

SPECTROFLUOROMETRIC CHARACTERIZATION OF OIL FROM PYROLYSIS OF SCRAP TIRES

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Abstract

Almost all kinds of fuel applied in combustion engines come from refining industry, in which crude oil serves as basic raw material. However, there are also searched other sources of hydrocarbons which can be used directly or as additives to conventional fuels. The most popular in this regard are vegetable oils such as rapeseed oil, from which are produced esters used as fuel for diesel engines. On the other hand, as additives to gasoline can be used alcohols derived from the fermentation of agricultural products. Another way to obtain liquid hydrocarbons is pyrolysis of scrap tires. In this article, such pyrolytic product is analysed in terms of its fluorescence properties compared to the fluorescent properties of substances derived from the distillation of the pyrolysis product in three following temperatures: 160, 204 and 350 °C. All the tested substances show relatively strong fluorescence in ultraviolet range. Fluorometric spectra were performed applying the spectrofluorometer Hitachi F-7000 FL with 1x1 cm quartz cuvette. Studied substances were previously diluted in n-hexane to obtain concentration 4 ppm. Amount of fluorescent peaks and their positions depends on kind of distillate. Ipso facto fluorescence method seems be suitable much more – than chemical analyse – for quick identification of substances constituting a components of distillate obtained from pyrolytic product.

Keywords: *fuels, used car tires, pyrolysis, fluorescence*

1. Introduction

The main fuels for combustion engines are hydrocarbon mixtures obtained from refining crude oil. In some cases, esters produced from vegetable oil are used as fuel for diesel engines, in other cases alcohols obtained from fermentation of various agriculture products [1] are used as additive to gasoline. Liquid hydrocarbons can be also produced by pyrolysis of tire wastes [2-4]. Main liquid products of such pyrolysis are C₆-C₂₄ organic compounds (mainly aliphatics) and aromatics. The temperature of pyrolysis higher the amount of aromatics with respect to hydrocarbons is greater. Pyrolysis of tires is usually conducted in temperature 300-400°C. For example when temperature 500°C then about 70% of aromatics (the rest – aliphatics) whereas for 300°C – half-and-half [5]. Quantitative distribution of kinds of pyrolytic products depends also on rate (quick or slow) of process [6] There are a lot of detailed technical solutions of the pyrolysis process – the relatively complete review were conducted by Quek and Balasubramanian [7] and Bridgwater [6]. In this article, we test possibility of characterisation of pyrolytic oil and its distillates by fluorescence – which is analytical method more simply, quick and chipper than high-pressure

liquid chromatography (HPLC) and gas chromatography (GC) or gas chromatography with a detector as mass spectrometer (GC-MS).

2. Material and method

Pyrolysis previously cut used car tires was conducted in the reactor in temperature 500°C for 8 h at the oxygen supply cut off. As a result of thermal decomposition of tires, the pyrolysis oil was obtained. Additional products of pyrolysis were pyrolysis gas, unspecified charred residues and steel components of tires. Physico-chemical characteristics of the oil are presented in Tab. 1.

Tab. 1. Physical-chemical properties of pyrolytic oil

Kinematic viscosity at 15 °C [kg/m ³]	0.932
Mass density at 40 °C [mm ² /s]	4.12
Content of sulphur [mg/kg]	1.08
Acid value [mg KOH/g]	4.45
Flash point [°C]	43.0
Oxidative stability [h]	> 20

The pyrolysis oil was subjected to a distillation process in the laboratory set equipped with a cylinder, three-necked flask (fitted with a mercury thermometer and thermocouple) and spherical radiator receptacle. The distillation was carried out in three temperature ranges. Initially, the sample was heated to 160°C to give approx. 4% light naphtha. The pyrolysis oil was then heated to 204°C, which allowed extracting approx. 56% of the medium fraction of naphtha, and in the final stage of the distillation temperature was gradually increased to 350°C, whereby approx. 40% of the heavy fraction was obtained.

Transparency and colour of every distillate is different which shows Fig. 1. Visually intensity of fluorescence in ultraviolet is similar for every distillate, which is shown in the same figure.

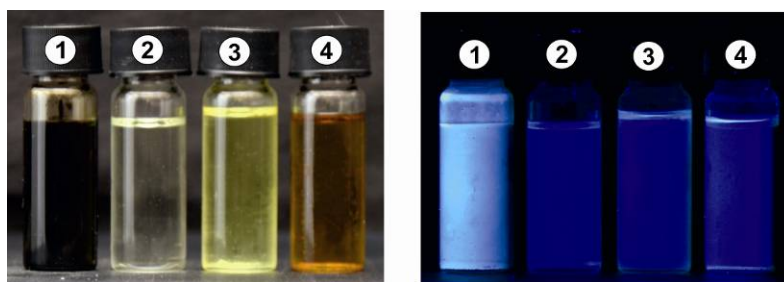


Fig. 1. Samples of pyrolytic oil (1) and distillates: 160 °C (2), 204 °C (3), 350 °C (4) Left: in visual range of light spectrum, right: in ultraviolet lamp lighting

Each sample was diluted in n-hexane to concentration 4 ppm (by weight). Excitation-emission spectra (Seems) were determined using spectrofluorometer *Hitachi F-7000 FL*. The instrument settings: Excitation Start: 200.0 nm, Excitation End: 480.0 nm, Excitation Sampling Interval: 5.0 nm, Emission Start WL: 260.0 nm, Emission End: 700.0 nm, Emission Sampling Interval: 5.0 nm, Scan speed: 1200 nm/min, Excitation Slit: 10.0 nm, Emission Slit: 10.0 nm, Photomultiplier Voltage: 400 V.

3. Results

Numerical form of Seems is a matrix consisted of $89 \times 57 = 5073$ fluorescence intensities (57 excitation wavelengths, 89 emission ones). The resulting matrix is the matrix for the solution

of oil minus the matrix for n-hexane (diluter). Fig. 2 presents visualized matrixes as EEMs in 3D version, every of four in the same scale of fluorescence intensity.

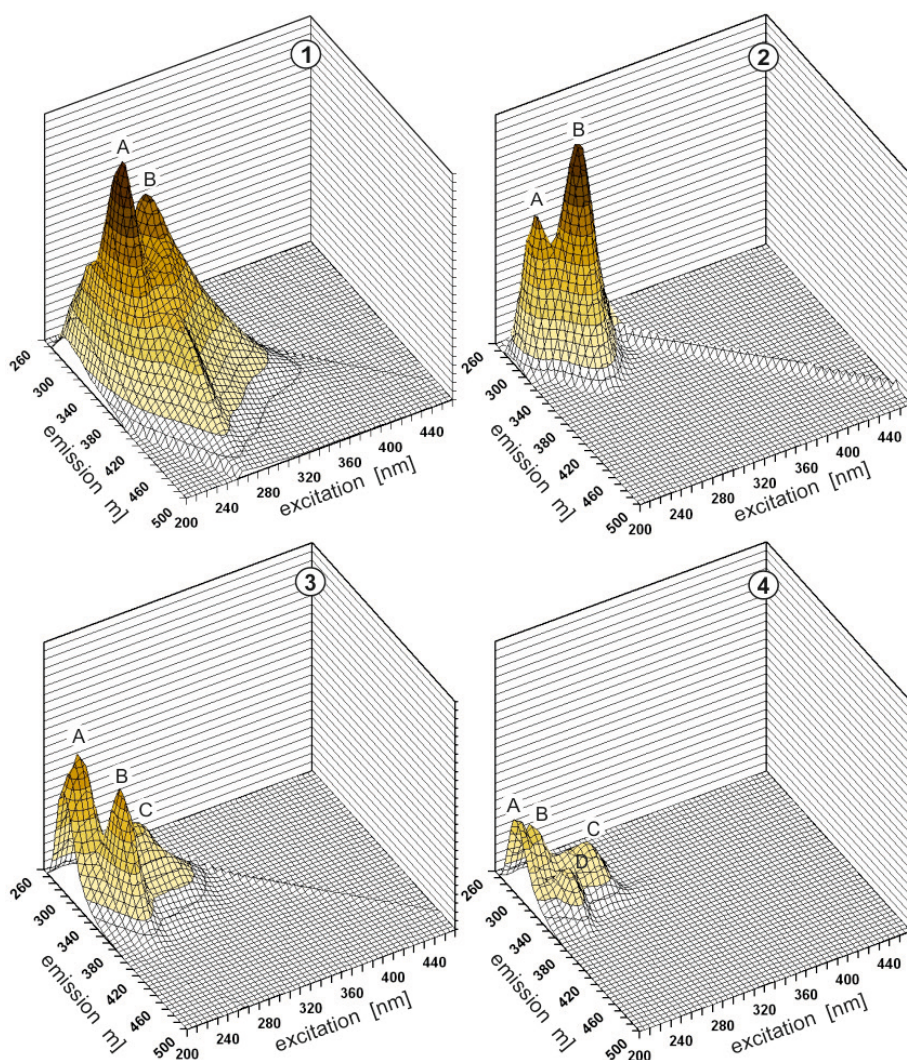


Fig. 2. Excitation-emission spectra of studied oils diluted in n-hexane (4 ppm); every spectrum in the same scale of intensity of fluorescence

The same results as in Fig. 2 are presented in Fig. 3, but as contour chart, furthermore every spectrum is normalised to the maximal peak. In both figures are pointed characteristic fluorescence peaks (by capitals). In fluorescence spectrum for pyrolytic oil, (sample No. 1) only two peaks are clearly visible. Certainly, other peaks exist also, but they are overshadowed by two very intensive peaks. The distillate 160°C is characterised also by two peaks, but they are positioned in other points than for pyrolytic oil. Distillate 204°C has three peaks, whereas distillate 350°C up to four.

4. Discussion

Each analysed sample of oil exhibit fluorescence. Such phenomenon proves that they contain fluorescence centres, which are polycyclic hydrocarbons. Distillates obtained from pyrolytic oil emit similar light in visual range (VIS) if exposed to light from ultraviolet (UV) (Fig. 1). However the vast majority of fluorescence photons are emit in UV. Intensity of fluorescence strongly depends on wavelength in which is analysed as well as on wavelength of light used for excitation of fluorescence.

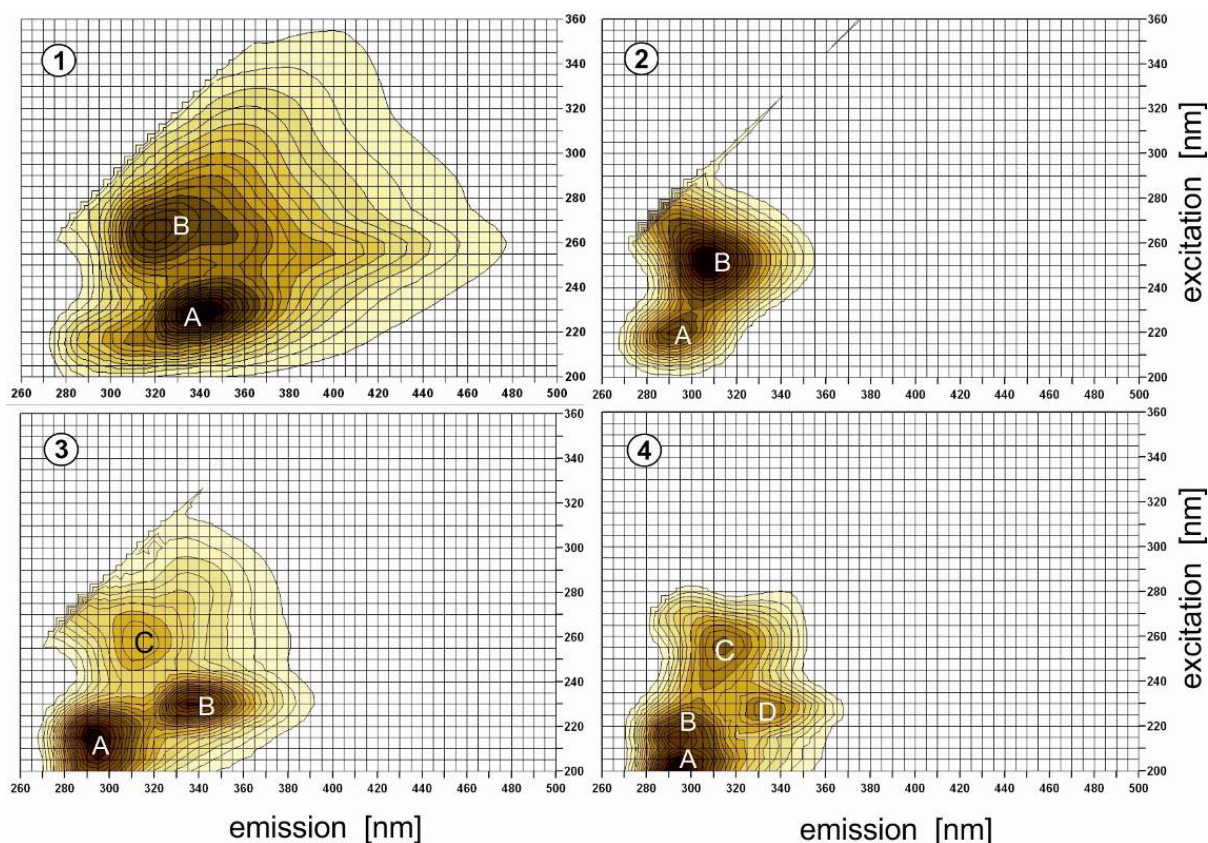


Fig. 3. Excitation-emission spectra for the same samples as in Fig. 2 but normalised to the maximal peak

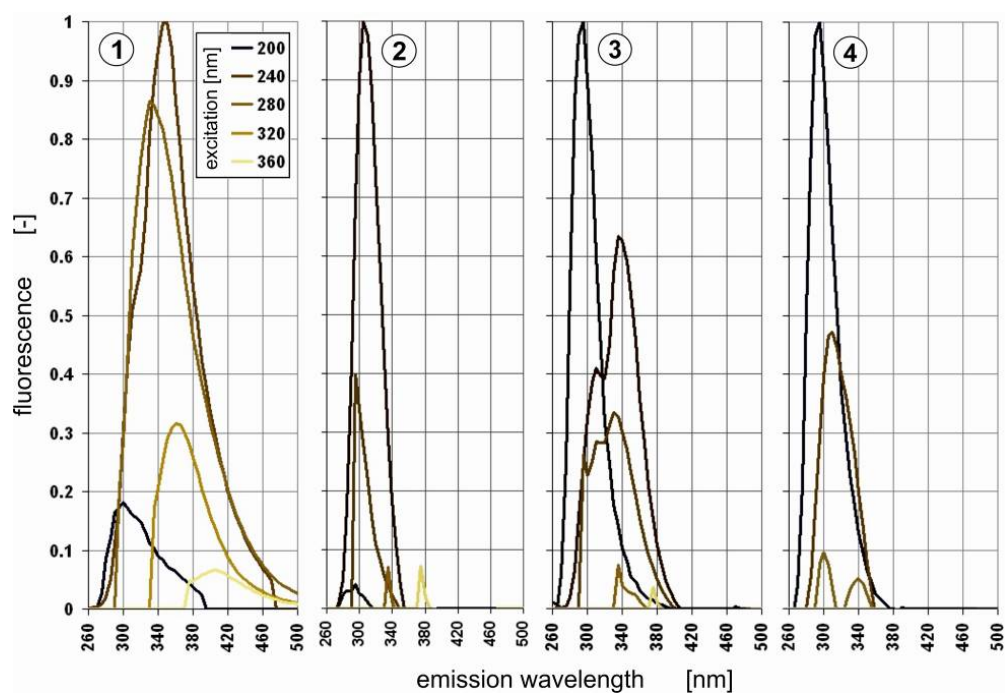


Fig. 4. Fluorescence spectra normalised to maximal value found for defined excitation wavelengths

To illustrate how spectra of fluorescence depends on excitation wavelength, from the matrixes visualised in Fig. 2 and 3 only spectra for 5 different excitation wavelengths were extracted and drawn in Fig. 4. Greatest intensity of fluorescence was observed when sample No. 1 (pyrolytic oil) and sample No. 2 (distillate 160°C) were subjected to excitation for 240 nm, whereas for sample No. 3 (distillate 20°C) and sample No. 4 (distillate 350°C) – for 200 nm.

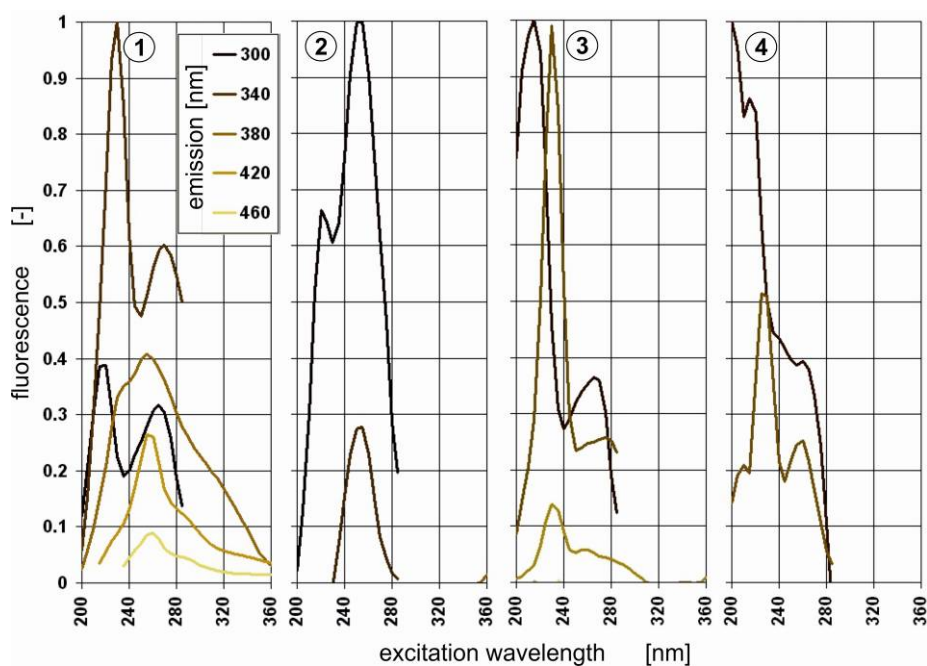


Fig. 5. Excitation spectra normalised to maximal value found for defined emission wavelengths

On the other hand, in order to illustrate how excitation spectra depends on emission wavelength, spectra for 5 different emission wavelengths were extracted and drawn in Fig. 5. It is worth noting that fluorescence can be expected in UV and blue part of VIS for pyrolytic oil, whereas not for distillates. Therefore, in Fig. 1 most intense fluorescence is observed for sample No. 1.

Shapes and positions of peaks of fluorescence spectra of each analysed oils depend on kind and amount of hydrocarbons, which exhibits fluorescence properties. They are mainly polycyclic aromatic hydrocarbons (PAHs) [8]. It should be noticed that the final fluorescence spectrum depends on light absorption processes not only in PAHs, but also in other hydrocarbons. Therefore, the fluorescence spectrum depends on chemical composition of the studied oil. It may be assumed, that temporal changes of oil (due to more or less stability) – in this case in pyrolytic oil and in its refinery products – should result in clearly noticed changes of their fluorescence spectra.

In this article we applied oil concentration in the solvent (n-hexane) extremely low (4 ppm) to maximally eliminate absorption of emitted light is quartz cuvette as well as reemission processes. It is possible, that higher concentration be suitable for other targets, like oil detection and identification of type of oil on the basis of shape of fluorescence or excitation spectra or even on excitation-emission spectra. It is still waiting to be studied.

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