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NEW INVESTIGATIONS ABOUT DECREASING OF SULFUR FROM DIESEL FRACTION

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Abstract

Sulfur content of diesel fuel has been cut down to ultra low levels by environmental regulation in many countries with the aim of reducing diesel engine's harmful emissions and improving air quality. As a result, research on the production of ultra low sulfur diesel has gained enormous interest in the scientific community worldwide.

The present paper considered some possibilities for decreasing of sulfur content in diesel fractions by different methods. It's established that extraction processes with selective solvents decrease sulfur content in different degree. It was calculated distribution coefficients of the systems. It was applying an adsorption process for purifying of middle distillated fractions from unlikely components. The obtained results show the possibility for looking for new techniques for optimization of the adsorption process.

Key words: solvent; oil fraction; extraction.

1. Introduction

The aim of the present article is to show the decreasing of sulphur content in diesel fractions by different methods, as well as to calculate the distribution coefficients of obtained systems.

Diesel-powered cars generally have a better fuel economy than equivalent gasoline engines and produce less greenhouse gas emission. Their greater economy is due to the higher energy per-litre content of diesel fuel and the intrinsic efficiency of the diesel engine. While petro diesel's higher density results in higher greenhouse gas emissions per litre compared to gasoline, the 20–40% better fuel economy achieved by modern diesel-engine automobiles offsets the higher per-litre emissions of greenhouse gases, and a diesel-powered vehicle emits 10-20 percent less greenhouse gas than comparable gasoline vehicles [1-4]. Biodiesel powered diesel engines offer substantially improved emission reductions compared to petro diesel or gasoline-powered engines, while retaining most of the fuel economy advantages over conventional gasoline-powered automobiles. However, the increased compression ratios mean that there are increased emissions of oxides of nitrogen (NOx) from diesel engines. This is compounded by biological nitrogen in biodiesel to make NOx emissions the main drawback of diesel versus gasoline engines.

In the past, diesel fuel contained higher quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. In the United States, more stringent emission standards have been adopted with the transition to ULSD starting in 2006 and becoming mandatory on June 1, 2010 (see also diesel exhaust). U.S. diesel fuel typically also has a lower cetane number (a measure of ignition quality) than European diesel, resulting in worse cold weather performance and some increase in emissions [3].

High levels of sulfur in diesel are harmful for the environment because they prevent the use of catalytic diesel particulate filters to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxide (NOx) adsorbers (still under development), to reduce emissions. Moreover, sulfur in the fuel is oxidized during combustion, producing sulfur dioxide and sulfur trioxide that in presence of water rapidly convert to sulfuric acid one of the chemical processes that results in acid rain. However, the process for lowering sulfur also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Biodiesel and biodiesel/petrodiesel blends, with their higher lubricity levels, are increasingly being utilized as an alternative. The U.S. annual consumption of diesel fuel in 2006 was about 190 billion litres (42 billion imperial gallons or 50 billion US gallons) [5].

Poor quality (high sulphur) diesel fuel has been used as a palladium extraction agent for the liquid-liquid extraction of this metal from nitric acid mixtures. Such use has been proposed as a means of separating the fission product palladium from PUREX raffinate that comes from used nuclear fuel. In this system of solvent extraction, the hydrocarbons of the diesel act as the diluents while the dialkyl sulphides act as the extractant. This extraction operates by a solvation mechanism. So far, neither a pilot plant nor full scale plant has been constructed to recover palladium, rhodium or ruthenium from nuclear wastes created by the use of nuclear fuel [6].

2. Experimental

The physico-chemical properties of used raw-material are given in Table 1. The physico chemical characteristics of selective solvents are presented in Table 2. The solvents N-methylpirolidone, DEG, MEG and furfural were selected on the base of previous investigations [7]. The selection of solvents was done by literal data, previous studies, physical properties and industrial aplying of coresponding solvents. The methodology of extraction processes in laboratory conditions are described in [7-10].

Table 1 Physico-chemical parameters of the raw material

Parameters	Middle distillated fraction
Density at 15 °C, kg/m^3	822,3
Density at 20 °C, kg/m^3	818,5
Sulfur content, ppm	1000
Arene content, % (m/m)	20,2
Polycyclic arene content, % (m/m)	5,6
Kinematic viscosity at 40 °C, mm^2/s	2,65
Ash content, % (m/m)	0,006
Coke residue, % (m/m)	0,03
Distilation characteristics	
IBP	197
50 %	262
90 %	336
95 %	343
EBP	360
Yield, % (v/v)	98,0

Table 2 Physical properties of selective solvents [13]

Solvent	d_4^{20} g/sm^3	Boiling point ^{O}C	Melting point, ^{o}C	Molar mass, g/mol
N-methylpyrolidone	1,03	202	24	99,1
Furfural	1,16	162	37	96,1
MEG	1,11	198	-12	62,1
DEG	1,12	244	-6	106,1

The ratio raw material: selective solvent and additives was 1:1 and 1:2 with the aim to establish effectiveness of our mixtures and contact time from 35, 50, 55 and 60 minutes to be established the effective time of contact. The temperature of the processes was determined experimentally and kept about 40-50°C.

The obtained products were investigated by BSS EN ISO 20846 - determined the sulfur content, and BSS EN 12916 - measured arene content. The obtained results for changing of sulfur, arene content and polycyclic arene hydrocarbons in treated raffinates are given in Tables from 3 to 6.

We have calculated the distribution coefficients on the base of the obtained results for sulfur content by the follow way:

$$K = C_e/C_r \qquad (1)$$

where: C_e – concentration of sulfur compounds in extract, mol/l; C_r - concentration of sulfur compounds in raffinate, mol/l.

The data are presented on the follow figures.

Table 3 Effect of contact time under sulfur and arene content in raffinates at selective purifying of middle distillated fraction with N-methyl pyrollidone

Contact time, min	Sulfur content, ppm	Arene content, % (m/m)	Yield of product, %(v/v)
ratio	*raw material*	*solvent =*	*1:1*
35	432,5	15,1	98,5
40	422,1	14,6	98,0
45	401,2	13,9	97,5
50	389,3	13,5	98,0
55	356,4	12,9	98,5
60	332,1	12,1	98,0
ratio	*raw material*	*solvent =*	*1:2*
35	387,5	14,3	98,5
40	367,4	13,6	98,0
45	342,1	12,9	97,5
50	311,6	11,8	98,0
55	278,1	11,5	97,5
60	265,3	11,3	98,5

Initial data: sulfur – 1000 ppm, arene hydrocarbons – 20.2 % (m/m), temperature – 50°C

Table 4 Effect of contact time under sulfur and arene content in raffinates at selective purifying of middle distillated fraction with furfural

Contact time, min	Sulfur content, ppm	Arene content, % (m/m)	Yield of product, %(v/v)
ratio	*raw material*	*solvent =*	*1:1*
35	444,4	13,6	98,0
40	398,1	12,1	98,5
45	354,3	12,0	97,5
50	322,6	11,7	98,0
55	256,3	11,5	98,5
60	223,4	11,0	98,0
ratio	*raw material*	*solvent =*	*1:2*
35	365,5	14,8	98,5
40	301,4	13,7	98,0
45	256,4	12,6	97,5
50	245,6	12,3	99,0
55	232,1	11,8	98,0
60	203,2	11,4	98,5

Initial data: sulfur – 1000 ppm, arene hydrocarbons – 20.2 % (m/m), temperature – 50°C

Table 5 Effect of contact time under sulfur and arene content in raffinates at selective purifying of middle distillated fraction with MEG

Contact time, min	Sulfur content, ppm	Arene content, % (m/m)	Yield of product, %(v/v)
ratio	*raw material*	*solvent =*	*1:1*
35	818,5	18,5	99,0
40	801,2	17,6	99,2
45	756,2	17,1	98,5
50	701,3	16,1	98,9
55	712,2	16,5	99,0
60	689,5	15,7	98,5
ratio	*raw material*	*solvent =*	*1:2*
35	755,2	17,1	98,5
40	678,5	16,5	99,0
45	666,3	16,1	98,5
50	632,1	15,8	99,1
55	622,5	15,1	99,0
60	616,2	14,8	99,1

Initial data: sulfur – 1000 ppm, arene hydrocarbons – 20.2 % (m/m), temperature – 50 °C

Table 5 Effect of contact time under sulfur and arene content in raffinates at selective purifying of middle distillated fraction with DEG

Contact time, min	Sulfur content, ppm	Arene content, % (m/m)	Yield of product, %(v/v)
ratio	*raw material*	*solvent =*	*1:1*
35	425,3	17,1	98,5
40	411,1	16,5	98,0
45	389,5	16,2	98,5
50	365,4	15,4	98,0
55	322,1	14,7	99,1
60	299,9	14,1	98,5
ratio	*raw material*	*solvent =*	*1:2*
35	325,2	13,0	98,6
40	311,4	12,9	98,5
45	301,1	12,5	98,7
50	299,9	12,1	98,0
55	287,6	12,0	99,0
60	289,7	11,7	98,5

Initial data: sulfur – 1000 ppm, arene hydrocarbons – 20.2 % (m/m), temperature – 50 °C

Table 7 The change of sulfur and arene hydrocarbons content of middle distillated fraction after adsorption treatment

Temperature, °C	Sulfur content after treatment, ppm	Arene hydrocarbons content after treatment %(m/m)	Yield of product, %(v/v)
	contact time:	*4.5 hours*	
15	658,0	18,2	55,0
20	456,3	17,5	70,0
25	265,3	16,7	45,0
30	75,5	12,3	42,3
	contact time:	*6.0 hours*	
15	523,0	16,2	65,0
20	251,1	15,5	56,0
25	112,7	13,7	45,0
30	65,2	11,3	40,0

Initial data: sulfur – 1000 ppm, arene hydrocarbons – 20.2 % (m/m), temperature – 50 °C

On the base of previous investigations and for purpose of this work for decreasing sulfur and arene content we use adsorption method for purifying of raw material. The methodology and experimental conditions of this process in laboratory conditions are given in [11]. It's essentially to notice that adsorption column is filled with Al_2O_3.

It was established that the adsorption process is the most effective at contact time – 4, 5 and 6 hours. On figure 3 is shown the distribution coefficients of sulfur compounds depend from temperature change.

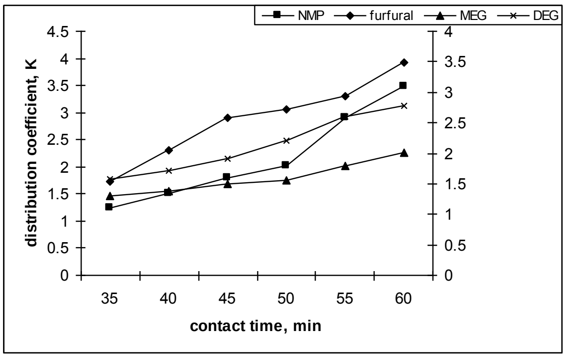

Fig. 1 Dependence of distribution coefficients from contact time of extraction with polar solvents /ratio raw material: polar solvent = 1:1

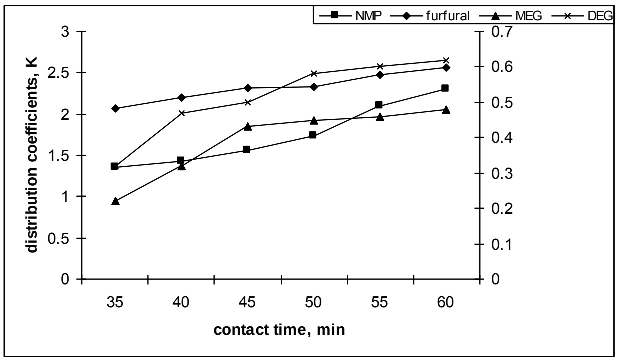

Fig. 2 Dependence of distribution coefficients from contact time of extraction with polar solvents /ratio raw material: polar solvent = 1:2/

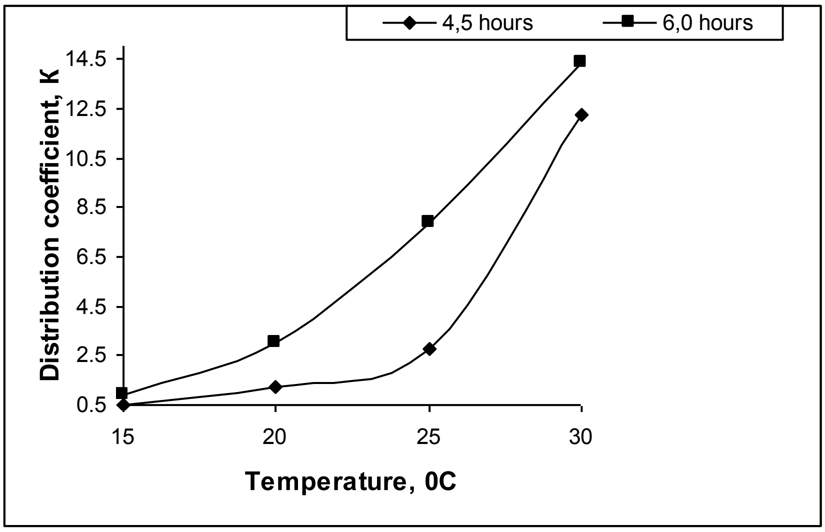

Fig. 3 Dependence of distribution coefficient from temperature of adsorption treatment

3. Results and Discussion

The presented data and results show that extraction method is a perspective method for obtaining of fuels, which require of Bulgarian standards for sulfur, arene and polycyclic arene hydrocarbons content. The done investigations present that from chosen of us selective solvents the most effective are – N-methyl pyrollidone, furfural and DEG. The optimum conditions of extraction processes with them are: contact time – 60 min, ratio investigated raw material: selective solvent = 1:2 and temperature – 50°C. The worse effective solvent from chosen from us is MEG.

It must notice that when we increase quantity of solvent toward raw material, the content of sulfur compounds, arene and polycyclic arene degrease in raffinates observable.

The calculated distribution coefficients of separated systems: middle distillated fraction: solvent proved experimental data and results which give a possibility for applying of method and looking for decisions for obtaining of lower cost fuel such as corresponding of requirements of Bulgarian State Standard, as well as methods and methodology for utilization of obtained wastes.

The experimental investigations present that the most effective contact time is 6 hours and temperature is 30 °C at applying of adsorption process. It's necessary to notice that the obtained yield of obtained purifying products is to a great extent lower than the yield that is obtained at extraction processes. The change of decreasing of sulfur compounds, arene and polycyclic arene hydrocarbons is lower, too.

4.Conclusions

1. It's investigated a possibility to decreasing sulfur and arene hydrocarbons content from middle distillated fraction by extraction with selective solvents. It's established that whole selected from us selective solvents decrease sulfur content in different degree. The most effective polar solvents from used from us solvents are N-methyl pyrollidone, furfural and DEG.

2. It's calculated the distribution coefficients of investigated systems: middle distillated fractions: selective solvents. The obtained data confirm obtained experimental results.

3. It's applied the adsorption process for purifying from sulfur and arene compounds of middle distillated fraction. The obtained results show the possibility for looking for new techniques for optimization of the process and it's applying for purifying of middle distillated fractions from unlikely components.

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