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Determination of sulfur content of diesel fuels and diesel fuel-like fractions of waste polymer cracking

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Abstract

The element content of low and high sulfur containing diesel fuels was measured by different analytical methods: energy-dispersive X-ray fluorescent (EDXRF) and inductively coupled plasma atomic emission (ICP-OES) spectroscopy methods. Then results were compared. High sulfur containing diesel fuels were from heavy diesel engines and diesel fuel-like liquids obtained by thermal degradation of waste polymers. In case of X-ray analysis also the effect of the used thin foils with different chemical compositions (polypropylene, polycarbonate, polyester) on the accuracy was investigated. According to data considerable differences and deterioration of accuracy was observed in the respect of foils in case of both low and high sulfur containing hydrocarbons. Results indicated appropriate correlation between experimental results measured by both two methods, but differences could be observed in the correlation, which could be explained with different ratio of C/H of samples.

Keywords: Energy dispersive X-ray fluorescence spectroscopy; Inductively coupled plasma atomic emission spectroscopy; Sulfur content; Waste plastic degradation

1. Introduction

The concentration of sulfur and its proper determination play an important role regarding fuels and products of petrochemical industry. The problem of appropriate determination of sulfur is important both from environmental and analytical aspects, because some specifications order to the compulsion decrease of the concentration of sulfur (e.g. from 2005 their maximum concentration is 50 mg/kg in fuels in the countries of European Union) [1–3]. Furthermore the reduction of sulfur content generates further analytical problems. On one hand, the development of hydrodesulfurazition processes was quicker than that of qualification standardized methods and instruments. On the other hand, at present there are great ambitions to create the harmony between different methods [4,5].

It is not left out of consideration that there are some part of industrial area, where diesel oils with high sulfur content are allowed and used (e.g. heavy special diesel engines). It means that a suitable technique for the determination of sulfur content in fuels has to possess measuring ability for the analyte in a wide range of concentrations (from the unit of ppm to %). There are numerous spectroscopic techniques to analyze the qualitative and quantitative elemental composition of fuels and lubricants: inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS), flame or graphic furnace atomic absorption spectroscopy (AAS) or by X-ray fluorescent spectrometry (XRFS) [5–14]. Each technique has advantageous properties in terms of analytical figures of merit. The atomic absorption and emission techniques are typically used for analysis of the products of hydrocarbon industry. The ICP technique is a fast analytical method, but needs preliminary sample preparation (e.g. digestion). Whereas the energy dispersive X-ray fluorescent spectrometry is a non-destructive, furthermore cost-effective method of elemental analysis of the samples. According to our experience an ideal analytical technique has to posses quick and easy sample preparation, sample homogeneity, simultaneous multi-element detection capability and naturally appropriate precision, repeatability and reproducibility. Application of EDXRFS to determine the sulfur content of hydrocarbon mix-

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tures obtained by cracking of waste polymers is a new route of analysis.

Nowadays both the consumption and the production of plastics is increasing by 4–5% annually. According to data, the amount of plastic waste was more than 30 Mt only in the European region. The increasing consumption of plastic materials and their wastes could generate considerable environmental problems, because their suitable handling is an also unsolved problem. This is one reason of others that there are numerous ambitions to stimulate the development of recycling and reusing processes of waste polymers. Because of the high rate of their application polyethylene, polypropylene and polystyrene are mainly investigated. These polymers may be subjected to cracking methods where the long carbon chain of polymer are cracked into lighter hydrocarbons with shorter chains, giving a mixture of hydrocarbon gases, liquids and heavier products [15–21]. One possible way for the utilization of products issued from polymer cracking is the application as fuels. The main advantage of such fuel-like fractions is the low sulfur content.

In this work, we studied comparatively the results of different analytical techniques (EDXRFS and ICP-OES) for the assay of commercial high sulfur containing diesel fuels from heavy engines and liquids obtained by thermal cracking of waste polymers.

2. Experimental

2.1. Samples

Diesel fuels with high sulfur content of diesel current generator from Paks Nuclear Power Plant (Hungary) (from the mark of DS-1 to DS-13), and liquid fractions of batch cracking process of waste polymers (polyethylene (CS-1) and mixture of polyethylene and polystyrene (CS-2)) were used. The degradation of plastic waste was carried out in a horizontal tube reactor, which was described in our previous publication [22]. The cracking equipment consisted of three main parts: an extruder, a reactor and a separator. The preheated polymer was driven from the extruder into the reactor, where the polymers were melted and cracked into lighter fragments. These fractions were separated by atmospheric and vacuum distillation to naphtha, diesel fuel, light and heavy oils. The liquid products of the cracking reactions were analyzed by a gas chromatograph and by infrared analysis (SHIMADZU IR-470 Infrared Spectrophotometer). Table 1 shows the main properties of samples.

Table 2
EDXRFS operating conditions

Target	S Ka line
Detector	Si-PIN
Foil	Polycarbonate, polypropylene, polyester
Voltage	6 kV
Current	300 μA
Filter	None
Medium	Helium
Measure time	180 s

According to data significant differences were observed among commercial and experimental samples. Commercial diesel fuels contained only paraffins, olefins and napthens, whereas diesel fuel-like fraction obtained by the cracking of high-density polyethylene and polystyrene contained also aromatics (CS-2).

2.2. Instruments and sample preparation

2.2.1. PHILIPS MiniPal PW 4025/02 energy dispersive X-ray spectrometer

For measurements a non-polarized energy dispersive X-ray fluorescent spectrometer (PHILIPS MiniPal PW 4025/02) was used. The spectrometer powered by PW 4051 MiniPal/MiniMate Software V 2.0A and the software also features an integrated deconvolution function that separates closely spaced peaks in the spectrum that the system would otherwise be unable to resolve. The spectrometer was equipped with a 9 W Rh-side window tube anode and Si-PIN detector. The anode angle was 90° with respect to the central ray. The fluorescent X-rays were detected with a Si-PIN detector with beryllium window, and the raw signal was counted with a counter fitted with 2048 channel. The special de Kat sample holder and thin films (polycarbonate, polypropylene and polyester) were obtained from Philips Analytical B.V. The operating conditions for this experiment are summarized in Table 2. Samples did not need pre-treatment in this case. The part of sample holder was put together and filled with sample then it was analyzed.

2.2.2. GBC Integra XM type ICP spectrometer

The sulphur determination was carried out with a GBC Integra XM type ICP-OES spectrometer (Australia) (Table 3). After performing the background equivalent concentration experiment

Table 1
The main properties of measured liquid fractions

Sample	Density, g/cm^3	*M*, g/mol	Paraffin, %	Olefin, %	Naphten, %	Aromatic, %
DS-1	0.829	224.8	46.1	21.0	32.8	-
DS-2	0.840	216.4	51.5	23.7	24.8	-
DS-3	0.839	225.9	49.6	24.8	25.6	-
DS-4	0.843	219.4	51.5	25.8	22.7	-
DS-5	0.839	220.4	46.1	21.5	32.4	-
DS-6	0.839	227.7	51.5	24.8	23.7	-
CS-1	0.808	234.1	53.7	46.3	-	-
CS-2	0.801	225.9	39.8	36.7	-	23.5