Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc

Petroleum & Coal 46 (2), 13-18, 2004

EXTRACTION APPROACH FOR DESULPHURIZATION AND DEAROMATIZATION OF MIDDLE DISTILLATES

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Received 3 August 2004;received in revised form 4 November 2004; accepted xx November 2004

Abstract

Reduction of sulphur content in diesel to near zero levels plays a significant role for improving air quality. Hydrodesulphurization is the most developed desulphurization technology today. However meeting the 10 ppm sulphur limit in the diesel fuel requires expensive revamps of the existing hydrotreating units or building of new grass root units. This specification also necessitates running the units at higher severity which is related to higher energy consumption and higher amount of emissions of CO_2 release in the atmosphere. Extraction of sulphur and aromatic compounds from the middle distillates offers another opportunity for desulphurization and dearomatization of diesel fractions at low temperatures without participation of hydrogen. This process allows a substantial reduction in the energy consumption. It was found in this study that by extraction of heating gas oil and hydrotreated diesel with the selective solvents, methanol, furfural, and ethylene glycol the sulphur content could be reduced sevenfold and the aromatics content threefold respectively. The extraction of the sulphur compounds from the hydrotreated diesel was about 40% more efficient than that of the heating gas oil, while the extraction of the aromatics from the hydrotreated diesel was twice as high as that from the heating gas oil. This indicates that the chemical nature of the middle distillate fractions plays a significant role on the efficiency of the extraction process.

Key words: extraction, desulphurization, dearomatization, diesel

Introduction

Sulphur compounds and aromatic hydrocarbons containing in diesel fuels are the main contributors to air pollution during the fuel combustion in the diesel engines. The sulphur compounds form sulphur oxides (SOx) while the aromatic hydrocarbons contribute to formation of nitrogen oxides (NOx) and soot particles known as particulate matter (PM). These cause acidification and impair human health.

In order to improve the air quality and the environment the European parliament approved Directive 2003/17/EC where the limit of sulphur content in petrol and in diesel was set 10 ppm coming in force since

01.01.2009 with an interim limit of 50 ppm effective as from 01.01.2005.

Attainment of these ultra low levels of sulphur in the motor fuels is a big challenge for the modern refining. Among the desulphurization technologies available today the hydrodesulphurization is the most developed. Unfortunately the ultra deep hydrodesulphurization of middle distillates require units operating at higher pressures, higher severity, higher catalyst activity, bigger catalyst volume, new reactor internals, and advanced process control [1]. All the lot substantially increases the costs of oil refining and also increases the emissions of CO_2 release in the atmosphere. This justifies the search of alternative approaches for desulphurization of middle distillates.

The aim of this work is to investigate the feasibility of desulphurization and dearomatization of middle distillates by extraction with selective solvents.

Experimental

Two distinct middle distillate fractions (heating gas oil and hydrotreated diesel), with properties given in Table 1, have been used for the extraction experiments. The selective solvents, methanol, furfural, and ethylene glycol (Merck-Schuchardt) were used as purchased. The solvents have been selected on the basis of literature data and commercial application. The procedure of the extraction experiments is described in [2].

Table1 Physico-chemical properties of middle distillate fraction under study

Properties	Heating gas oil	Hydrotreated Diesel
Distilation properties (^{0}C)		
Initial boiling point	257	222
10% recovered	290	244
30% recovered	307	262
50% recovered	316	289
70% recovered	327	315
90% recovered	360	360
End boiling point	390	375
Refractive index n_d^{20}	1.4609	1.4703
Density at 20 ^{0}C (kg/m^3)	862.5	841.4
Viscosity at 20 ^{0}C (mm^2/s)	11.3	5.22
Content (% mass.)		
of aromatics	29.85	27.1
of sulphur	0.47	0.2
Cetane index	56.2	55.5

Results and discussion

The change of sulphur level and aromatics content in both middle distillates after extraction with methanol, furfural, ethylene glycol as well as with 40% NaOH in methanol at different temperatures and feedstock : solvent ratios is illustrated in Tables 2 and 3. It is evident from these data that all used solvents remove sulphur from both feed stocks. Increasing the temperature close to the critical temperature dissolution of the separate systems, the removal process of sulphur containing compounds from the middle distillate fractions through extraction with the solvents studied becomes more efficient. Decreasing the feedstock : solvent ratio also increases the efficiency of the extraction process.

It can be seen that the degree of desulphurization and dearomatization is different for both feeds indicating that the chemical nature of the feedstock plays a significant role on the efficiency of the extraction process. The extraction is more efficient with the hydrotreated diesel, where the sulphur level in the raffinate can be reduced by a factor of 7 and the aromatics content can be reduced by a factor of 3, while with the heating gas oil these values are 5 and 1.6 respectively, under the conditions studied.

Figures 1 and 2 show the relationship between the sulphur and the aromatics content in the raffinates obtained from both feeds. These data indicate stronger relationship between the sulphur and the aromatics content in the raffinates obtained from the hydrotreated diesel than those obtained from the heating gas oil. The slope of the line Aromatics = f (Sulphur) for the hydrotreated diesel is 126.8 against 54.8 for the heating gas oil. Extrapolated values for the aromatics content at 0 % sulphur for the hydrotreated diesel and the heating gas oil are 5.9% and 16.2% respectively. By using these values and those of the aromatic content in the initial feedstocks it can be calculated that 21% of the aromatics in the hydrotreated diesel contain sulphur while in the heating gas oil 13.7% of the aromatics contain sulphur.

These data suggest that in the heating gas oil some part of the sulphur is not an aromatic type. This may be the reason for the lower degree of desulphurization of the heating gas oil. However this can not explain the lower dearomatization degree of the same feed.

The hydrotreated diesel should contain only aromatic type of sulphur because the non-aromatic type of sulphur is easily removed during hydrotreatment. Obviously the solvents used in the study are more selective to the extraction of the aromatic compounds containing in the hydrotreated diesel. Additional investigations are needed to explain the observed phenomenon.

Table 2 Change of the sulphur content (%) and of the aromatics content(%) in the heating gas oil during extraction with selective solvents

Solvent	Temperature, ^0C	Feedstock:Solvent ratio	Raffinate sulphur, %	Raffinate aromatics, %	Raffinate yield, %	Extract yield, %
Methanol	50	1:1	0.25	27	80.1	19.9
		1:2	0.16	20	82.7	17.3
		2:1	0.27	30	72.7	27.3
	30	1:1	0.31	32.1	77.1	22.9
		1:2	0.22	31.4	80.3	19.7
	20	1:1	0.32	35	67.5	32.4
		1:2	0.25	33.8	76.3	23.7
Furfural	60	1:1	0.22	32	77.2	22.8
		1:2	0.11	30	86.3	13.7
		2:1	0.26	31.5	78.6	21.4
	80	1:1	0.18	25	69.1	30.9
		1:2	0.09	20	80.8	19.2
		2:1	0.21	27	78.6	21.4
Ethylene glycol	90	1:1	0.25	27.7	76.5	23.5
		1:2	0.19	19	81.3	18.7
		2:1	0.27	31.8	82.5	17.5
	50	1:1	0.26	33	81.7	18.3
		1:2	0.21	27	87.9	12.1

Table 3 Change of the sulphur content (%) and of the aromatics content(%) in the hydrotreated diesel during extraction with selective solvents

Methanol	50	1:1	0.06	15	87.5	12.6
		1:2	0.035	9	72.4	27.6
		2:1	0.08	20	65.6	34.4
	30	1:1	0.08	17	61.1	38.1
		1:2	0.05	11	93.2	6.8
	20	1:1	0.09	19	73.4	26.6
		1:2	0.06	13	86.5	13.5
Furfural	60	1:1	0.056	14	86.2	13.8
		1:2	0.0302	10	83.4	14.6
		2:1	0.07	16	82.8	17.2
	80	1:1	0.05	13	87.2	12.8
		1:2	0.0288	8	86.9	13.1
		2:1	0.053	15	77.5	22.5
Ethylene glycol	90	1:1	0.07	11	83.4	16.6
		1:2	0.041	9	86.5	13.5
		2:1	0.09	14	84.6	15.4
	50	1:1	0.09	15	77.9	22.1
		1:2	0.05	13	76.8	23.2

Solvent	Temperature, ^{0}C	Feedstock:Solvent ratio	Raffinate sulphur, %	Raffinate aromatics, %	Raffinate yield, %	Extract yield, %
4. 40% NaOH in methanol	90	1:1	0.08	16	80.2	19.8
		1:2	0.05	14	82.8	17.2
		2:1	0.09	17	76.4	23.6
	50	1:1	0.09	17	79.5	20.5
		1:2	0.05	13	80.4	19.6

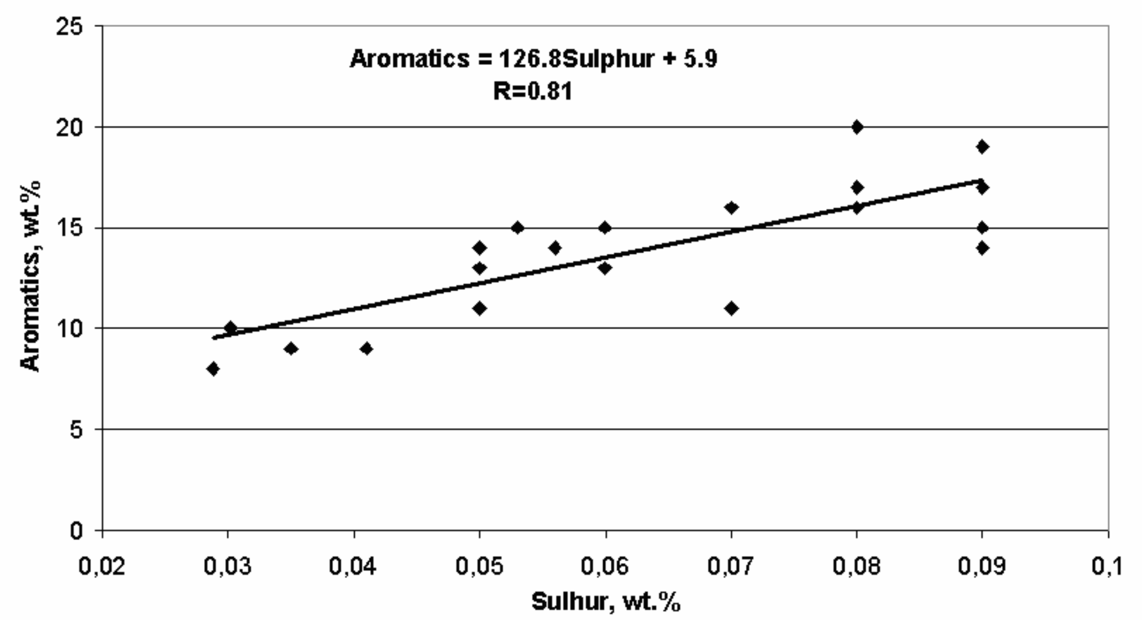

Figure 1 Relationship between sulphur and aromatics in the hydrotreated diesel

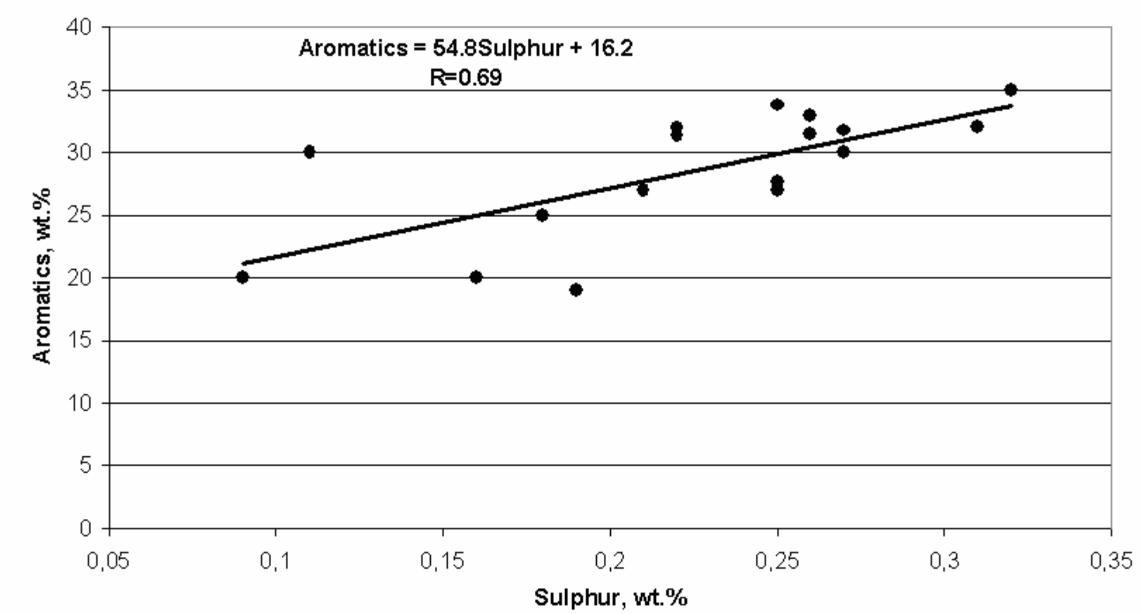

Figure 2 Relationship between sulphur and aromatics in the heating gas oil

Conclusions

The extraction of the heating gas oil and the hydrotreated diesel with methanol, furfural, and ethylene glycol removes the sulphur in the middle distillates.

Increasing the temperature close to the critical temperature dissolution of the separate systems improves the extraction efficiency. Decreasing the feedstock to solvent ratio also improves the efficiency of the extraction process.

Furfural was found to be the most efficient solvent for the studied middle distillate fractions. The degree of desulphurization and of dearomatization of the hydrotreated diesel was higher. Additional investigations are needed to explain the observed difference in the desulphurization and dearomatization degree between both middle distillate fractions.

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