METHOD OF DECREASING OF UNLIKELY COMPONENTS IN GASOLINE

Yordanka Ts. Tasheva*, Petko St. Petkov, Isay D. Lazarov

Department "Industrial management and technologies", Faculty of Social sciences, Burgas University "Prof. Dr Assen Zlatarov", 8010 Burgas, Bulgaria e-mail:jtasheva_2006@abv.bg; pst_petkov@abv.bg; bpr@bpr-bg.com

Abstract

Desulphurization of FCC gasoline and diesel fuels has been investigated by chemical oxidation of sulphur containing compounds with hydrogen peroxide in the presence of an acid catalyst such as formic acid and acetic acid, followed by extraction of the oxidized compounds using acetonitrile. Oxidative desulphurization (ODS) of diesel fuel was found to be very promising approach for the reduction of up to 92% of sulphur at low temperature (50 C) and atmospheric pressure. The direct extraction of diesel oil without any oxidation has resulted in about 45% sulphur removal, however such direct extraction also removed other aromatic hydrocarbons and affected the yield.

In this paper is considered the possibility to use a extraction method as purifying method from sulfur compounds and benzene from Bulgarian gasoline fractions.

1. Introduction

The sulfur content in motor and diesel fuels is continuously reduced by regulations to lower levels. The current specification in Europe and the USA calls for a maximum sulfur content of 50 ppm in gasoline and diesel by 2005 [1,2], and this level will be reduced to below 10 ppm by the year 2010 [1]. The current industrial method for removal of sulfur from fuels is hydrodesulphurization (HDS), which requires high temperature and high pressure, making HDS a very costly option for deep desulphurization. Moreover, HDS is not effective for removing heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivates especially 4,6-dimethyldibenzothiophene (4,6-DMDBT). There are many research and development efforts both on the conventional hydrodesufurization and on alternative methods such as selective adsorption, biodesulfurization, and oxidation/extraction (oxidative desulphurization) etc. for removing these refractory sulfur compounds from petroleum products [3-12].

Oxidative desulphurization (ODS) has been given much attention as an alternative technology for deep desulphurization. The ODS is basically a two-stage process, oxidation, followed by liquid extraction. In the ODS process, the sulfur containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulfooxides and sulfones. These are preferentially extracted from light oil due to their increased relative polarity [7, 9, 13, 14]. Any unused oxidant that remains in the light oil can be removed by water washing and extracting. The oxidized compounds can be extracted from the light oil by using a non-miscible solvent. Depending on the solvents used for extraction, the oxidized compounds and solvent are separated from light oil by gravity separation or centrifugation. The light oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods,

such as absorption using silica gel and aluminum oxide. The solvent is separated from the mixture of solvent and oxidized compounds by a simple distillation for recycling and re-use.

Benzothiophene, Dibenzothiophene (DBT), 4-methyldibenzothiophene, and 4, 6-dimethyl-dibenzothiophene are typical thiophenic compounds prevailing in diesel fuels. Using a hexadecane solution of these model compounds, experiments were carried out to compare the reactivity of the different benzothiophenes in oxidesulfurization (ODS) with several polar solvents. V_2O_5/Al_2O_3 catalyst, hydrogen peroxide as oxidant and the solvents: N,N-dimethylformamide (DMF), 2-ethoxyethanol (EEOH), acetonitrile (MeCN) and gamma-butyrolactone (BuL) were used. The experimental results showed that removal of benzothiophenes contained in diesel can be carried out efficiently in conditions here studied, with a yield to sulfones higher than 80%, depending on the reactivity of each S-compound and solvent used. DBT was completely removed but the yield to DBT sulfone with MeCN was only 95%. According to the solvent used, benzothiophenes reactivities decrease in the order: MeCN > BuL > EEOH > DMF. It was found that an important fraction of the eliminated compounds in the diesel phase, is not totally transformed to its corresponding sulfone, it is only removed as sulfur compound by extraction, without undergoing ODS reaction. Depending on the thiophenic compound, it was possible to remove about 70-85% of benzothiophenes by physical extraction process, using the best solvent (DMF) and only close to 30-60% with MeCN [4].

The majority of technology available today for the production of ultra-low sulfur fuels relies on the use of hydrogen and high pressure, and therefore uses capital-intensive equipment.

Oxidative desulphurization offers lower capital alternative to hydrodesulphurization (HDS).

Several other oxidative desulphurization technologies have been introduced based on hydrogen peroxide and require the recycle of an organic acid co-oxidant. Lyondell Chemical Company's oxidative desulphurization (ODS) process uses a hydro peroxide oxidant, eliminating the need to recycle the co-oxidant acid. The company has demonstrated this process in a small continuous pilot unit for several refinery streams, with our focus being predominately on diesel fuel. This process has the capability to produce a clear, colorless diesel with less than 10 ppm of sulfur. Progress has also been made on extending this technology to treat heavy pyrolysis gasoline and FCC gasoline [10].

2. Experimental

Under experimental desulphurization were used fractions of gasoline, which are produced in "Bulgarian Petrol Refinery" Ltd - Sofia. Their physico-chemical properties are given in Tables 1 and 2.

Table 1. Physico-chemical properties of gasoline fraction, named NG

Parameters	Values	Parameters	Values
Octane number		Xylene, % (m/m)	8,8
RON	75,6	Toluene, % (m/m)	2,1
MON	74,4	Benzene, % (m/m)	1,1
Distillated characteristics		Sulfur content, ppm	110
- 50 % distillated at, ºC	100	Olefins, % (m/m)	4,5
-90 distillated at %, ºC	142	Paraffin, % (m/m)	75,3
Oxygen, % (v/v)	0,19	Arenes, % (m/m)	20,2

Table 2. Physico-chemical properties of gasoline fraction, named BAS

Parameters	Values	Parameters	Values
Octane number		Xylene, % (m/m)	6,3
RON	75,1	Toluene, % (m/m)	3,3
MON	74,6	Benzene, % (m/m)	1,03
Distillated characteristics		Sulfur content, ppm	70
- 50 % distillated at, ºC	91	Olefins, % (m/m)	4,0
-90 distillated at %, ºC	127	Paraffin, % (m/m)	79,9
Oxygen, % (v/v)	0,18	Arenes, % (m/m)	16,1

We have been used the follow solvents: N- methylpyrrolidone, furfural and diethylene glycol. The choice of the solvents was made by literal data, physical properties and application in manufactory at the last. The part of physical properties of the solvents is given in Table 3.

Table 3.Physical properties of used selective solvents from us

Solvent	Density at 20 °C, g/sm^3	Boiling point, °C	Melting point, °C	Molecular mass, g/mol
N-methylpyrrolidone	1,03	202	24	99,1
Fufural	1,16	162	37	96,1
Diethylene glycol	1,12	244	-6	106,1

The method of the extraction was given in [13]. The specific conditions of the separate processes are the follow: temperature of the laboratory extraction process: 25°C; time of the processes: 15, 20, 25, 30 minutes; and the ratio raw-material: solvent = 1:1 and 1:2.

It was determined sulfur content by BDS EN ISO 20846 (UV-spectroscopy) and content of benzene in obtained raffinates by BDS ISO 12916 (liquid chromatography).

3. Result and Discussion

The obtained results after treatment of gasoline fractions are given in Tables 4 to 9.

On the base of the obtained results were calculated the coefficients of distribution of sulfur compounds by the follow equation: $K = C_e/C_r$ (1), where: C_e – concentration of sulfur compounds in extract, mol/l; C_r - concentration of sulfur compounds in raffinate, mol/l.

Table 4. Results of variation of sulfur and benzene content in gasoline fraction NG after treatment with furfural

№	Contact time, min	Sulphur content, pm	Benzene content, %
	Ratio feedstock:	Furfural = 1:1	
1	10	37,2	0,16
2	15	26,1	0,14
3	20	24,3	0,13
4	30	22,1	0,12
	Ratio feedstock:	Furfural = 1:2	
1	10	9,8	0,14
2	15	9,1	0,12
3	20	7,6	0,11
4	30	5,6	0,10

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC
Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

Table 5. Results of variation of sulfur and benzene content in gasoline fraction NG after treatment with N-methylpyrrolidone

№	Contact time, min	Sulphur content, pm	Benzene content, %
1	10	31,2	0,22
2	15	28,6	0,18
3	20	25,7	0,16
4	30	25,5	0,14
	Ratio feedstock:	N-methylpyrrolidone =	1:2
1	10	8,7	0,11
2	15	8,2	0,09
3	20	7,7	0,08
4	30	5,8	0,08

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC
Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

Table 6. Results of variation of sulfur and benzene content in gasoline fraction NG after treatment with diethylene glycol

№	Contact time, min	Sulphur content, pm	Benzene content, %
1	Ratio feedstock:	DEG =	1:1
2	10	41,4	0,66
3	15	40,8	0,61
4	20	39,2	0,57
	30	38,7	0,55
1	Ratio feedstock:	DEG =	1:2
2	10	9,9	0,26
3	15	9,7	0,24
4	20	8,4	0,19

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC
Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

Table 7. Results of variation of sulfur and benzene content in gasoline fraction BAS after treatment with furfural

№	Contact time, min	Sulphur content, pm	Benzene content, %
1	Ratio feedstock:	DEG =	1:1
2	10	41,4	0,66
3	15	40,8	0,61
4	20	39,2	0,57
	30	38,7	0,55
1	Ratio feedstock:	DEG =	1:2
2	10	9,9	0,26
3	15	9,7	0,24
4	20	8,4	0,19

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC
Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

Table 8. Results of variation of sulfur and benzene content in gasoline fraction BAS after treatment with N-methylpyrrolidone

№	Contact time, min	Sulphur content, pm	Benzene content, %
1	Ratio feedstock:	DEG =	1:1
2	10	41,4	0,66
3	15	40,8	0,61
4	20	39,2	0,57
	30	38,7	0,55
1	Ratio feedstock:	DEG =	1:2
2	10	9,9	0,26
3	15	9,7	0,24
4	20	8,4	0,19

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC
Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

Table 9. Results of variation of sulfur and benzene content in gasoline fraction NG after treatment with diethylene glycol l

№	Contact time, min	Sulphur content, pm	Benzene content, %
1	Ratio feedstock:	DEG =	1:1
2	10	41,4	0,66
3	15	40,8	0,61
4	20	39,2	0,57
	30	38,7	0,55
1	Ratio feedstock:	DEG =	1:2
2	10	9,9	0,26
3	15	9,7	0,24
4	20	8,4	0,19

Initial data: ratio feedstock: solvent = 1:1, 1:2, temperature – 25ºC; Initial sulfur content – 110 ppm, benzene content – 1,1 % (m/m)

On Figure 1 to 4 are given the dependence of coefficients of distribution from the time of contact. The obtained results from extraction processes in laboratory condition of gasoline fractions show that all solvents extracted sulfur and benzene from raw-materials.

It was observed that increased ratio investigated raw-material: solvent (1:2) led to increase of the decreasing of sulfur and benzene content at two investigated raw-materials. It must notice, that when increase the amount of the solvent, the quantity of sulfur compounds and benzene content decrease noticeable. The most effective combination is: investigated raw-material: furfural, time of contact – 30 minutes.
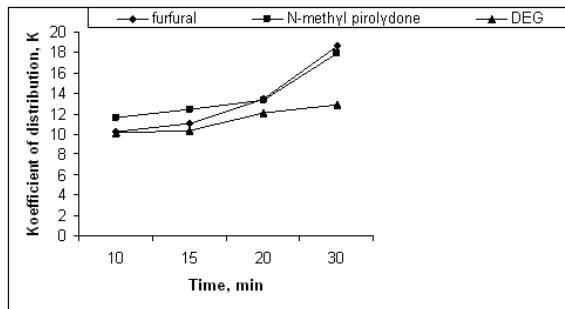

Fig.1. Dependence of coefficients of distribution from time of extraction of gasoline fraction NG at ratio raw material: solvent = 1:1
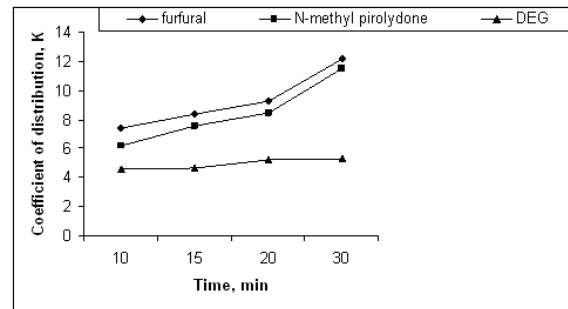

Fig.2. Dependence of coefficients of distribution from time of extraction of gasoline fraction NG at ratio raw material: solvent = 1:2
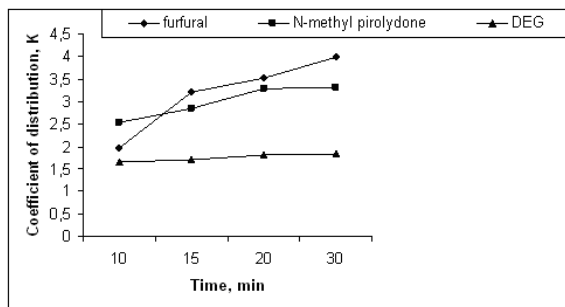

Fig.3. Dependence of coefficients of distribution from time of extraction of gasoline fraction BAS at ratio raw material: solvent = 1:1
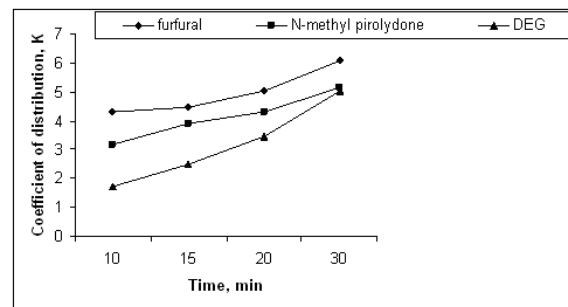

Fig.4. Dependence of coefficients of distribution from time of extraction of gasoline fraction BAS at ratio raw material: solvent = 1:2

The data given in Table 5 show that the solvent N-methylpyrrolidone purifies the gasoline fraction from sulfur compounds and benzene not enough effectively, but it must notice, that obtained raffinates have appropriate contents of sulfur and benzene according to Bulgarian standard.

The results from extraction treatment with diethylene glycol show that obtained products answer of the requirement of Bulgarian standard for sulfur and benzene content, too.We obtained the most decreasing of sulfur content and benzene at extraction treatment of raw-material NG at ratio gasoline NG : solvent =1:2 and time of contact 30 minutes.

On the Figures from 1 to 4 are presented the dependences of the coefficients of distribution of sulfur compounds from the time of extraction processes.

It`s clear, that the highest values of coefficients of distribution are obtained using solvent furfural at extraction of gasoline fraction BAS, the coefficients of distribution using solvent N-methylpyrrolidone are lower, and the values of coefficients of distribution using solvent diethylene glycol are the lowest. The calculated results confirm experimental data, that the solvent furfural is most selective toward sulfur compounds and benzene from used from us other solvents.

4. Conclusions

1. It was proved that all used from us solvents led to decrease of sulfur content and benzene in gasoline fraction after extraction treatment.
2. The most effective solvent for extraction of used from us gasoline fraction is furfural at the follow conditions: raw-material: solvent = 1:2, temperature – 25ºC and time of the contact – 30 minutes.
3. It's established that using extraction method for purify of gasoline fraction, produced of "Bulgarian Petrol Refinery" are obtained gasoline fuels according to requirements of Bulgarian standard and European norms for sulfur content and benzene.

References

[1]   Rall D.J., Fuel, 82, № 4, 2003, p.1819.
[2]   Taylor N.A., J.A. Hugill. Oil and Gas Journal, 89, № 33, 2001, p. 57-59.
[3]   Porier M.A., P.J. Falkiner, J.P. Campebele, Exxon Research and Engineering Co., 2000.
[4]   Bosman A., L. Datsevitch, A. Jess, Chem. Commun., 2001, p.2494.
[5]   Babich I.V., A.J. Moulijn, Fuel, 82, 2003, p.607-631.
[6]   Sarazin P., J. Bonnardot, Hydrocarbon Processing, 2005.
[7]   Patent USA 7097760.
[8]   Pospíšil M., Blažek, J.: 41 Int. Petr. Conference, Bratislava, 2003.
[9]   Patent EP 1310544.
[10]   Wiltskire J., BP Technol. Mag., 32, 2000, p.10.
[11]   Patent USA 6338794 B_1.
[12]   Patent USA 62547661 B_1.
[13]   Tasheva J., P. Petkov, Sl. Ivanov, I. Lazarov, Oxid. Commun., 28, 2, 2005, 286.