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Extractive purification of hydro-treated gas oil with *N*-methylpyrrolidone

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Abstract: The purification of hydro-treated gas oil by liquid–liquid extraction with *N*-methylpyrrolidone as solvent was studied. The results showed that this method, under appropriate experimental conditions, reduced the sulphur content of the gas oil from 174 to 28 ppm, the nitrogen content was decreased from 58 to 15 ppm, the aromatics content was diminished from 27.1 to 13.8 % and the polycyclic aromatic hydrocarbons were totally extracted. The obtained refined gas oil could be used to produce clean diesel fuel, thus protecting the environment.

Keywords: diesel fuel; desulphurization; denitrification; de-aromatization.

INTRODUCTION

Diesel is extensively used as a fuel both in highway transportation vehicles (*e.g.*, cars, buses and trucks), and non-highway transportation systems (*e.g.*, locomotives, marine vessels, farm equipment, *etc.*).[1–3] Gas oil cuts contain a complex mixture of hydrocarbons having different molecular weights and boiling points, which are mainly composed of paraffins, naphthenes and aromatics together with small amounts of organic sulphur and nitrogen compounds.[1,2,4] The sulphur present in the diesel fuel is a major source of air pollution. During combustion in the diesel engines, the sulphur compounds burn to form harmful sulphur oxides (SO_x) and sulphate particulates, and the nitrogen compounds are oxidized to nitrogen oxides (NO_x).[4] Aromatic hydrocarbons reduce the quality of diesel fuel and increase the emissions of particulate matter and polycyclic aromatic hydrocarbons (PAH).

Many environmental problems and health hazards are caused by exhaust emissions from diesel engines, which contain SO_x, NO_x, CO, CO_2, particulate

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matter and unburned hydrocarbons. For these main reasons, fuels specifications in many countries worldwide reduce the content of sulphur, nitrogen and aromatic hydrocarbons in diesel fuel to lower levels.[5] Hydro-treating is one of the most important processes in petroleum refining; it helps to improve the characteristics of diesel fuel to make it meet the required specifications and pollution standards.

The gas oil hydro-treating process is a catalytic process in which gas oil obtained from either primary distillation of crude oil or conversion processes (visbreaking, coking and catalytic cracking) is treated under hydrogen pressure.[6,7] This process helps obtain a quality diesel fuel with low contents of sulphur, nitrogen and aromatics together with a better stability and a high cetane number.[1,5–7] The performance of gas oil hydro-treaters is affected by operating conditions, such as reactor temperature, liquid hourly space velocity (*LHSV*), hydrogen partial pressure and recycle gas to oil ratio.[1,5] Kinetics studies showed that the rates of hydrogenation of dibenzothiophene, benzothiophene, and thiophene homologues are low,[1,5,8] but they can be increased by increasing the temperature and/or the hydrogen partial pressure and decreasing the space velocity, which leads to large capital investments and high specific power consumption.[1,5] The use of higher operating severity for lowering sulphur levels to ultra low levels in conventional gas oil hydro-treaters have practical limitations related to cycle length, throughput, design pressure, hydrogen availability, thermodynamic equilibrium, *etc*. In view of this, alternative desulphurization methods that do not use hydrogen for catalytic decomposition of organosulphur compounds have been the subject of recent studies.

Oxidative desulphurization (ODS) is a promising technology for the reduction of sulphur at low temperatures (≈50 °C) and atmospheric pressure.[1,9] In ODS, the organic sulphur compounds are oxidized by adding one or two oxygen atoms to the sulphur using appropriate oxidants without breaking any carbon–sulphur bonds, yielding sulphoxides and sulphone, respectively. These oxidized compounds are then extracted or adsorbed due to their increased relative polarity. Thus, the ODS is a two stage process; oxidation, followed by liquid extraction or adsorption.

Desulphurization by adsorption (ADS) is an unconventional process of removing sulphur which is based on the ability of a solid sorbent to selectively adsorb organosulphur compounds from refinery streams.[10] Based on the mechanism of interaction the sulphur compound with the sorbent, ADS could be divided into two groups: desulphurization by physical adsorption and reactive adsorption desulphurization.

Biodesulphurization (BDS) has drawn wide attention recently because of its green processing of fossil fuels, which allows the removal of the sulphur present in organosulphur compounds by bacteria.[1] The process operates in the presence of water and oxygen under mild operating conditions (*i.e.*, at room temperature and pressure) and requires no hydrogen.[9] Several bacterial species have now been identified for BDS; these include *Arthrobacter*, *Brevibacterium*, *Pseudomonas*, *Gordona* and *Rhodococcus* spp.

Extractive desulphurization is based on the fact that organosulphur compounds are more soluble than hydrocarbons in an appropriate solvent.[10] The most attractive feature of the extractive desulphurization is the applicability at low temperature and low pressure. The process does not change the chemical structure of the fuel oil components. As the equipment used is rather conventional without special requirements, the process can be easily integrated into the refinery.[10] To make the process efficient, the solvent must be carefully selected to satisfy a number of requirements. To be recycled, the solvent must have a boiling temperature different to that of the sulphur-containing compounds. It must be inexpensive to ensure economic feasibility of the process.[1] The solvents used for this process can be divided into two categories: conventional organic solvents and ionic liquids.

Studies on extractive refining of non-hydro-treated gas oil cuts with various selective organic solvents and extraction systems have been performed.[11–14] *N*,*N*-Dimethylformamide (DMF), acetonitrile, dimethylacetamide (DMA), methyl cellosolve, tetrahydrofurfuryl alcohol,[13,14] furfuryl alcohol and phenol have been used for the extractive purification of atmospheric distillate gas oil fractions.[15] In extractive refining of atmospheric gas oil, dibenzothiophene derivatives and polycyclic aromatic hydrocarbons, which are the most difficult to remove in hydro-treating, should be extracted most readily.[15] Aromatic components containing nitrogen (carbazole, indole, and quinoline homologous) are even more easily extracted with polar solvents.

At the St. Petersburg State Institute of Technology, *N*-methylpyrrolidone (NMP) was tested for the purification of different types of gas oil.[16] In 2006, atmospheric gas oil was treated with NMP in the presence of undecane and the results showed that the raffinates obtained are promising as diesel fuel components.[17] In 2011, refining of delayed-coking light gas oil using DMF, NMP and phenol with 8 % water as extractants was investigated; the quality of the raffinate obtained in a one stage extraction using water-free NMP was higher than for purification with phenol and DMF.[18] In 2013, a study was conducted on a light visbreaker gas oil, phenol with 10 % water was used as a solvent for the light fraction, and NMP for the heavy fraction. The obtained raffinates could be used to produce ecological diesel fuel.

The aim of this work was to study the capabilities of *N*-methylpyrrolidone for the desulphurization of hydro-treated diesel cut under different experimental conditions. This desulphurization should be accompanied by the de-aromatization and the denitrification of the diesel fraction.

EXPERIMENTAL

N-Methylpyrrolidone (NMP) is a dipolar aprotic solvent having a normal boiling temperature of 202 °C and a density of 1.028 g mL^{-1} at 25 °C. In this study, *N*-methylpyrrolidone from Sigma–Aldrich (purity ≥ 99 %) was used as the extraction solvent. To increase the extraction selectivity and the raffinate yield, some water was added to the NMP. A hydrotreated gas oil fraction was supplied by the Kstovo Oil Refinery (OOO LUKOIL-Nizhegorodnefteorgsintez). The physicochemical properties of this feedstock are presented in Table S-I of the Supplementary material to this paper.

The laboratory purification of the gas oil fraction with NMP was performed in a glass extractor in which a pre-set temperature was maintained with a thermostat and intense stirring was realized with a glass stirrer during 30 min (Fig. 1). Some experiments were performed in a single-stage while other in a five-stage process.[19] The multistage extraction was performed in counterflow following the scheme simulating the operation of an extraction column (Fig. 2). The experimental conditions of the extraction operations are listed in Table I.

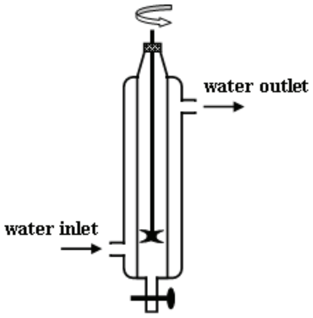

Fig. 1. Glass extractor.

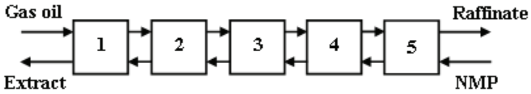

Fig. 2. Five-stage extraction in counter flow.

TABLE I. Experimental conditions of extractive purification of hydro-treated gas oil from the Kstovo Oil Refinery with NMP

Exp. No.	Solvent: feed weight ratio	Water content in NMP, wt. %	Extraction stage	*t* / °C
1	1:1	1	1	40
2	2:1	1	1	40
3	2:1	3	1	40
4	2:1	1	1	60
5	1:1	1	5	40
6	2:1	1	5	40
7	1:1	3	5	40
8	2:1	3	5	40
9	1:1	3	5	60

In the extraction process with NMP, an oil-rich raffinate phase and a solvent-rich extract phase are formed. After decantation, the heavier extract phase collected at the bottom of the extractor was separated. The raffinate was washed with distilled water to remove traces of NMP and then dried with calcium chloride before being analyzed.

RESULTS AND DISCUSSION

The yields of the raffinate and extract obtained in each experiment are given in Table II. The refractive index of these phases was determined by a classic Abbe refractometer at room temperature and the obtained values were adjusted to the standard temperature of 20 °C using the Eq. (1):

$$n_D^{20} = n_D^{T} + 0.00045\,(T - 20\ ^\circ\text{C}) \tag{1}$$

TABLE II. Yields and characteristics of the raffinates and extracts obtained after extractive purification of the hydro-treated gas oil with NMP

Exp No.	Yield[a], wt. %		Refractive index, n_D^{20}		Density at 15 °C	
	Raffinate	Extract	Raffinate	Extract	Raffinate	Extract
1	95.8	4.2	1.4619	1.4902	0.8235	0.9892
2	77.0	23.0	1.4601	1.4760	0.8165	0.9792
3	88.3	11.7	1.4590	1.4823	0.8122	0.9834
4	60.0	40.0	1.4616	1.4734	0.8223	0.9763
5	83.0	17.0	1.4594	1.4791	0.8139	0.9811
6	59.0	41.0	1.4584	1.4746	0.8104	0.9785
7	95.2	4.8	1.4586	1.5027	0.8111	0.9987
8	81.6	18.4	1.4581	1.4798	0.8095	0.9817
9	87.4	12.6	1.4596	1.4809	0.8146	0.9825

[a] For 100 wt. units of feedstock

The density of phases was measured using an electronic densimeter Anton Paar type DMA 48 at 15 °C. In Table II, it could be seem that the refractive index and density for the raffinates and extracts vary with the experimental conditions, indicating the change in their composition. The density of the raffinate phase is governed by the density of the gas oil, whereas the density of the extract phase is governed not only by the density of the solvent, but also by the amount and the type of dissolved hydrocarbons in the solvent. The difference in density between these phases allowed their separation by decantation.

The sulphur content in the raffinates was determined by X-ray fluorescence spectroscopy according to the standard test method ASTM D4294 and the sulphur concentration of the extracts was deduced by material balance. The results are presented in Table III. The degree of sulphur extraction is calculated as the ratio between the weight of sulphur extracted and the initial weight of sulphur in the feedstock.

Interesting results were obtained in experiment No. 8 performed in five stages at 40 °C. The solvent:feed ratio of this experiment was 2:1; the water content in NMP was 3 wt. %. The raffinate was collected with a yield of 81.6 % and its sulphur content was the lowest, 28 ppm. The degree of sulphur extraction in this experiment was 86.9 %.[20] Since the refractive index of aromatic compounds is higher than that of the paraffinic materials, the lower value of the refractive index for raffinate No. 8 indicates the lowest content of aromatic compounds.

TABLE III. Sulphur content of raffinates and extracts obtained after extractive purification of the hydro-treated gas oil with NMP

Exp No.	Sulphur content, wt. ppm		Degree of sulphur extraction, wt. %
	Raffinate	Extract	
1	102	1816	43.8
2	74	509	67.3
3	51	1102	74.1
4	98	288	66.2
5	63	716	69.9
6	32	378	89.1
7	35	2931	80.9
8	28	821	86.9
9	66	923	66.8

Experiment No. 7 could be more economical from the point of view of the process than experiment No. 8. Under the same conditions as extraction No. 8 and with a lower amount of solvent, extraction in experiment No. 7 allowed a raffinate to be obtain with only 7 ppm higher sulphur content than raffinate No. 8, but the yield of raffinate No. 7 (95.2 %) was significantly better than that obtained in experiment No. 8. The energy expended for regeneration of *N*-methylpyrrolidone by distillation in the case of experiment No. 8 would be greater than that used for experiment No. 7. In the extractive purification of gas oil realized according to experiment No. 7, the quantities of fuel and energy lost would be less important compared to those with experiment No. 8.

The Europe-wide regulation for diesel quality (EN 590) limits the sulphur content of diesel fuel to 10 wt. ppm and the maximum content of polycyclic aromatic hydrocarbons tolerated is 8 wt. %. For these reasons, raffinate No. 8 having the lowest sulphur content and the lowest refractive index was selected for further analysis.

Effect of the solvent:feed weight ratio on the desulphurization

The experiments Nos. 1 and 2 are performed under the same conditions with ratios of solvent:feed equal to 1:1 and 2:1, respectively. This increase in the solvent ratio decreased the yield and the sulphur content of the raffinate. The same results were obtained by comparing experiments Nos. 5 and 6, or experiments Nos. 7 and 8.

Effect of the water content in N-*methylpyrrolidone on the desulphurization*

The water contents in NMP used as the extraction solvent in experiments Nos. 5 and 7 were 1 and 3 %, respectively. The increase of this water content increased the yield of raffinate and decreased its sulphur content. The same results are obtained by comparing experiments Nos. 2 and 3, or experiments Nos. 6 and 8. Kumar *et al.*[21] studied the removal of sulphur compounds from straight-run gas oil (SRGO), light cycle oil (LCO) and coker gas oil (CGO) using NMP. The SRGO was obtained from the atmospheric distillation of crude oil; the LCO was produced in the fluidized catalytic cracking process (FCC) of heavy feed and the CGO from the coking process of heavy fractions. The obtained results showed that adding water increased both the yield and sulphur content of raffinates. This different result could be explained by the fact that these gas oils were produced from crude oils of different origins and they were treated by different processes. The composition of these cuts was certainly different from that of the hydro-treated gas oil used in the present study. The effect of water content in NMP on the efficiency of desulphurization depends on the nature of the hydrocarbons contained in the feedstock, in particular with regard to the organosulphur compounds.

Effect of extraction stage number on the desulphurization

The experiments realized in five stages gave raffinates with lower yields and lower sulphur contents compared to the raffinates obtained under the same experimental conditions but with a single stage.

Effect of temperature on the desulphurization

The raffinate of experiment No. 4 performed at 60 °C was collected in a lower yield and with higher sulphur content than the raffinate of experiment No. 2 performed at 40 °C. The same results were obtained by comparing the raffinates of experiments Nos. 9 and 7 realized at 60 and 40 °C, respectively; the increase in temperature decreased the degree of sulphur extraction. Mokhtar *et al.*[22] found the same effect of temperature on the desulphurization of a synthetic gas oil with DMF as solvent. The selected model compounds were thiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene, which are the most difficult sulphur compounds to hydrogenate, and these types of compounds represent the largest proportion of sulphur compounds contained in hydro-treated gas oils. Adzamic *et al.*[23] studied the extractive desulphurization of FCC gasoline with two solvents, sulfolane and furfural, the results showed that an increase of temperature from 50 °C reduced the desulphurization efficiency with sulfolane but had no significant effect on the extractive desulphurization with furfural. In their studies, Kumar *et al.*[20,21] reported that an increase in the extraction temperature increased the degree of sulphur removal and simultaneously decreased the raffinate yield. This result was obtained for the extractive desulphurization of different types of gas oil using DMF, DMA and NMP. The observed results indicate that the impact of temperature on the efficiency of the process is related to the nature of the sulphur compounds present in the feedstock, *i.e.*, the composition and the origin of the petroleum fractions determine the choice of the solvent and the operating parameters of the process.

Denitrification and de-aromatization of the hydro-treated gas oil

The nitrogen contents of the hydro-treated gas oil and the raffinate of experiment No. 8 were determined using a Kjeldahl distillation apparatus according to the standard test method ASTM D3228 and the results are shown by the histogram in Fig. 3. The extraction conditions of experiment No. 8 (Table II) reduced the nitrogen content of the gas oil from 58 to 15 ppm.

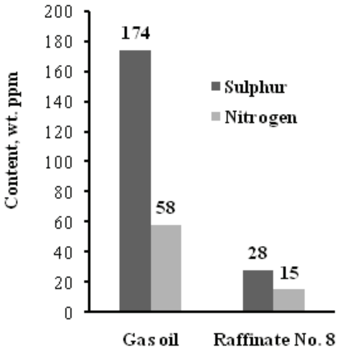

Fig. 3. Sulphur and nitrogen contents in the gas oil and raffinate No. 8.

The hydro-treated gas oil and the raffinate No. 8 were analyzed by high performance liquid chromatography with refractive index detection according to the standard test method ASTM D6591. This analysis determined the total aromatics content and the polycyclic aromatic hydrocarbons (PAH) content of these samples and the results are shown in Fig. 4. The experiment No. 8 reduced the

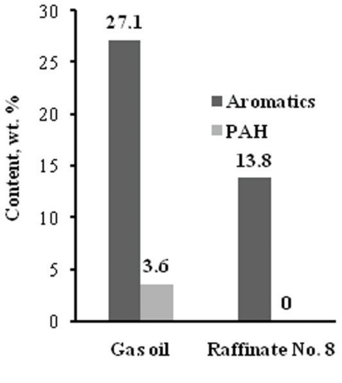

Fig. 4. Aromatics and PAH contents in gas oil and raffinate No. 8.

aromatics content of the gas oil from 27.1 to 13.8 wt. % and allowed the total amount of polycyclic aromatic hydrocarbons to be extracted.

CONCLUSIONS

The extractive desulphurization of a hydro-treated gas oil fraction from the Kstovo Oil Refinery was performed under different experimental conditions. The results showed that the desulphurization was improved by increasing the solvent ratio, increasing in water content of NMP and increasing the number of extraction stages. A higher temperature extraction was unfavourable for the desulphurization process.

N-Methylpyrrolidone had a high capacity for the removal of undesirable components from the hydro-treated gas oil cut. In the extractive purification performed in experiment No. 8, 86.9 % of the sulphur was removed, the nitrogen content was reduced by 3.8 times, the aromatics content was 2 times lower and the polycyclic aromatic hydrocarbons were totally extracted. The refined gas oil became cleaner for the environment met the European standard (EN 590) in terms of the polycyclic aromatic hydrocarbons content, but not concerning the sulphur content. For these two required specifications, the purified gas oil respected the Algerian (NA 8110) and Russian (GOST R 52368-2005) standards.

The combination of hydro-treatment and extractive purification is a promising method for producing ecological diesel fuels.

SUPPLEMENTARY MATERIAL

Properties of the hydro-treated gas oil from the Kstovo Oil Refinery are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding authors on request.

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ИЗВОД

ЕКСТРАКТИВНО ПРЕЧИШЋАВАЊЕ ХИДРОТРЕТИРАНОГ ГАСНОГ УЉА ПОМОЋУ *N*-МЕТИЛПИРОЛИДОНА

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Проучавано је пречишћавање хидротретираног гасног уља екстракцијом течно–течно помоћу *N*-метилпиролидона као растварача. Резултати су показали да овај метод, под одређеним експерименталним условима, смањује садржај сумпора у гасном уљу са 174 на 28 ppm, садржај азота са 58 на 15 ppm, садржај аромата са 27,1 на 13,8 % и потпуно екстрахује полициклични ароматичне угљоводонике. Овако добијено рафинисано гасно уље може да се користи да би се добио за околину чист дизел за гориво моторних возила.

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