTG) compounds content of selected abused cooking oil samples

Sample No.	% Polar compounds	% Polymerised-triglyceride compounds
9	31.6	10.1
361	40.0	35.0
385	48.2	43.6
413	61.8	56.3
639	63.0	41.9
765	51.6	45.4
893	55.4	49.1
976	38.2	27.3
1039	25.2	18.8

Table 2: Calorific values (MJ kg⁻¹) of selected abused cooking oil samples

Sample No.	CV values
9	39.2
361	38.5
385	38.4
413	38.0
639	39.6
765	38.4
893	38.6
976	38.9
1039	39.2
Benzoic acid	26.45 ^[13]
Typical coal (A)	25.0-27.0

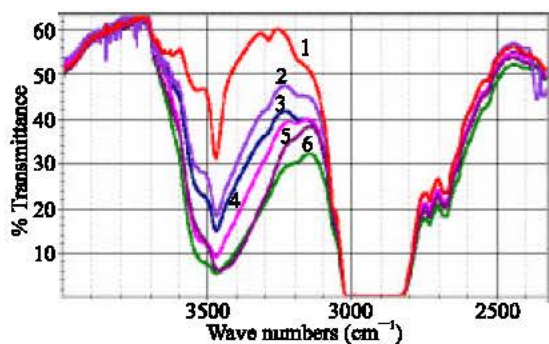


Fig. 1: The most obvious difference between the virgin sunflower oil (1, red) and the degraded oils (2-6) is at the O-H stretch band around 3500 cm^{-1}

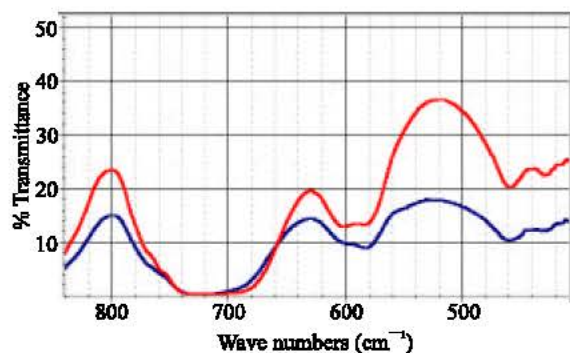


Fig. 2: IR spectrum of the virgin oil (bottom, blue) and the most oxidised oil sample (top, red)

Figure 1 clearly indicates the difference in the infrared spectra of the virgin oil and the used sunflower oil. It is particularly obvious in two regions, the first of them being at the O-H stretching frequencies 3550 to 3450 cm^{-1} ^[11,12] where the degraded oils are more pronounced than the virgin sunflower oil. The second region represents the twin bands around 2750 cm^{-1} where the C-H stretching vibration of the CHO functional group occurs^[11,12]. These latter bands are more intense in the degraded oils showing that oxidation has taken place. This is in agreement with previous observations^[1] that aldehydes (especially malonaldehyde) and epoxides are common oxidation products of sunflower oil heated for an extended time.

The broad band from 800 to 600 cm^{-1} in Fig. 2 represents the C-H out of plane deformation vibration for the alkene (C=C) functional group^[11,12]. In this band of frequencies the virgin sunflower oil has a broader and more intense peak than the degraded oils. This is to be expected in view of the high percentage of polyunsaturated compounds present in sunflower oil. The virgin oil in which no oxidation of these compounds has yet occurred, would naturally display a more intense peak in this area than the used cooking oil sample. Further

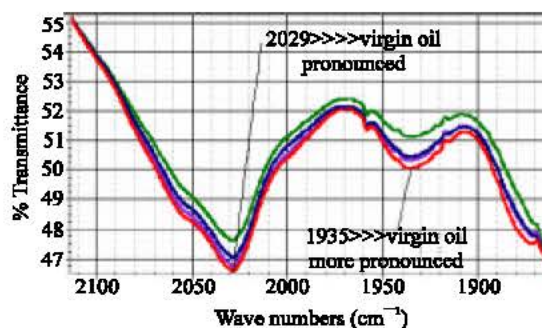


Fig. 3: The virgin oil spectrum (bottom one) has slightly more pronounced peaks at the alkene overtone frequencies

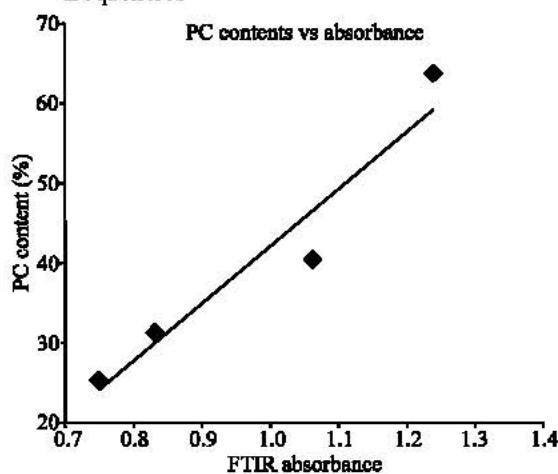
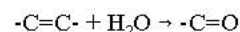


Fig. 4: Relationship between the absorbance at 3469 cm^{-1} and the %PC in selected used cooking oil samples

proof of the oxidation reaction can be found at the overtone peaks (2030 and 1935 cm^{-1}) for the series of strong C=C absorptions that are found between 1500 and 980 cm^{-1} (Fig. 3). At these frequencies, the virgin sunflower oil peak is slightly more pronounced than those of the degraded oils.

In organic chemistry an oxidation reaction is a reaction whereby the carbon atom loses electron density by forming a chemical bond with an electronegative species like oxygen. Since sunflower oil is highly unsaturated, carbonyl bonds typical of aldehyds, ketones and organic acids can be easily formed, especially at high temperatures. The process can be represented by the simplified chemical reaction:



From the work presented in this communication, it can be concluded that the spectroscopic technique employed was very successful to observe the chemical changes that took place while sunflower oil is being used as a cooking

agent. The discrimination between virgin and abused oil, was clearly demonstrated by means of FTIR spectroscopy and one could even obtain an indication of the type of oxidation that occurred during the process of degradation.

Figure 4 illustrates the quantitative relationship between the absorbance values obtained at 3469 cm^{-1} in the spectra and the percentage polar compounds present in each of some of the limited number of samples available. It seems that a linear relationship with a reasonable correlation coefficient of 0.93 exists between these two parameters. The data set in this investigation is too small to make any conclusive deductions in this regard, but it does demonstrate that there is more than a good possibility to utilise FT-IR spectroscopy as a quantitative tool to monitor the degradation of cooking oil in terms of the polar compound content present as a result of degradation. More work is planned to investigate this observation further in future. At this stage it can only be stated that the use of FT-IR clearly succeeded as a qualitative tool to illustrate differences between used and virgin sunflower oil.

Although it can be argued that the limited amount of work presented in this short communication can be extended to cover much more detail, the original goals of the investigation were very successfully achieved.

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