Properties of Fatty Acids Methyl Esters from Used Frying Oils

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Fatty acid methyl esters (FAME) are used as alternative diesel fuel made from renewable sources. The attention is oriented to the materials that do not compete with food and feed production. Significant potential as an alternative low-cost biodiesel feedstock present used frying oils (UFO). The chemical changes of triacylglycerols which take place during frying can be so extensive that the properties of the FAME made from UFO (UFOME) should not meet all requirements of the standard EN 14 214. The key problem is FAME oligomers which lower the ester content and increase the viscosity. In this work, the results of oligomer content determination using gel permeation chromatography (GPC) and gas-liquid chromatography (GLC) are presented. Effective method for oligomer removal from UFOME is their final treatment based on UFOME distillation in vacuum film evaporator.

1. Introduction

The EU's objective is to replace 10 % of fuel consumption with alternative fuels by the year 2020. First generation biofuels - liquid fuels for transportation based on vegetable oils (Fatty Acid Methyl Esters - FAME), or sugar beat, sugar cane and starch-containing agricultural products (bioethanol) have limited resources, high price and are unable to replace fossil fuels on a large scale. Without subsidies and subsidy-related measures biofuels would not be able to compete against fossil fuels. In the decades to come natural triacylglycerols (TAG) will continue to form an important part of renewable energy resources, especially as raw materials for preparation of liquid fuels for transportation purposes.

FAME are used in standard diesel engines without engine conversion as alternative fuels from renewable resources usually combined with fossil diesel. The solution of their high price is utilization of cheap sources of oils and fats such as non-edible oils, oils with increased acid content, and used oils/fats (UFO). UFOs are found in relatively large quantities (Mittelbach, 1996) in the course of preparation of meals or fast-food products by frying on an industrial scale. Frying is the most demanding cooking process in terms of working temperature where fats are heated in the presence of air, light and water to the temperature of 160 to 200 °C for a fairly long time. Hydrolytic, oxidation, cracking and polymerization reactions occur in the oil during such frying and lead to the

formation of undesirable products with different polarity, stability and molar mass. Most of these products, e.g. dimeric and polymeric acids, dimeric acylglycerols and polyglycerols, remain as radical reactions products in the oil, increasing the frying oil viscosity.

UFO were in the past used as an admixture in compound feeds for livestock (Iglhaut et al, 1998). Harmful substances thus returned via animal meat to the food chain. For these as well as other serious reasons (BSE – bovine spongiform encephalopathy), there has been a ban on UFO use in compound feeds in the EU from 2002. Naturally, alternative UFO use for diesel fuel preparation has emerged recently.

UFO price is substantially lower than that of fresh oils/fats. UFO is obtained from producers usually free of charge, the only cost item being transportation and processing. While fresh oils and fats usually meet the requirement for low acidity and low water content, this is not always the case with UFO. Currently, there is no known UFO parameter(s) allowing us to decide whether future FAME from UFO (UFOME) will be compliant with the EN 14 214 standard. In principle, the technology of FAME production from UFO does not differ from the standard FAME production using fresh vegetable oils or animal fats (Cvengroš and Cvengrošová, 2004). However, previous experience with FAME production from UFO indicates that chemical changes occurring in vegetable oils and animal fats during frying cause that UFO do not always yield standard FAME products. Despite a high conversion degree of AG to FAME, FAME obtained from UFO often demonstrate insufficient ester content - EC (content of methyl esters), increased viscosity, reduced oxidation stability, raised carbon residue value (CCT value) etc.

Content of polymeric TAG according to official method (AOAC, 1996) and content of polar substances (AOAC, 1984) are used as UFO quality evaluation criteria. The content of polymeric substances should not exceed 12 % by weight, the content of polar substances 24 % by weight (Gertz, 2000). The content of polymers is closely linked to the content of polar substances as dimerization and oligomerization are steps succeeding oxidation processes. There is a linear relation between the content of polymeric TAG and content of polar substances having a high correlation coefficient R^2 value of approx. 0.98 (Gertz, 2000; Sánchez-Muniz and Bastida, 2003). Both UFO quality assessment methods are time-consuming, complicated and costly, requiring special reagents, which is why simpler procedures are being sought providing relevant data. Viscosimetry, NIR spectroscopy, NMR spectroscopy and dielectrimetry (Hein et al, 1998; Al-Kathani, 1991;Wegmueller, 1994) are used for this purpose. Band intensity in the region 4700 to 4900 cm^{-1} is used in NIR spectroscopy to evaluate oxidation and oligomerization changes (Hein et al, 1998). Mittelbach and Enselsberger (1999) mention HPSEC (GPC) chromatogram for heat-exposed rapeseed oil with obvious presence of dimeric and trimeric TAG. The importance of the distillation in UFOME final treatment was emphasized by Verhé et al (2009).

2. Materials and Methods

2.1Materials
18 UFO samples obtained from UFO collector INTA Šalgovce and two samples of fresh FRITOL oil (Palma Bratislava) and lard (JAV AKC Vlčany) were evaluated. UFO

samples were heated to approximately 50 °C, filtered and deacidified and dried on a molecular evaporator MO 15 at the temperature of 180 °C and pressure of 20 – 50 Pa. Subsequently, treated UFO in each sample was transformed into UFOME by standard alkaline-catalyzed two-step transesterification with methanol and treated by filtration and washing (Cvengroš and Považanec, 1996). Conversion of AG to FAME was determined by GLC (Cvengroš and Cvengrošová, 1994), EC by GLC according to EN 14 103. Conversion rate for all UFOME tested exceeded 98 %, which is a value corresponding to the MAG, DAG and TAG content below the admissible value according to the EN 14 214 standard. 12 UFOME samples showed ester content between 98 to 101 % (EN 14 214 minimum value 96.5 %); 6 samples had a lower ester content ranging from 83 to 94.5 %. FAME standards from the fresh rapeseed oil and lard as well as UFOME from selected samples were distilled on a molecular evaporator at about 140 °C and 20 Pa to the evaporation degree over 95 %. Distillation residues and distillation products were evaluated separately.

Methyl esters of dimeric fatty acids (diFAME) were prepared by esterification with methanol of distilled dimeric fatty acids obtained under the commercial name of UNIDYNE 22 (Chemotex Děčín) finally treated on the molecular evaporator MO 15. The diFAME acid value was 1.4 mg KOH/g.

2.2 Methods

Molecular weights and molecular weight distributions for samples were obtained by measurements carried out by means of gel permeation chromatography (GPC). Conversion of acyglycerols (AG) to FAME was determined by the method referred to in (Cvengroš and Cvengrošová, 1994). The method is based on the comparison of FAME peak areas in the sample prior to and after the sample treatment with an efficient transesterification agent. The wiped-film laboratory molecular evaporator of the MO 15 type was used for distillation (Cvengroš, 1990)..

3. Results and Discussion

Figure 1 demonstrates a GPC record for commercially available fresh vegetable oil FRITOL, Figure 2 GPC record for selected used frying oil (UFO 1). GPC is a standardized method used for determination of polymers in frying oils/fats (AOAC, 1996). While the elimination curve for the fresh oil is smooth, having only one peak, the curve for the used oil is more complicated, featuring two additional flat peaks for dimers and trimers. Figures 1 and 2 show that GPC provides unambiguous information about oligomeric content in UFO.

UFOME were prepared from a set of 18 UFO samples by the standard procedure involving pre-treatment in a short-path wiped-film evaporator where at the temperature of 185 °C and pressure of 20 – 50 Pa UFO were dried and deacidified to achieve the acid value under 1.0 mg KOH/g. The above-mentioned pre-treatment subsequently resulted in the conversion of AG to FAME exceeding 98 %. After two-step transesterification with methanol (MeOH) and G-phase separation the excess MeOH in the UFOME prepared was distilled off in a laboratory rotary evaporator (t ~ 90 °C, p ~ 1.5 Pa, time 15 min) and subsequently UFOME were cooled, filtered, extracted with water (2 % by weight), centrifuged in a centrifuge (at about 1500 *g*) and dried. In the samples of treated UFOME, viscosity, conversion rate and EC were determined; in

selected samples also oligomer content by GPC was ascertained. Table 1 shows values for some UFOME samples and for the FAME standard prepared from the fresh rapeseed oil with final FAME treatment by distillation on a short-path evaporator.
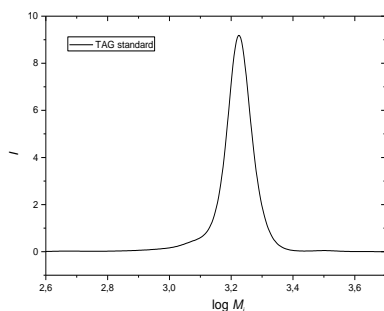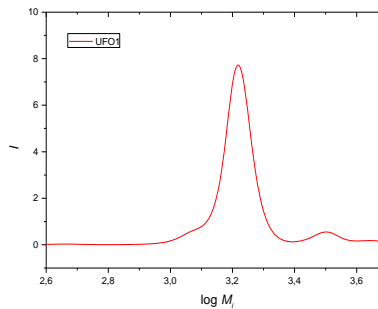

Figure: 1 GPC of fresh oil FRITOL *Figure 2: GPC of UFO 1*

Viscosity values in Table 1 reveal that UFOME viscosities are slightly higher than those of the FAME standards, but still within the range of the EN 14 214 standard. The table also indicates that the GLC-based EC information and oligomer content information obtained from GPC have a relatively good correlation. In determining the EC, GLC thus provides indirect information about oligomeric content too.

Table 1 Some parameters of used UFO and UFOME

Sample	AV of UFO* (mg KOH/g)	ν at 40 °C (mm^2 s^{-1})	Conversion (%)	EC from GLC (%)	EC from GPC (%)
UFOME 1	0.5	5.045	99.8	88.5	90.7
UFOME 2	0.5	5.023	97.4	91.5	93.8
UFOME 3	0.3	4.988	99.9	93.7	93.1
UFOME 4	0.5	4.551	99.1	96.2	95.6
FAME**	–	4.267	–	–	100

*AV of UFO after pretreatment, ** standard FAME - distilled FAME made from fresh rapeseed oil, EC – ester content

Figure 3 shows a GPC chromatogram of four UFOME samples from Table 1 and a chromatogram of the FAME standard. UFOME chromatograms, too, demonstrate two further peaks for UFOME dimer and trimer. The record obtained for the standard sample has only one peak for monomer methyl esters. According to GLC as well as GPC, none of the UFOME presented has EC over the required value of 96.5 %.

Figure 3 also features a chromatogram of UFOME 2 distillation residue, constituting 5 % by weight of the input amount. Three peaks account for monomer, dimer and trimer methyl esters. Distillation residue chromatogram peaks overlap the peaks of the UFOME chromatogram.

Figure 4 presents GPC chromatograms of the above-mentioned distillation residue and methyl esters of dimeric fatty acids (diFA). The dimers were prepared by esterification

of diFA with MeOH. diFA contain a small portion of trimers, which is confirmed by the elimination curve shape.
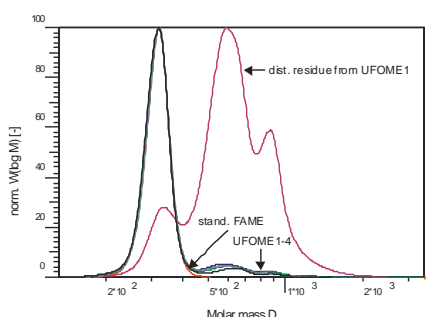

Figure 3: GPC of four UFOME from Table 1 (UFOME 1 – UFOME 4), for standard FAME and for distillation residue (5 %) of UFOME 1
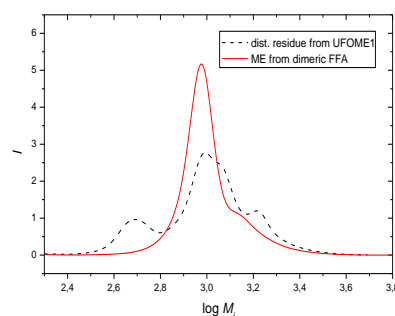
Figure 4: GPC of distillation residue from UFOME 1 (5 %) and synthetic methyl esters from dimeric fatty acids

UFOME final treatment based on vacuum distillation in wiped-film evaporator represents system approach by solving the problem of oligomers in UFOME. It is clear, that the molecules of dimeric UFOME with double molar mass compared to that of monomeric (cca 300 resp. 600 g mol^{-1}) remain in distillation residue and do not enter the distillate. The presence of oligomers in common UFOME is also indicated by different viscosity of distilled and undistilled UFOME as well as by lower EC according to GLC. Viscosities of selected UFOME are as follows: for UFOME 2 distilled 4.501 mm^2 s^{-1} and undistilled 5.023 mm^2 s^{-1} at 40 °C, for UFOME 3 distilled 4.398 and undistilled 4.988 mm^2 s^{-1}.

Distillation of FAME solves several problems at the same time (Cvengroš and Cvengrošová, 1994). The conversion of AG to FAME stops to be the key problem because di- and triacylglycerols with negligible volatility stay in the residue, the distillate are neutral FAME as the free fatty acids are bound in the form of undistillable soaps, the water content of the distillate is practically zero, ash content is also equal to zero, the process is simpler and various cleaning methods (extraction, washing, filtration, centrifugation, drying, chemical treatment, etc.) can be omitted, the distillation is economically more efficient. It is necessary to pay attention to the effective separation of free glycerol in the raw FAME, as the rate of glycerol evaporation is comparable with that of FAME, and they distill together.

4. Conclusion

GPC study of UFO and UFOME has shown that both substances contain oligomers, which reduce the ester content below the required level in UFOME even when the conversion of AG to FAME is high. An efficient way for elimination of oligomers from UFOME is their final treatment based on UFOME distillation in a film evaporator. GLC allows obtaining information about oligomeric content. Naturally, GLC cannot provide information on the oligmeric content in UFO without UFO being transformed to

UFOME. Such information should be valuable in the screening of suitable or unsuitable UFO. For this purpose it will be necessary to use also other methods alongside the GPC, particularly spectral methods.

Acknowledgement

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