Spectroscopic studies of the quality of WCO (Waste Cooking Oil) fatty acid methyl esters

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Abstract. Different kinds of biodiesel fuels become more and more attractive form of fuel due to their unique characteristics such as: biodegradability, replenishability, and what is more a very low level of toxicity in terms of using them as a fuel. The test on the quality of diesel fuel is becoming a very important issue mainly due to the fact that its high quality may play an important role in the process of commercialization and admitting it on the market. The most popular techniques among the well-known are: molecular spectroscopy and molecular chromatography (especially the spectroscopy of the electron absorption and primarily the infrared spectroscopy (FTIR)).The issue presents a part of the results obtained with the use of spectroscopy of the electron absorption and in majority infrared spectroscopy FTIR selected for testing samples of the acid fats WCO (Waste Cooking Oil) types. The samples were obtained using laboratory methods from sunflower oil and additionally from waste animal fats delivered from slaughterhouses. Acid methyl esters were selected as references to present the samples. In order to facilitate the spectroscopic analysis, free glycerol, methanol, esters and methyl linolenic acid were measured.

1 Introduction

The massive expansion of internal combustion engines is associated from the outset with the use of primarily crude oil as an energy source. In almost one hundred years old history of generally understood automotive industry the only fuel hydrocarbon fractions were extracted from crude oil, which still remains the most important energy source. In this respect, it also has a very large impact on the global

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political and economic situation. However, the modern world realized that global deposits of oil are largely reduced and the the ever-increasing consumption causes a serious ecological threat such as a greenhouse effect caused by CO_2 gas. This fact has become a powerful driving force for many research programs around the world to search for alternative fuels which would partially or completely replace the conventional fossil fuels and cast little threat to the environment[1-4]. In this context, the fuel constituents derived from renewable sources such as bio fuels seem to play the most important role. Among the various types of bio fuels the biodiesel (most often defined as the fatty acid methyl esters (FAME)) is most attractive. It should be noted that the application of FAME either as fuel for compression engines or ignition or as a gas component considerably changes the properties which have been known so far. Significant differences in chemical structures of hydrocarbons present in diesel and FAME differentiate the behavior of these products and affect their handling, storage conditions as well as the engine compartment. Currently, practically every vegetable or animal fats can be used as a raw material for the production of various types of biodiesel. The most commonly manufactured raw materials are edible vegetable oils and rapeseed oils, soy, sunflower or even palm oil.

Those raw materials, referred to as the first generation, do not resolve major issues such as reduction of CO_2 emission and may even increase problems on the food market [5-6]. Focusing attention on acquisition of raw materials seems to be the solution to this situation. II generation i. e. edible plant oils such as algae and microalgae [7], Jatropha [8] or used vegetable oil can be obtained from households or restaurants.

There are two main factors which prove that waste oil (WCO) is nowadays one of the most promising raw materials for the production of biodiesel [9-12], namely the wide availability of the raw material and the very low production cost. Due to the increasing consumption, the amount of waste oils is growing very quickly. For example, only in the United States about 10 million tons of the WCO is generated annually. This in turn requires environmentally friendly methods for WCO disposal and in this context the use of WCO as a raw material for biodiesel production is considered economically advantageous [13]. It has been estimated that the low cost of biodiesel production from WCO may help in overcoming the economical barriers. Currently the biodiesel production cost is ~1.5 times higher compared to that of conventional diesel, and only this fact speaks much for the opportunity to introduce biodiesel on a larger scale. It is estimated that more than 70% of the cost of biodiesel production is cost-per-acquisition of raw material [14-15]. It should be pointed out that the price of the WCO is 2-3 times lower compared to the price of crude vegetable oils, which can substantially lower the production costs of the same fuel in the form of biodiesel. Also, a significant reduction in the costs of waste disposal is an additional worth-mentioning advantage [16]. Due to the structural transformations taking place in frying oil over time [16], the chemical and physical properties of WCO oils differ from those of fresh oil. As a result of the frying temperature (approx. 190 °C) as well as the presence of O_2 and H_2O from fried products, similar physical and chemical changes occur both in the food, and in oil medium used for frying. These changes can result in the formation of various compounds that often have very complex and unidentified structures, such as free fatty acids (FFA) [17-19]. The presence of solids together with significant quantities of H_2O in the test products (those may come with fried products and are introduced during the washing) may also be problematic. Hence, the fact that the profile of fatty acids composition and the free fatty acids content in raw materials affect physicochemical properties of derived bio fuels is undisputable.

The use of WCO for biodiesel production requires an appropriate technology with advanced pretreatment processes and selection of relevant transesterification reaction parameters. Various contaminants such as water, organic compounds and substances which cannot undergo saponification lower the transesterification yield and overall quality of biodiesel product. The quality of products obtained must be controlled by suitable analytical techniques, one of which is infrared FTIR spectroscopy [20-24].

The main purpose of current work is the application of infrared spectroscopy and FTIR-spectroscopic properties of WCO oils for assessing the suitability of the WCO for the production of biodiesel.

2 Materials and Methods

2.1 Materials

All fatty acid methyl esters tested were obtained from fresh oils using laboratory methods. All frying oils (WCO), waste animal fats and bio-commercial oils used for the experiments meet the requirements of EN 14214:2006 standard.

The following oil materials were used:

1. Refined sunflower oil underwent five cycles of frying potato French fries. Single cycle consisted of heating the oil up to the temperature of 180°C followed by an insertion of vegetable material.

2. Refined sunflower oil underwent five cycles of frying fish fingers. The production cycle was carried out in the same way as in 1.

3. Waste animal fats, were obtained from a slaughterhouse. They were melted down by their slow heating up to the temperature of 60°C (under greatly reduced pressure in order to prevent its degradation). Remains of poured, drained fat were centrifuged and decanted. The raw materials obtained were subjected to esterification in a lab reactor (V = 1000 ml) and adjustable temperature stabilization.

The reaction time and mixing speed were based on the available literature [25-27]. In order to begin the trans-esterification reaction the experiments were carried out in temp. of 55 °C. After reaching the desired temperature all tested oil samples were treated by a catalytic mixture consisting of methanol and NaOH. The reaction mixtures were stirred for 2 h using power agitator.

In order to completely separate the Glycerin and esters obtained, the mixture was subjected to 8 h long sedimentation process. The esters were then washed twice with hot water (at 80°C) and dried to remove the remaining alcohol and catalyst used.

Then, each of the selected studies of esters was tested with regard to the peroxide number (LN) [PN-ISO 3960], number of acid (LK) [PN-ISO 660] and composition of higher fatty acids that are marked by gas chromatography. The gas chromatography with nitrogen has been used as the carrier gas, packed column (2.5 m with stationary phase PEGA, which consisted of polyethylene glycol adipate embedded GAS medium-chromium-Q) and a flame ionization detector.

2.2 Methods

Spectroscopic methods. Electronic absorption spectra were recorded at 23°C on double-beam UV-Vis spectrophotometer Cary 300 Bio (Varian, USA) equipped with a thermostated cuvette holder with a 6×6 multicell Peltier block. The temperature was controlled with a thermocouple probe (Cary Series II, Varian, USA) placed directly in the quartz cuvette. The spectra were recorded from 200 to 600 nm.

The measurements of ATR-FTIR background-corrected spectra were carried out in solvents using a HATR Ge trough (45° cut, yielding 10 internal reflections) crystal plate for liquids and were recorded with a 670-IR spectrometer (Varian, USA). Typically, 25 scans were collected, Fourier-transformed, and averaged for each measurement. The IR absorption spectra at

a resolution of one data point per 1 cm-1 were obtained in the region between 4000 and 400 cm-1. The instrument was purged with argon for 40 min before and then during the measurements. The Ge crystal was cleaned with ultra-pure organic solvents (Sigma-Aldrich Co.). All experiments were carried out at 20 °C.

3 Results and discussion

Infrared spectrometry (FTIR) is a commonly used tool for analysis of the carbonyl group-containing compounds and for determination of the petroleum products. Its use for determination of the FAME content is based on the fact that the carbonyl C=O vibration, which usually occurs at approximately 1700-1800 cm^{-1} is practically negligible in hydrocarbon fraction, while in case of FAME it is highly intense. It is well-known that esters give highly specific and strong absorption bands caused by vibrations of their C=O and C-O valence bonds.

The absorption band of the carbonyl group C=O in saturated aliphatic esters usually appears at 1735-1750 cm^{-1}. The aryl and α, β-Unsaturated structure may cause slight shift of this band towards a shorter wavenumber values (i. e. 1715-1730 cm^{-1})[28]. The C-O stretching vibration emerges within a much broader range (1100-1300 cm^{-1}), and is also observed in the spectra of other organic compounds such as carboxylic acids, ethers, or alcohols. Methyl esters belonging to the long-chain fatty acids often give rise to absorption maxima at approximately 1250, 1205, and 1175 cm^{-1}[29]. In case of FAME the most characteristic band has its maximum at approximately 1175 cm^{-1}[30].

Other characteristic of a hydrocarbon chain bands which occur in EMKT and ON are:

-methyl (-CH$_3$) and methylene (-CH$_2$-) groups C-H stretching vibrations (both symmetrical and non-symmetrical), present at 2870 and 2965 cm^{-1} (former), and 2925, and 2850 cm^{-1} (latter)[31].

- bending vibrations of the C-H bond: in methyl group present at 1375, 1450 cm^{-1} (and 1438 cm^{-1} in compounds containing carbonyl group); in methylene group at 1465 (scissoring vibration), and 721 cm^{-1} (rocking vibrations)[32].

Interestingly, in the spectra of hydrocarbon fraction of diesel within the range of 1700-1800 cm^{-1} another characteristic band is present, while it is absent in the FAME spectrum. This suggests the presence of various oxidation products (aldehydes, ketones, carboxylic acids) or various oxidation inhibitors, for example -mediated inflammatory diseases. In addition, poor absorption of some in the vibrations of the maximum of approx. 1750 cm^{-1} can be attributed to the presence of small amounts (within 1%) (that is, polymers with carbonyl groups)[33].

Although the formation of such carbonyl compounds is unlikely in high-quality fuels, their presence may cause difficulties in the determination of FAME content. It should be noted, that despite those difficulties the band between 1750-1740 cm^{-1} is considered as optimal for the IR-based identification and quantitative analysis of FAME in medium oil fractions and lubricating oils[34].

Figure 1 shows the selected electron absorption spectra of the methyl esters from sunflower oil after frying French fries (black line) and fish (dashed line) and the spectrum of the selected commercial esters, dissolved in methanol (grey line).

The absorption maxima at approximately 270 nm, for all samples of oils selected for tests (279 nm for the methyl esters of rapeseed oil after frying French fries or fish and 281 nm for commercial esters) clearly indicate the origin of the band as the n→π* electronic transition within the carbonyl group (C=O)[35-38].

In case of commercial esters a very broad absorption set of bands is easily noticed (360 - 510 nm), which is not observed in the spectra of sunflower oil esters (after frying French fries and fish).

This region of the spectrum may be characteristic either of various fuel additives e.g. biocides (synthetic or natural) or pollutants. Studies carried out on other esters (not shown) revealed spectral features similar to those presented in Fig. 1.

The FTIR spectra of the investigated esters are given in Fig. 2. The samples were dissolved in appropriate organic solvent and dispersed at the surface of ZnSe crystal and then the solvent evaporated in an atmosphere of inert gas (N_2).

The samples of sunflower oils after frying both French fries and fish have the characteristic maxima at about 1744 cm^{-1} (1743 cm^{-1} for the methyl esters of rapeseed

oil) originating from carbonyl C=O for stretch.

The spectrum of methyl esters from oil after frying French fries compared to that of esters from oil after frying fish (Fig. 2, top) shows a remarkable difference in the band shapes within the range of 1770-1670 cm^{-1}. In particular, a clear decrease in the intensity of band at 1744 cm^{-1} is observed, most likely as a result of the formation of strong hydrogen bonding.

The band with the maximum at 1715 cm^{-1} neither is observed in the spectrum of commercial B100 nor in the spectra of the methyl esters of sunflower oil, clearly indicates a lack of ability to create this type of hydrogen bridges.
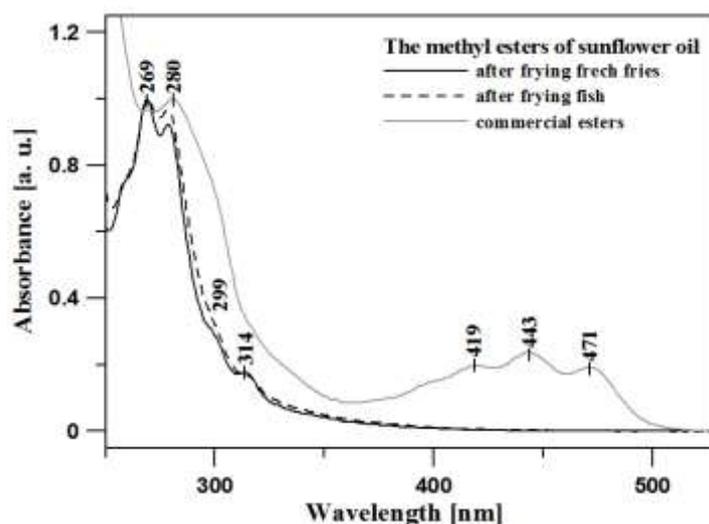

Fig. 1. Electronic absorption spectra of the methyl esters from sunflower oil after frying French fries (black line) and after frying fish (dashed black line) and esters commercial-B100 (grey line), dissolved in methanol (Mt-OH).
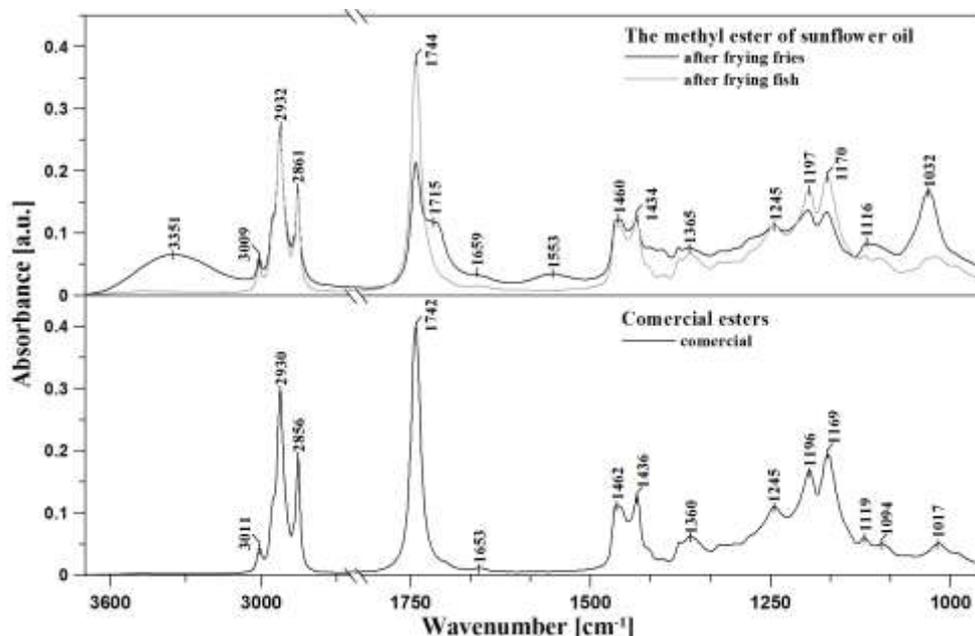
Fig. 2. ATR-FTIR absorption spectra of esters from sunflower oil after frying French fries (solid black line) and after frying fish (dashed black line) (top) and of commercial esters-B100, (bottom). All samples were dissolved in Mt-OH.

With the decrease in intensity of the band at 1744 cm^{-1} and the respective intensity increase of the band at 1715 cm^{-1} a simultaneous increase in intensity of the band at 1032 cm^{-1} associated with the C-O stretching vibrations is observed. This band is also clearly visible in the spectra of methyl esters from oil after frying French fries and fish, while in the spectrum of commercial esters it is least intensive, which is most likely associated with the greatest intensity of carbonyl C=O vibration in this spectrum. Bands in the area of 1100-1300 cm^{-1} also originate from C-O stretching, but only minimal differences are observed in this region between all spectra[34]. These bands together with a decreasing trend of hydrogen bonding between groups of C=O   H-O-H show small but noticeable increase in their intensity.

A similar trend is also observed in the spectrum of commercial esters. Interestingly, the area between 3680-3070 cm^{-1}, with a broad band showing the maximum at approximately 3351 cm^{-1} results from the presence of a high content of methanol and a significant amount of H$_2$O in the tested samples of esters[39]. This effect may also depend on whether the esters were used in frying French fries or fish. The studies have also revealed a glycerol content in the samples tested. the sample of commercial esters contains the lowest amount of glycerol. Analogical observation was made for methanol and methyl ester of linolenic acid content, which presence in the test esters is very well correlated with changes in the intensity of the bands at 3351 cm^{-1}[40-41]. An increased concentration of these compounds results in a significant decrease in intensities of these bands

Table 1. Positioning of FTIR absorption maxima with assignment of appropriate vibrations in bio fuels tested (for the methyl esters of sunflower oil after frying French fries, fish and for commercial esters-B100 recorded within the range of 3700-900 cm^{-1}.)

FTIR			
Position of bands [cm^{-1}]			**Type and origin of vibrations**
Esters of sunflower oil		**B100**	
3351w	3351st	–	ν (O-H) in H_2O
3009	3009	3011	ν(C-H)
2932	2932	2920	$CH_{2, s+as}$, $CH_{3, s+as}$ *aliphatic group of triglycerides*
2861	2861	2856	
1744st	1744w	1742s	C=O *group of Ester*
1715	–	–	
1659	1659	1653	ν(C=C)
1553	1553	–	ν(C=C)$_s$
1460	1460	1462	-C-H (in CH_2) *bending*
1434	1434	1436	=C-H (cis-) *bending*
1417	1417	1418	
1404m	1404m	1403m	ν (=C-H (*cis-*))
1376	1376	1377	-C-H $_s$ (in CH_3)
1365	1365	1360	-C-H $_s$ (CH_3) *bending*
1317	1317	1319	δ(CH)
1277st	1277st	1276m	δ(CH_2)
1245	1245	1245	-C-O *stretching*
1197	1197	1169	or -O-CH_2-C
1170	1170	1194	-C-O
1116	1116	1119	ν(C-C)
1132	1132	1117	
914m	914m	910m	-OH
860	860	859	ν(C-O-C)$_s$
839st	839st	840w	ν(C-O-C)$_s$ or ν(C-C)
721	721	722	-CH_2- *rocking*

ν – stretching vibrations, δ – bending vibrations, s – symmetrical, as – asymmetrical, st – strong, * denotes frequencies that may originate from the solvent used

4 Conclusions

This study presents the application of infrared spectroscopy and FTIR as a tool for analysis of the quality of the selected fatty acid-methyl esters as potential biodiesel components. The experiments primarily focused on the methyl esters obtained from waste oils WCO. The results obtained were compared with the spectra of commercial esters (B100) and comply to commercial standards EN 14214.

When using both spectroscopies: UV spectroscopy as well as FTIR infrared

spectroscopy, key areas have been examined. The essence of the examination was to determine suitability of the information of the spectral test on the WCO ester type in order to apply them as a bio fuel.

It has been proved that the analysis of key areas in the UV-Vis and FTIR spectra of the selected waste oils may serve as an inexpensive source of information on the composition of these oils and their suitability as raw materials for biodiesel production.

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