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Standard methyl esters from used frying oils

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HIGHLIGHTS

- UFOME (fatty acid methyl esters from used frying oils) show deficient ester content.
- Low ester content is linked with the presence of oligomers in used frying oils (UFO).
- UFO pretreatment by supercritical CO_2 extraction shows low separation efficiency.
- UFOME final treatment in film evaporator assures high quality of UFOME.
- GPC and NIR/MID are appropriate methods for UFO/UFOME quality study.

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ABSTRACT

Used frying oils (UFO) are an interesting and important source material for manufacturing of methyl esters (ME) as alternative fuels. The technology of methyl ester preparation from UFO (abbreviated as UFOME) is similar as in the case of fresh oils. However, in spite of a high degree of acylglycerol conversion into methyl esters, UFOME frequently exhibit insufficient methyl ester content, increased viscosity and density, reduced oxidation stability, increased carbon residue value, etc. Low ester content is related especially to the formation and presence of oligomeric products that result from reactions involving double bonds in acyls. A method suitable for studying changes in UFO and UFOME composition is NIR/MID spectroscopy, particularly bands at 2880 or 2930 nm. Out of 31 UFOME samples subject to evaluation, 16 samples with insufficient ester content of less than 96.5% had absorbance values above 1.80 at 2880 nm. On the other hand, all the remaining 15 samples with sufficient ester content above 96.5% after transesterification had absorbance values up to 1.80 at 2880 nm. Distillation treatment of UFOME samples with insufficient ester content gave rise to UFOME having ester content in line with the EN 14 214 standard. While distillation can be used to treat UFOME in order to obtain standard quality, no treatment at the UFO level is feasible for the time being. UFO extraction with supercritical CO_2 can be applied to achieve monomeric and oligomeric UFO separation, but the separation yield and grade are low and investment and operating costs excessively high.

1. Introduction

Sustainable alternative fuels have recently become a high priority in many countries and will play a large role in the industry and traffic also in the near future. Fatty acid methyl esters (FAME) are one of these sustainable fuels based on non-petroleum sources derived from either transesterification of triacylglycerols (TAG) or esterification of free fatty acids (FFA) with methanol (MeOH). FAME have many advantages, such as low emissions and non-toxicity, possess good lubricity, exhibit higher cetane number, contain no aromatics and consist of about 10% of oxygen by mass. These properties reduce CO emissions, hydrocarbons and particular matter in exhaust gases. Despite this FAME have not become a worldwide popular alternative fuels due to their high cost when compared with fossil diesel. A major obstacle to their commercialization is non-availability of raw material, competition with food and fodder production and its high price, which in the case of FAME amounts to 70–95% of the total cost [1–4]. There are several solutions available for handling the issue of high-priced inputs. A primary solution in this regard is focusing on cheaper sources of

Abbreviations: AG, acylglycerol; AV, acid value; DAG, diacylglycerols; EC, ester content; FAME, fatty acid methyl esters; FFA, free fatty acids; G, glycerol; GC, gas chromatography; GP, glycerol phase; GPC, gel permeation chromatography; HMWC, high molecular weight compounds; LMWC, low molecular weight compounds; MAG, monoacylglycerols; ME, methyl esters; NIR, near infrared spectroscopy; MID, middle infrared spectroscopy; OL, organic layer; PV, peroxy value; TAG, triacylglycerols; THF, tetrahydrofuran; UFO, used frying oils; UFOME, methyl esters made from UFO; W/F, the share of distillation residue from the feed.

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oils and fats, such as non-edible oils, oils with increased acid content and used oils/fats.

One category of used frying oils and fats (UFO) known also as used cooking oils (UCO) is found in large quantities in the industrial-scale process of meals and fast-food products preparation by frying. Processes taking place in oil/fat during frying are well known and have been described [4–9]. Degradation of hydroperoxides gives rise to saturated and unsaturated aldehydes, ketones, hydrocarbons, lactones, alcohols, acids and esters. Most of these products, e.g. dimeric and polymeric acids, dimeric acylglycerols and polyglycerols, remain in the oil/fat as products of radical reactions, increasing the frying oil/fat viscosity. Other products are subjected to further degradation via alkoxy radicals to volatile polar substances, such as hydroxy and epoxy acids, which, in turn, are released from the oil. Chemical changes occurring in the oil during frying result in an increased oil viscosity and free fatty acid content, color change, iodine number drop, change in refraction and the oil's increased foaming property. It is inevitable to thoroughly monitor frying oil quality in order to maintain an appropriate quality of oil and fried foods [10].

UFO quantities are relatively large and require a systemic solution. The potential estimated UFO quantity to be obtained from salvage worldwide is currently about 15 million tons a year [2]. Another piece of information, one that may prove useful for calculations, is 5 kg of UFO amount per inhabitant per year [11]. In the past, UFO were used as an admixture in compound feeds for livestock [12]. Harmful substances thus returned to the food chain via animal meat. 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 [1,2,13,14]. Consequently diesel fuel preparation emerges as an alternative use of UFO and owing to their low prices as compared to those of original fresh vegetable oils and animal fats; they become an interesting article with considerable potential. Incidentally, the oft-emphasized fact of lower UFO prices in comparison with fresh oils has been questioned recently. EU biofuel support measures under preparation stipulating that the quantity of second-generation biocomponents shall be multiplied by a factor of 2 when counted towards the biocomponent content in blended fuels have lead to various speculative actions. Thus, at present, the UFO price is somewhere higher than that of fresh oils/fats, which, by definition, will not be classified as second-generation biofuels.

UFO and UFOME as potentially alternative fuels have been treated in detail especially in a number of review articles [1,2,7,15–19]. The detailed reference list is focused particularly on the high degree of similarity in the preparation, properties and use of UFOME and FAME derived from pure oils/fats. The technology of FAME production from UFO is essentially the same as standard methyl ester (ME) production from fresh vegetable oils or animal fats [14]. Following UFO processing, involving, in particular, elimination of solids (food residues), acidity reduction and drying, classic transesterification and final treatment of raw FAME is carried out as in the case of fresh oils [1,13,15,20]. Various aspects have been described in this regard: sources, their quality and pretreatment, catalysts, reaction conditions, conversions, yields, final treatment as well as performance and emission characteristics. While fresh oils and fats usually meet the requirement for low acidity and low water content, this is not always the case with UFO. At present, however, there is no known UFO parameter(s) allowing us to decide whether future UFOME will be compliant with the EN 14 214 standard.

Despite a great degree of similarity between FAME and UFOME, the UFO/UFOME is an indefinable system of feedstock oils/fats additionally affected by chemical changes going back to its prehistory. However, previous experience with UFOME production indicates that chemical changes taking place in vegetable oils and animal fats during frying are so extensive that in some cases they restrain or even preclude the utilization of UFO for the preparation of UFOME to be used as fuel. UFO contain products of oxidation, hydration, degradation and polymerization processes. UFO are thus affected by their prehistory, and common FAME preparation procedures do not always yield standard FAME products. However, in spite of a high degree of acylglycerol conversion into methyl esters, UFOME exhibit increased viscosity, reduced oxidation stability, increased carbon residue value, etc. Moreover, the situation has changed after 2003 when a new parameter, methyl ester content subject to a minimum limit of 96.5%, was introduced in the EN 14 214 standard. Subsequently it was discovered that a considerable portion of UFOME production failed to comply with this parameter [21,22]. This has been attributed to the presence of polar substances and oligomeric (polymeric) structures [11,16,17,24]. To deacidify input UFO, which usually have increased acidity, a two-stage process is mostly used comprising acid-catalyzed esterification followed by alkali-catalyzed transesterification with methanol [1,13,15,17,25,26], providing an advantage of methanol esterification carried out at elevated temperature of about 120 °C and atmospheric pressure [27]. Vacuum distillation to remove FFA [14,15,26] and extraction pretreatment [23] have also been reported in this respect. UFOME final treatment procedures include silica gel adsorption, water-diluted acid washing and water washing [3,28]. While adsorption and extraction are effective to reduce acidity, peroxide number and methanol and glycerol content, their effects on the reduction of viscosity and density and on the increase of ester content is negligible [3,17]. On the other hand, UFOME final treatment using vacuum distillation of raw esters is a highly effective approach, yielding a high-quality product [8,14,15,17,26]. A whole range of procedures based particularly on spectral and chromatographic methods has been developed to evaluate the deep fryer's oil batch degradation. As regards chromatography procedures, it is GPC (HPSEC) that is mostly used [15,17,29–33]; among spectral methods NIR spectroscopy prevails [15,17,34–38]. Apart from other things, the NIR technique is also used for the determination of polar substance content in the region 4700–4940 cm^{-1} [34], and water and methanol content at 1000–4500 cm^{-1} [39]. As UFO quality evaluation criteria, particularly as regards termination of their use as frying oils, polymeric TAG content according to [40] and polar substance content [41] are used. The content of polymeric substances should not exceed 12% by weight, the content of polar substances 24% by weight [10,42].

The options for UFO treatment before esterification or transesterification to be carried out in order to eliminate polar substances and oligomers are limited. Commercial adsorption composites based on active coal, alumina, clay, silica gel, frypowder (rhyolite, citric acid, and water) and magnesol (magnesium silicate) preparations [43,44] do not adjust UFO viscosity and are rather suited for maintenance of deep fryer's oil. Supercritical CO_2 extraction of UFO intended to eliminate oxidized low-molecular weight products as well as oligomers has been described in [5] and UFO extraction with supercritical ethane in [42].

UFOME are used in standard diesel engines without engine conversion as alternative fuels from renewable sources, usually blended with fossil diesel [2]. If they meet quality parameters stipulated in the EN 14 214 standard, their performance and emission characteristics are similar to those of FAME obtained from fresh oils [16].

The objective of the present work is to design a method for evaluating UFO or UFOME quality based on the quality of final methyl esters expressed in terms of ester content as well as designing a method for UFO or UFOME treatment that would guarantee final UFOME parameters compliant with the EN 14 214 standard.