FLUORESCENCE SPECTROSCOPY INVESTIGATION OF DEGRADATION OF RAPESEED OIL METHYL ESTERS

RAPŠU EĻĻAS METILESTERU DEGRADĀCIJAS FLUORESCENCES SPEKTROSKOPIJAS PĒTĪJUMI

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Key words: biodiesel, degradation, fluorescence spectroscopy

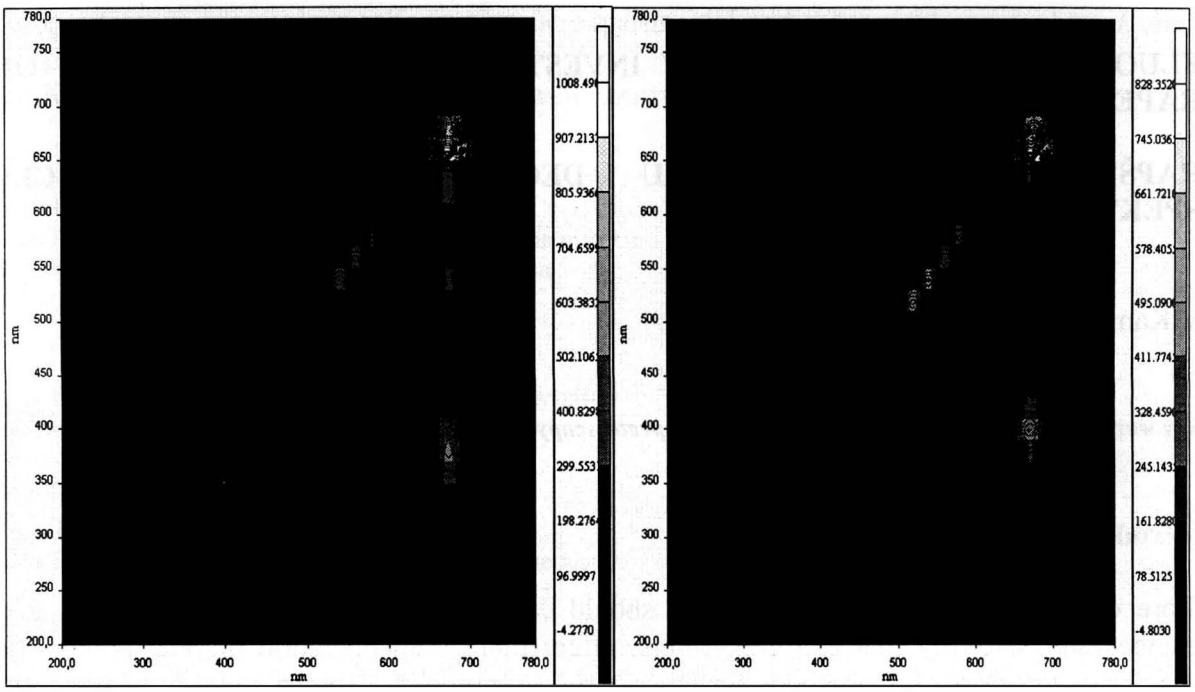
Introduction

Store of biodiesel for prolonged period should cause formation of sediments, boost acid number and viscosity that can clog filters, affect fuel pump operation or plug combustor nozzles or injectors. Test methods for laboratory estimation the storage stability of biodiesel are being developed. The measurements of acid number and viscosity by determined time, temperature and other experimental conditions appear promising. However, correlation of such test results with actual storage stability will be difficult therefore monitoring a quality of bulk fuel during prolonged storage and real plan to replace aged fuel with fresh product seems to be a better solution of the problem. In order to realize such monitoring stored fuel should be periodically sampled and its quality assessed by a fast and effective measurement. In this paper we investigate the possibility of application the fluorescence spectroscopy for this purpose. Fluorescence measurements are used in fuel analysis for example for the determination of sulfur content [1]. In spite of non extensive putting into practice the fluorescence spectroscopy should be one of the most promising techniques for fast and complex fuel analysis because enhanced selectivity and high sensitivity. Several forms of fluorescence spectroscopy – conventional, total luminescence and synchronous scanning fluorescence may be effective for this purpose.

Results and Discussion

In order to achieve a rapid biodiesel degradation samples were heated at 200 and 250 ^{o}C respectively. Three dimensional contour maps of total luminescence spectra of biodiesel before heating and during the heating at 200 ^{o}C are shown in Fig.1. The spectra are constructed in such a way that one axis represents the emission and other the excitation wavelength, while the contours are plotted by linking points of equal fluorescence intensity. As it is evident from this figure the fluorescence characteristics of biodiesel have changed dramatically during the heating. From there total luminescence spectra are very sensitive visual indicator of quality.

As evident from Fig.1 before heating the characteristic and more intensive fluorescence is placed in the region excitation 200-700 nm – emission 200-800 nm.



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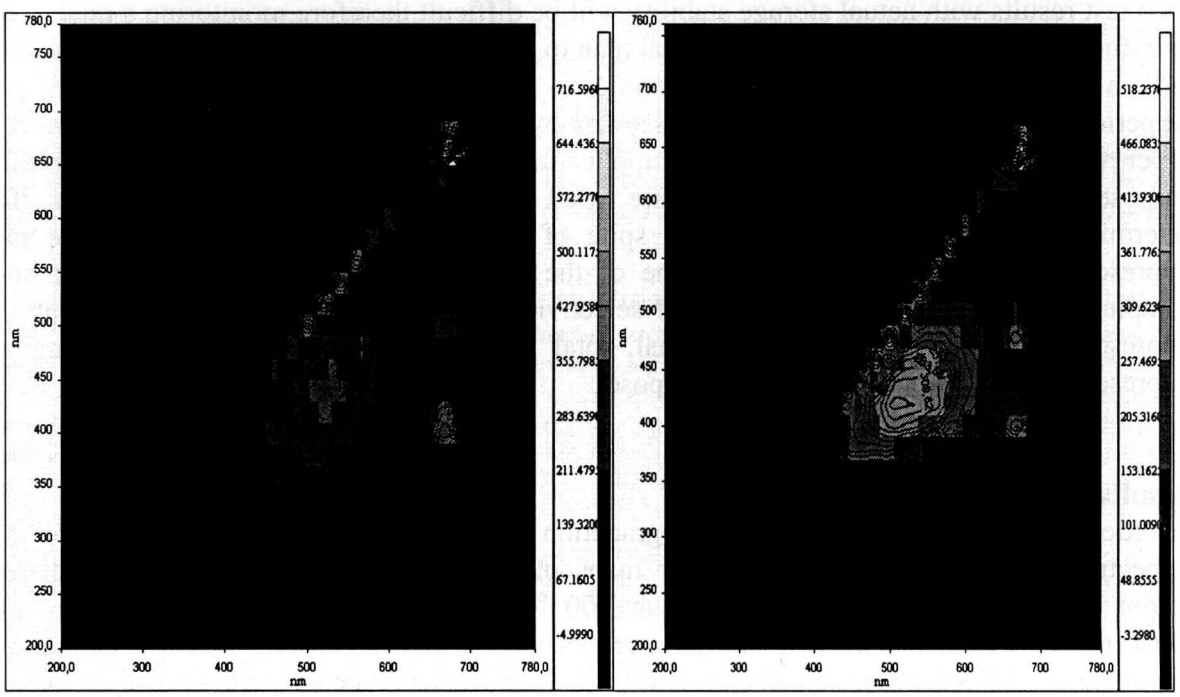

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Fig.1. *Contour maps of total luminescence spectra of biodiesel before heating (0) and during heating at 200 °C (heating time: 1 – 15 minutes, 2 – 30 minutes, and 3 – 60 minutes). Horizontally - emission wavelengths.*

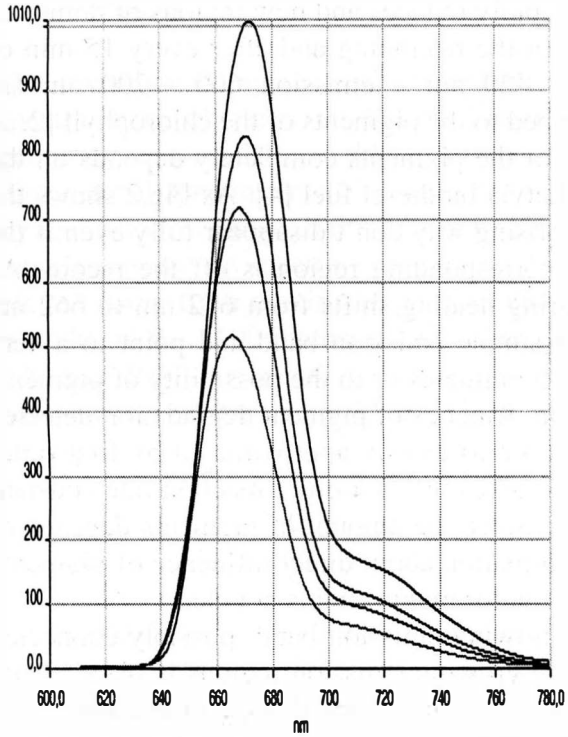

Fig.2. Decrease of long wave emission band during heating of biodiesel. Excitation at 660 nm.

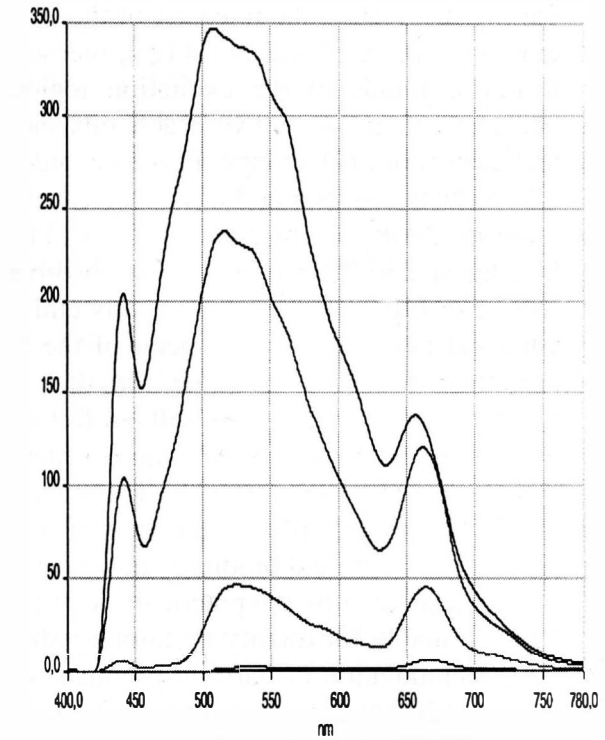

Fig.3. Increase of emission bands during heating of biodiesel in the region 400 – 700 nm. Excitation at 440 nm.

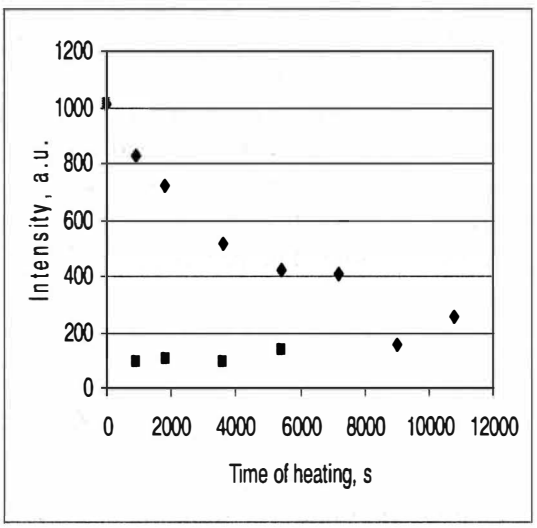

Fig.4. Long wave emission band maxima intensity change during heating of biodiesel. Excitation at 660 nm. ♦ – heating at 200 °C, ■ – heating at 250 °C.

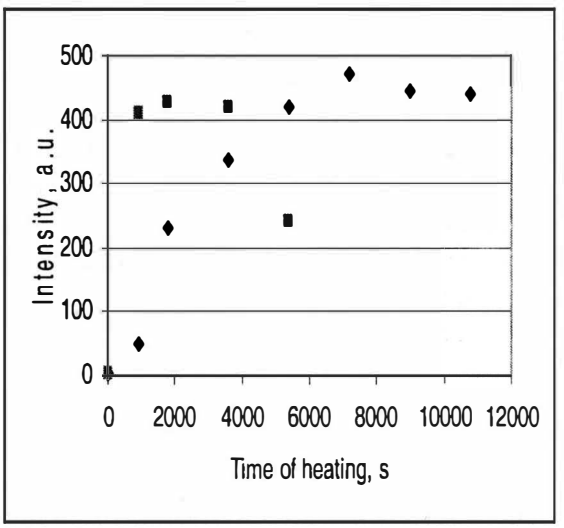

Fig.5. Emission intensity change during heating of biodiesel in the region 400 – 700 nm. Excitation at 440 nm. . ♦ – heating at 200 °C, ■ – heating at 250 °C.

During the heating the intensity of this emission rapidly reduces and new regions of dominate emission appear (Fig.2 and Fig.3, measurements at the beginning and after every 15 min of heating). Bands in the excitation region 350 - 420 nm – emission 660 - 700 nm are characteristic not for all vegetable oils and is ascribed to the pigments of the chlorophyll [2, 3] and carotenoid [4] groups. Presence and amount of the pigments completely depends on the oil products processing, but is characteristic for Latvia biodiesel fuel [4]. As Fig.2 shows the intensity during the heating drops fast, but in surprising way don't disappear fully even if the heating at 250 °C was done and absorbance in corresponding region is off the record. As shown in Fig.2, the maxima of this emission during heating shifts from 672 nm to 662 nm what indicate complex character of the formally simple emission band and point to a very high thermal stability of some from the chlorophyll pigments or to the possibility of pigments to structure reorganizations without full destruction. Kinetics of pigment degradation detected by fluoresce intensity at 670 nm (excitation at 660 nm) can by approximated by first order reaction equation (R^2 = 0,993). This approximation gives the first order reaction rate constant at 200°C k = 8,49 10^{-5} $s^{-1}$and the half-life 3544 s. Since the amount of pigments depends of processing of oil and biodiesel and there isn't information about direct influence of pigments on biodiesel quality, the practical use of this emission for monitoring is not clear.

More valuable for quality monitoring should be growing emission band, possibly connected with accumulation of harmful products. One of the growing emission regions is placed from 400 nm till 700 nm. As shown in Fig.3 the emission during the initial stage of heating grows in all 400-700 nm region, int. al. the band at 662 nm is growing too, what once again point at the complex nature of the long wave emission band. Accordingly to those measurements, formation of molecules with extended π-electron system with pigment like structure and fluorescence band at 662 nm during the heating occur. The growing complex emission in the broad region 400–600 nm (excitation at 440 nm) points to the formation of several molecules with extended π-electron system. During the heating its concentration grow, then reach maxima and than began to decrease. Accordingly to the fluorescence intensity at 517 nm in formation stage there isn't a first order reaction kinetic and rate approximation request an additionally investigations. Simply one can evaluate only the initial rate and time of reaching the maxima. The initial rate and time of reaching the maxima at 200 °C is 0,106 a.u./s and 8000 s and at 300 °C 0,808 a.u./s and 2000 s respectively. The increase of temperature influences the product formation less then the pigment degradation. For practical monitoring only the determination of initial rate of reaction should be valuable. The practical significance of initial rate determination in growing emission regions for biodiesel quality assessment will be a purpose of further investigation.

Conclusions

The fluorescence characteristics of biodiesel during destruction changed dramatically and the total luminescence spectra are very sensitive visual indicator of quality. For practical quantitative monitoring the determination of initial rate of reactions in growing regions of fluorescence should be valuable.

Experimental

The investigated rapeseed oil methyl ester was product of Ltd. "Delta Riga". Fluorescence spectra were obtained on Perkin Elmer luminescence spectrometer LS 45. Right angle geometry was used for undiluted biodiesel samples in a 10 mm fused-quarz cuvette. Three dimensional spectra were obtained by measuring the emission spectra in range 200 - 780 nm by excitation in range 200 - 780 nm, spaced by 10 nm. Three dimensional contour maps of total luminescence spectra were produced using the standard program. All contour maps were plotted using from maxima dependent changing scale range of fluorescence intensities (from 0 - 600 till 0 - 1100 intensity units). For fast degradation the 100 ml biodiesel was heated at 200 and 250 °C respectively in glass vessel in dark using Velp Scientifica Manuals DK 6 equipement. After every 15 or 30 minutes storage at the given temperatures biofuel was sampled.

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Kampars V., Ratyeva S. Fluorescence spectroscopy investigation of degradation of rapeseed oil methylester.
In order to find fast and simple techniques for biodiesel fuel quality monitoring, total luminescence and conventional spectra in region 400-800 nm of biodiesel before heating and during the heating at 200 °C and 250 °C were investigated. The fluorescence characteristics during biodiesel degradation changed dramatically and the total luminescence spectra are very sensitive visual indicator for quality. In the long wave region not only degradation of pigments, but also formation of pigment-like substances were observed. For practical

quantitative monitoring the determination of initial rate of reactions in growing regions of fluorescence should be valuable.

V. Kampars, S. Rajeva. Rapšu eļļas metilesteru degradācijas fluorescences spektroskopijas pētījumi.
Lai atrastu ātru un vienkāršu biodīzeļdegvielas kvalitātes monitoringa tehniku, pētīti biodīzeļdegvielas totālās luminiscences un konvencionālie spektri 400-800 nm rajonā pirms un karsēšanas laikā pie 200 un 250 °C. Fluorescences raksturojumi biodīzeļdegvielas degradācijas laikā mainās būtiski un totālās luminescences spektri ir ļoti jūtīgs un uzskatāms kvalitātes indikators. Garo viļņu rajonā novēro ne tikai pigmentu degradāciju, bet arī pigmentiem līdzīgu savienojumu veidošanos. Praktiskam kvantitatīvam monitoringam visvairāk piemērota liekas reakcijas sākuma ātrumu noteikšana augošas fluorescences intensitātes rajonos.

Кампар В., Ратьева С. Исследование деградации метиловых эфиров рапсового масла методом флуоресцентной спектроскопии.
С целью разработки быстрого и эффективного метода мониторинга качества биодизельного топлива были изучены обычные и тотальные спектры флуоресценции в диапазоне 400-800 нм перед и в процессе нагревания топлива при 200 ип 250 °С. Установлено, что в процессе нагревания характеристики флуоресценции существенно меняются и тотальные спектры флуоресценции являются чувствительным и наглядным индикатором деградации. В в процессе нагревания в длинноволновом диапазоне налюдается не только разложение натуральных пигментов, но и оброзование пигментоподобных продуктов. Найболее удобным методом получения качественной характеристики стабильности топлива следует считать определение начальной скорости в спектральных областях с возрастающей интенсивностью.