

EXTRACTIVE DEAROMATIZATION AND DESULPHURIZATION OF A DISTILLATE GASOIL CUT WITH DIMETHYLFORMAMIDE

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ABSTRACT

Diesel fuels, whose relative share in fuel production is continuously on the rise due to the tendency towards dieselization of the automotive park, are still among the main polluters of the environment with sulphur dioxides and carcinogenic substances such as polycyclic arene hydrocarbons (PAHs).

Diesel fuels are obtained by blending gasoil components from the atmospheric distillation of crude oil and from secondary processes – mainly fluid catalytic cracking (FCC). Their quality is determined by the type of the crude, and the technology and properties of the different components. The straight run gasoils have better cetane characteristics compared with those from FCC. Their sulphur and arene hydrocarbon contents, however, do not meet the present and future requirements of Bulgarian and EU diesel fuel specifications.

In the present study, the possibilities for lowering the sulphur and arene hydrocarbon content levels in the distillate gasoil cuts by their extraction with a selective solvent – dimethylformamide in one or two stages is investigated.

The degree of purification of the initial sample is estimated from the change of the refraction index and the results from the NMR spectral analysis of the raffinates obtained in a two-stage dearomatization with DMF at a feedstock/solvent ratio of 1:3.

Keywords: diesel fuel, extractive dearomatization and desulphurization.

INTRODUCTION

The production of environmentally compatible diesel fuels requires detailed investigations on the comparison of technologies and properties of the obtained base fuel components, including also the sulphur and arene hydrocarbons content in them.

According to the present requirements for the quality of the diesel fuels in Bulgaria until the end of the year 2006 their sulphur content is limited to 350 ppm and that of polycyclic arene hydrocarbons - to 11 percent. From 01.01.2007 the sulphur should not exceed

50 ppm [1]. Hydrocatalytic processing is presently the basic method for dearomatization and desulphurization of the diesel fractions from atmospheric distillation and secondary processes to the prescribed levels.

In the recent years methods for lowering arene hydrocarbons and sulphur in the middle distillate fractions by extraction with selective solvents that are easily regenerated by rectification, have been rapidly developing. The developed novel extraction technologies could be radically reducing the cost of diesel dearomatization and desulphurization since they do not demand hydrogen and are carried out at atmospheric

pressure, and comparatively low temperatures. Sulphur reduction of road fuels by hydrogenation beyond the 2000 specifications down to 50 ppm increased the annualised costs to EU refineries by 0.8 to 0.9 G•/a. [2]

The studies on the extraction of the undesired components contained in the middle distillate diesel fractions are also of exceptionally great importance for widening the raw materials pool for diesel fuel production. [3]

The selection of extragents and optimum conditions for extraction dearomatization of distillate diesel fractions from Lukoil-Neftochim Bourgas is of particular interest to us since the latter is the major producer of diesel fuels in Bulgaria. For these fractions it has been reported by other authors [4] that in extraction of a Lukoil hydrotreated middle distillate fraction with the selective solvents, methanol, furfural and ethylene glycol the sulphur content can be reduced sevenfold (from 0.2 % to 0.029 %) and the aromatics content threefold (from 27.1 % to 8 %) respectively. Fuel oil from the same producer with sulphur content of 2.4% can be desulphurized to less than 1% sulphur by one stage extraction with dimethylformamide and other solvents. [5]

The aim of this work is to study the capabilities of dimethylformamide for the dearomatization and desulphurization of a non-hydrotreated distillate diesel cut by two stage extraction.

EXPERIMENTAL

A distillate diesel fraction produced in the oil-refinery of Lukoil Neftochim Bourgas and used as a component of the commercial diesel fuels was investigated. The physico-chemical characteristics of this feed stock are presented in Table 1.

For the accomplishment of the set tasks dimethylformamide (DMF, with normal boiling temperature 153°C and density 0.994 g m⁻³) was used for the extraction of the diesel fraction in the one or two steps.

The laboratory extraction of the diesel fraction with the selective solvent was carried out in a glass extractor in which a pre-set temperature was maintained with a thermostat and intense stirring was realized with a glass stirrer.

Table 1. Physico-chemical characteristics of the distillate diesel fraction under study.

Characteristics	Distillate diesel fraction
Density at 15°C, kg m ⁻³	855
Cetane number	55
Cetane index	41
Distillation characteristics, °C	
Initial boiling point	176
50 % recovered	317
90 % recovered	383
95 % recovered	410
End boiling point	420
Content of sulphur, %	2.0
Flash point in open crucible, °C	110
Freezing point, °C	minus 3
Refractive index, n_D^{20}	1.4780

¹H and ¹³C NMR spectra were taken in a deuteriochloroform (DCCl₃) solvent in a cuvette with a diameter of a 5 mm on a NMR spectrometer BRUKER DRX250, operating at 250.13 MHz (¹H) and 62.89 MHz (¹³C). Inverse Gated Decoupling was used for the quantitative determination of the ¹³C atoms in the NMR spectrum under the following conditions: pulse width of 5.6 µs (90°) and a delay between pulses of 3 s.

The NMR spectral analysis was performed according to the method of Schoolery [6] - 0.2 ml of DCCl₃ and 10 mg of chromium acetylacetonate (Cr AcAc) as a relaxation agent, was added to 0.4 ml of each sample.

RESULTS AND DISCUSSION

In the process of extraction of the distillate diesel fractions with DMF, raffinates and extracts are produced. Their yields and refraction coefficients have been determined. The results from the investigation are presented in Table 2.

It has been established that in the one-step extraction best results are achieved at ratios feed stock : solvent = 1 : 2 and 1 : 3. In the two-stage extraction with DMF and ratios of 1 : 2 and 1 : 3 the raffinates

Table 2. Extraction of the diesel fraction with dimethylformamide.

Ratio feed stock : solvent		Temperature, T, °C	Time, min	Stage extraction, Number	Yield, %		Refractive index, n _D ²⁰	
Diesel fraction	DMF				Raffinate	Extract	Raffinate	Extract
1	0.5	90	30	1	83.6	16.4	1.4720	1.5010
1	1	90	30	1	84.3	15.7	1.4710	1.5250
1	2	90	30	1	78.8	21.2	1.4650	1.5060
1	3	120	30	1	69.1	30.9	1.4640	1.5130
1	1	90	30	2	86.8	13.2	1.4670	1.5000
1	2	90	30	2	42.9	57.1	1.4610	1.4730
1	3	120	30	2	41.4	58.6	1.4595	1.4820

Table 3. Sulphur content of the diesel fraction and raffinates in the two-stage extraction with dimethylformamide at ratios of 1 : 2 and 1 : 3.

Variant	Refractive index, n _D ²⁰	Content of sulphur, %
Feed stock	1.4780	2.0
Raffinate, ratio 1 : 2	1.4610	0.68
Raffinate, ratio 1 : 3	1.4595	0.33

Table 4. ¹H and ¹³C NMR analysis of the distillate diesel fraction (176 – 420° C) and raffinate.

	Mol % of Total ¹ H	
	Distillate diesel fraction	Raffinate
% Ar-H	4.7	0.9
% Al-H	95.3	99.1
% Ar-H/Al-H	4.7/95.3 (1:20.3)	0.9/99.1 (1:110)
% α-H	4.9	1.1
% β-H	90.4	97.9
% H on terminal CH ₃	32.9	32.3
% Ar-C	14.5	2.7
% Al-C	85.5	97.3
Ar-C/Al-C (mol % of total C)	14.5/85.5 (1:5.9)	2.7/97.3 (1:36.0)
Ar-H/Ar-C	1/3.1	1/3.0
Al-H/Al-C	1.11/1	0.98/1
Factor of aromaticity, Fa	0.14	0.03

obtained display the lowest refractive coefficient. The sulphur content of these samples has been determined by X-ray fluorescent analysis on a LAB-X3000 device. The results are presented in Table 3.

Table 3 shows that the sulphur content has diminished by about 3 times in raffinate No. 1 and by about 6 times in raffinate No. 2.

NMR spectral analysis has been performed of the feed stock under study and of the raffinate from the two-stage extraction dearomatization of the diesel fraction with DMF at ratio of 1 : 3.

The proton (¹H) NMR spectra were divided into regions of interest based upon the chemical shifts of specific proton types. These areas were as follows: H_{dar}, ¹H of condensed di- and polyarene rings (δ 7.2 – 9.0); H_{mar}, ¹H of monoarene rings (δ 6.0 – 7.2); H_α, ¹H on carbons α-position to aromatic system (δ 2.1 – 4.0); H_β, ¹H on 2° and 3° carbons in aliphatic chains and naphthene rings (δ 1.1 – 2.1); and H_γ, ¹H on 1° methyl groups (δ 0.2 – 1.1). [7]

The carbon ¹³C NMR spectra were divided into regions of interest based upon the chemical shifts of arene-, aliphatic- and naphthene carbons: C_{ar}, C in arene rings (δ 100 - 170) and C_{al}, C in aliphatic chains and naphthenic rings (δ 0 – 70). Knowing the integral intensities of the signals in the ranges under observation the factor of aromaticity of the investigated product can be easily cal-

culated with a method described in [8].

From the data of the ^1H and ^{13}C NMR-spectral analysis of the feed stock and that of the raffinate, obtained by the two-stage extraction with DMF at ratio 1:3, additional structural characteristics have been calculated as suggested in [7]. The results are presented in Table 4. The data presented clearly demonstrate that the amount of protons in arene hydrocarbons (% Ar-H) decreases about 5 times. The number of the hydrogen atoms from substitutes at the α -position as opposed to the arene rings in the feed stock is greater than that in the raffinate by 4.5 times. The number of the β -hydrogen atoms and those from the terminal CH_3 -groups remains comparatively unchanged. The factor of aromaticity (Fa) has also undergone a 5-fold decrease. The ^1H and ^{13}C NMR-spectral analysis confirms the good effect in the raffinate obtained in the two-stage extraction dearomatization of the distillate diesel fraction with DMF at a feed stock / solvent ratio of 1 : 3. The protons in the arene hydrocarbons and the factor of aromaticity are five times lower.

CONCLUSIONS

By two-stage extraction with DMF, the initial sulphur content of the distillate diesel fraction at ratios of feed stock / solvent of 1 : 3 can be lowered from 2.0% down to 0.33% sulphur.

In the raffinates the content of the arene hydrocarbons is also decreased. The raffinate obtained in the

two-stage extraction at a feed stock / solvent ratio of 1 : 3 has five times lower content of arene hydrocarbons.

Increasing desulphurization and dearomatization levels by using two-steps extraction and by increasing feed stock / solvent ratio leads to lower raffinate yields.

The results obtained from ^{13}C NMR-spectral analysis are in accord with those from the ^1H NMR – investigation, which gives us grounds to further use NMR analysis in our studies.

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