Desulfurization of FCC gasoline by extraction with sulfolane and furfural

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ORIGINAL SCIENTIFIC PAPER

Extractive desulfurization of FCC gasoline with two solvents (sulfolane and furfural) was studied. Experiments have been carried to determine more suitable solvent with respect to process parameters including temperature, batch time, solvent / FCC gasoline ratio and extraction times. Results show that lower sulfur content in raffinate was achieved with sulfolane at temperatures around 50 °C and solvent / FCC gasoline ratio above 2. This was also verified with statistical analysis of the extractive desulfurization with sulfolane by 2^3 full factorial design. Maximum desulfurization efficiency was obtained at high levels of temperature and sulfolane / FCC gasoline ratio; time in researched range of values had small impact and minimum sulfur content in raffinate of 196 mg kg^{-1} was obtained at higher levels of temperature, time and sulfolane / FCC gasoline ratio. Mathematical model that can be used for predicting sulfur content in raffinate after extractive batch process with sulfolane was statistically developed and proven with analysis of variance.

Key words: liquid extraction, FCC gasoline, desulfurization, sulfolane, furfural, mathematical modeling

INTRODUCTION

It is well known that the presence of sulfur in the hydrocarbon fuels has negative influence on the environment (increase of adverse emissions in atmosphere), as well as on efficiency and lifetime of catalytic converters in cars and engines in general. Current EU restrictions regarding sulfur content in diesel and gasoline fuels are 50 mg kg^{-1} and are valid till 2009 when new restrictions of 10 mg kg^{-1} will take effect.[4]

Motor gasoline is a blend of several kinds of gasolines, mostly produced with secondary conversion processes (catalytic cracking, reforming, alkylation). FCC (Fluid Catalytic Cracking) gasoline is one of the most important compounds of commercial gasoline, with overall contribution of sulfur up to 98%. This is why FCC gasoline desulfurization is highly necessary.[7]

Conventional method for hydrocarbon fuels desulfurization is catalytic hydrotreating technology (HDS) which reduces sulfur by its conversion to H_2S. The HDS process is highly efficient in removing tiols, sulfides and disulfides; however it is less effective for thiophenes and its derivatives. The sulfur compounds that remain in the motor fuels are mainly thiophene and its derivatives, which make deep-desulfurization by HDS extremely difficult. Also, to ensure higher product quality it is necessary to increase catalyst or reactor volume, which significantly reduces economy of the process. Because of this, it is necessary to investigate new processes of fuel desulfurization as the existing HDS process supplement. Some of the new promising methods for fuel desulfurization are adsorption, extraction, oxidative extraction, precipitation, membrane and biochemical processes.[6,12,15]

Extraction method is based on better solubility of sulfur compounds and aromatic hydrocarbons in relation to non aromatics in appropriate polar solvent. Particular extraction processes vary with the type of solvent used which necessitates different process conditions while the successful extraction can only be achieved in the layer forming region. Thus, the process efficiency, for the most part, depends on the correct solvent selection, which means that compromise must be reached between solvent selectivity and capacity, and other properties including environmental and toxicological restrictions.[2,3,8,13,14,16,17,18]

In petroleum refining industry sulfolane and furfural are commercial extraction solvents mostly used for aromatics extraction from different petroleum fractions.[1,5,9,10] Since part of the sulfur in petroleum is present in the form aromatic compounds[4], these two solvents are interesting candidates for extraction desulfurization of FCC gasoline.

Design of experiments (DOE) is statistical method used for process characterization, modeling and optimization. Implementation of DOE allows us to see how parameters interact and how the whole system functions, which couldn't be possible with experiments with just one parameter variation, till others are kept constant. Other advantage of DOE is a possibility to see the way interdependent factors react in the wider range of values, without experiment with all possible combinations. With DOE empirical mathematical models are obtained, which enables us to predict response for all possible inlet factors combinations. With these models it is possible to optimize critical factors and identify best combination of values.[2]

In this paper, possibility of extractive desulfurization of FCC gasoline with boiling point of 155 °C, with sulfolane and furfural as extraction solvents was explored. Influence of process parameters on the desulfurization efficiency was determined in order to select more efficient solvent. The statistical study of the process was

Table 1. Physical and chemical properties of the FCC gasoline

Property	Value
RON (Research octane number)	90.8
Density at 20 °C (kg m^{-3})	710.6
Total sulfur (mg kg^{-1})	760
Kinetic viscosity at 40 °C (mm^2 s^{-1})	0.557 9
Boiling range (°C):	
IBP	39.8
50%	78.3
95%	139.4
Dry point	149.9

achieved with two-level full factorial design with three process parameters. The effect of each parameter and their interactions were determined, as well as the statistical model for the process.

Table 2. 2^3 full factorial design and results of experiments

Run no.	Real Value			Coded Value			$S_{i,\,exp}$
	X_1	X_2	X_3	X_1	X_2	X_3	(mg kg^{-1})
1	30	30	4	- 1	+1	+1	214
2	30	30	2	- 1	+1	- 1	295
3	50	30	2	+1	+1	- 1	293
4	50	30	4	+1	+1	+1	196
5	30	30	4	- 1	+1	+1	206
6	30	10	4	- 1	- 1	+1	294
7	30	10	4	- 1	- 1	+1	198
8	30	30	2	- 1	+1	- 1	283
9	30	10	2	- 1	- 1	- 1	410
10	50	30	2	+1	+1	- 1	311
11	30	10	2	- 1	- 1	- 1	512
12	50	30	4	+1	+1	+1	206
13	50	10	4	+1	- 1	+1	204
14	50	10	4	+1	- 1	+1	308
15	50	10	2	+1	- 1	- 1	304
16	50	10	2	+1	- 1	- 1	357

EXPERIMENTAL

Materials

A sample of fluid catalytic cracking (FCC) gasoline was obtained from INA d.d. Oil Company. The main properties of the raw gasoline are listed in Table 1.

Furfural (Riedel de Haën, R.G) was fractionally distilled at reduced pressure under nitrogen atmosphere and only the colorless middle fraction was collected. Analytical-grade sulfolane was obtained commercially from Sigma–Aldrich.

Extraction experiments

The extractive desulphurization experiments were carried using a semiautomatic apparatus, Fig. 1, developed for batch extraction. The apparatus is controlled via a personal computer. The calculated volumes of FCC gasoline and extracting solvent were warmed to the desired temperature and than mixed together. The extraction mixture was then stirred at 700 rpm for a desired period of time at the process temperature. The extraction was conducted at different temperatures raging from 20 to 70 °C, solvent / feed ratios from 0.2 to 6 and extraction times from 5 to 40 minutes. The extraction mixture was then left for 8 hour to ensure adequate separation of the phases. After extraction with sulfolane, purification of the raffinate was necessary, because certain quantity of the sulfolane remained in the raffinate and obstructed the sulfur analysis. After complete phase separation, 25 ml of the raffinate phase was transferred to another vessel and purified with 25 ml of distilled water for 15 minutes at 25 °C and 700 rpm. The mixture was then left for 24 hour to separate. The total sulfur content was measured using wave dispersive X-ray fluorescent spectrometer, according to standard method ISO 20884.

Statistical study

Statistical design of experiments refers to the process of planning the experiment so that appropriate data that can be analyzed by statistical methods will be collected,

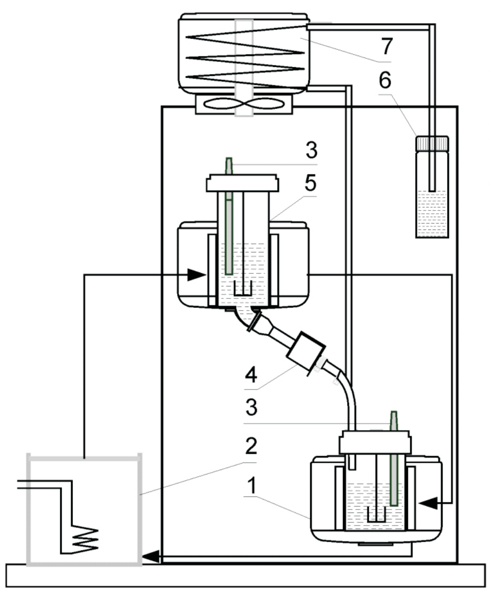

Fig. 1. Batch extraction apparatus
Sl. 1. Aparatura za šaržnu ekstrakciju

resulting in valid and objective conclusions. Factorial experiment is useful tool for dealing with several factors, in which factors are varied together, instead of one at a time. In order to investigate influence of process parameters and their interactions on the response, 2^3 full factorial design was applied. By this design in each complete trial and replication of the experiment all combinations of the levels of the factors are investigated. 2^3 factorial design contained 18 runs in which 3 parameters (temperature, time and solvent / FCC gasoline ratio) were varied over two levels (+1 for high and –1 for low value). 2^3 full factorial design with parameters actual and coded values and results of experiments are presented in Tab 2. Experimental runs and replications were carried out randomly according to the developed design to ensure reproducibility and to reduce standard error. The statistical calculations were made using software tool Design-Expert, Stat-Ease, Inc.

RESULTS AND DISCUSSION

In this study, effects of process parameters: temperature, time and solvent / FCC gasoline ratio, as well as the effect of extraction times on sulfur content in FCC gasoline were investigated. Obtained experimental data are presented in Figs.2-5. After selection of the solvent with higher efficiency toward sulfur compounds removal; experiments according to the 2^3 full factorial design were conducted and obtained results are presented in Tabs. 2. and 3. and Figs. 6. to 9. After extraction with sulfolane, it was necessary to remove retained sulfolane from raffinate.

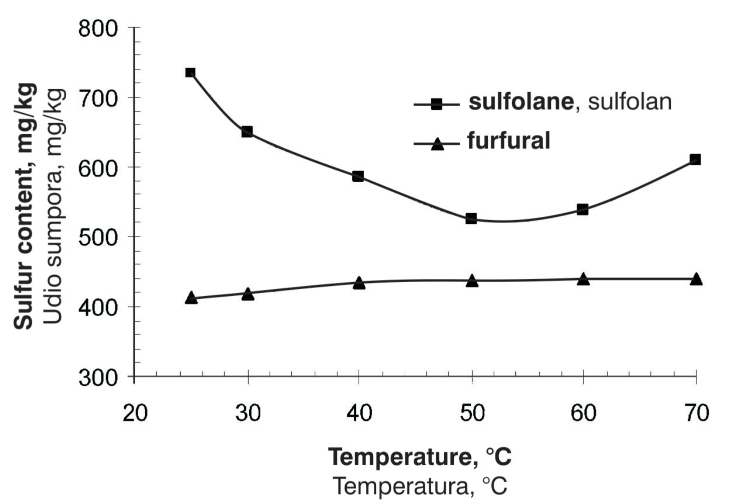

Fig. 2. Effect of temperature on the extraction of sulfur at t = 10 min and solvent / FCC gasoline ratio = 1

Sl. 2. Utjecaj temperature na učinkovitost ekstrakcijske desulfurizacije sulfolanom pri t = 10 min i omjeru otapalo / FCC = 1

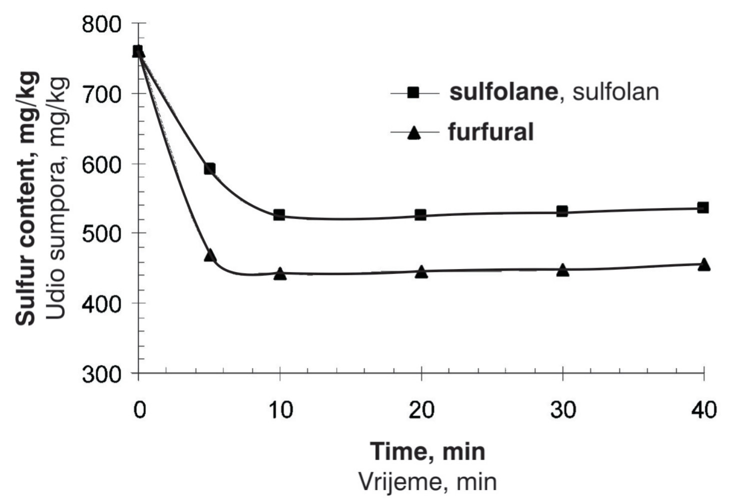

Fig. 3. Effect of time on the extraction of sulfur at T = 50 °C and solvent / FCC gasoline ratio = 1

Sl. 3. Utjecaj vremena na učinkovitost ekstrakcijske desulfurizacije sulfolanom pri T = 50 °C i omjeru otapalo / FCC = 1

Effect of temperature

With the increase of the extraction system temperature, heterogeneous area and fluid density are decreasing, resulting in extraction efficiency increase. Fig. 2 represents effect of temperature on extractive desulfurization with sulfolane and furfural. Sulfolane results indicate that maximum desulfurization efficiency of 526 mg kg^{-1} sulfur content was achieved at 50 °C. Since further increase of temperature reduces desulfurization efficiency, it can be assumed that process is exothermic and is ruled by Van't Hoff law. On the other hand, extraction with furfural results indicate negative impact of temperature on the desulfurization efficiency, although this effect is very small and sulfur content values were around 430 mg kg^{-1} for all temperatures. Because of this, it can be concluded that temperature has no significant effect on the extractive desulfurization with furfural. Further experiments of process parameters effect research were conducted at 50 °C because maximum desulfurization efficiency of extraction with sulfolane was obtained at this temperature.

Effect of time

The data obtained for 5 different times of extraction with sulfolane and furfural (Fig. 3) indicate that the optimum duration for extraction process was 10 minutes, where the lowest sulfur content in raffinate is observed for both of the solvents. With further increase of extraction duration till 40 minutes, desulfurization efficiency decrease is noticed, as sulfur content is increased for 12 mg kg^{-1} in respect to sulfur content obtained at 10 minutes duration. This sulfur content increase with time can be explained by reextraction effect of sulfur transfer from solvent back to raffinate.

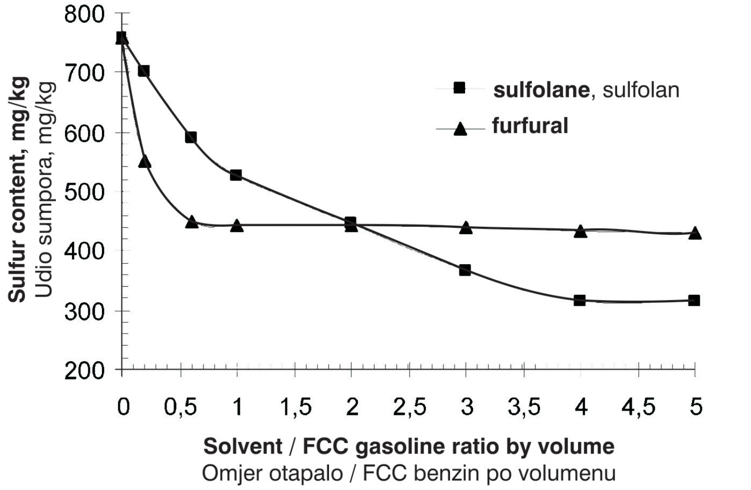

Fig. 4. **Effect of solvent / FCC gasoline ratio on the extraction of sulfur at T = 50 °C and t = 10 min**
Sl. 4. Utjecaj omjera otapalo / FCC benzin na učinkovitost ekstrakcijske desulfurizacije sulfolanom pri T = 50 °C i t = 10 min

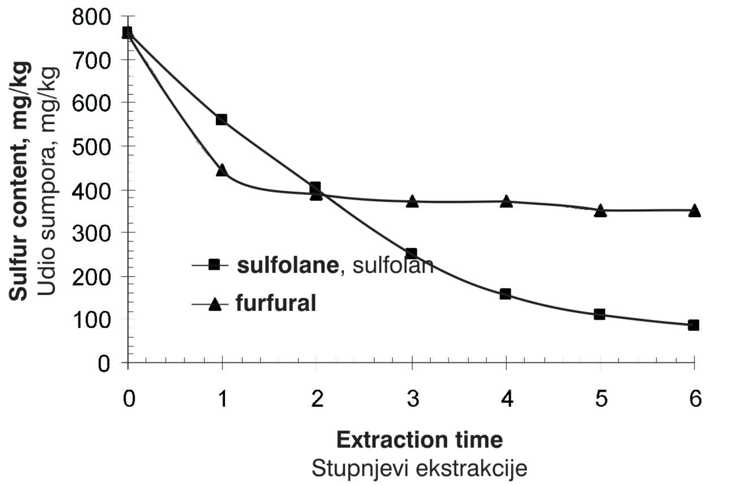

Fig. 5. **Effect of extraction times on the extraction of sulfur at T = 50 °C and t = 10 min**
Sl. 5. Utjecaj stupnjeva ekstrakcije na učinkovitost ekstrakcijske desulfurizacije sulfolanom pri T = 50°C i t = 10 min

Effect of solvent / FCC gasoline ratio

The effect of solvent / FCC gasoline ratio on the extraction of sulfur with sulfolane and furfural is presented in Fig. 4. It can be noticed that desulfurization efficiency increase for extraction with sulfolane occurred till solvent / FCC gasoline ratio of 4, where minimum observed sulfur content in raffinate was 314 mg kg^{-1}. With further solvent / FCC gasoline ratio increase, further desulfurization efficiency increase hasn't been observed. With solvent / FCC gasoline ratio increase, for extraction with furfural, desulfurization efficiency had also increased, but in lower extent. It is observed that the sulfur content in raffinate decreased till solvent / FCC gasoline ratio of 1, where its minimum was 443 mg kg^{-1}. Further solvent / FCC gasoline ratio increase didn't have any significant influence.

Effect of extraction times

As shown in Fig. 5. extraction times increase desulfurization efficiency of extraction with sulfolane and furfural. Experiment with 6 extraction times (10 minutes each) was conducted at 50 °C. Obtained data show that reduction of sulfur content for extraction with sulfolane from initial 760 mg kg^{-1} to final 83 mg kg^{-1} was achieved. For extraction with furfural final value of sulfur content in raffinate after 6 extraction times was 350 mg kg^{-1}.

Statistical analysis

The purpose of this statistical analysis was to determine most significant parameters in the batch process of extractive desulfurization. With chosen 2^3 full factorial design that contained 18 experiments, it was explained and quantified impact of 3 parameters (temperature, time and solvent / FCC gasoline ratio), as well as their interaction, on the response (sulfur content in raffinate). Data were collected in the way that made possible to obtain the mathematical model

Table 3. List of individual parameters and their interaction effects on total sulfur content; model and coefficient validation (ANOVA results)

Source	Studentized Effects (-)	Contribution (%)	Sum of squares (-)	Degrees of Freedom (-)	Mean square (-)	F-value (-)	F-test (-)
X_1	-29.625	3.57	3 510.56	1	3 510.56	36.98	0.0003
X_2	-72.125	21.19	20 808.06	1	20 808.06	219.18	< 0.0001
X_3	-117.625	56.38	55 342.56	1	55 342.56	582.94	< 0.0001
$X_1 X_2$	31.625	4.07	4 000.56	1	4 000.56	42.14	0.0002
$X_1 X_3$	30.625	3.82	3 751.56	1	3 751.56	39.52	0.0002
$X_2 X_3$	27.625	3.10	3 052.56	1	3 052.56	32.15	0.0005
$X_1 X_2 X_3$	-41.625	7.06	6 930.56	1	6 930.56	73.00	< 0.0001
Model	-	-	97 396.44	7	13 913.78	146.56	< 0.0001
Total	-	-	98 155.94	15	-	-	-
Residual	-	-	759.50	8	94.94	-	-

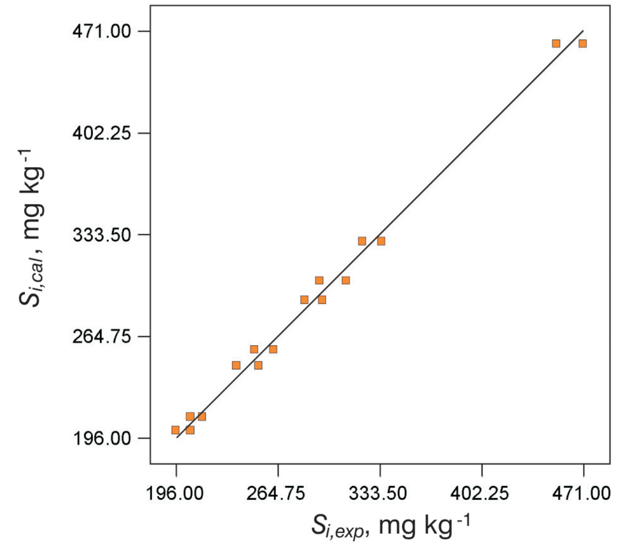

Fig. 6. Calculated ($S_{i,cal}$) versus observed ($S_{i,exp}$) values of sulfur content in FCC gasoline after extraction process

Sl. 6. Prikaz eksperimentalno dobivenih vrijednosti ($S_{i,exp}$) i vrijednosti dobivenih modelom ($S_{i,cal}$) za količinu sumpora u uzorku nakon procesa ekstrakcijske desulfurizacije

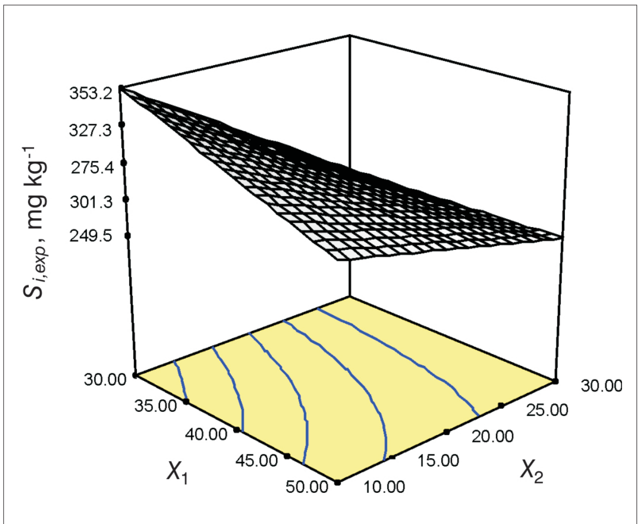

Fig. 7. Response surface and contour plot of sulfur content, $S_{i,exp}$, vs. X_1 and X2

Sl. 7. Ovisnost modelom procijenjenih vrijednosti sadržaja sumpora, $S_{i,exp}$, o X_1 i X_2

that describes extractive desulfurization with sulfolane for batch system illustrated in previous section. As sulfolane proven itself as a more efficient extractive solvent than furfural, factorial design was conducted for extractive desulfurization with sulfolane. 2^3 full factorial design with coded and real values of levels and results are presented in Table 2. Using obtained data, parameters effects and contributions, sum of squares, mean squares, degrees of freedom and F-test values required

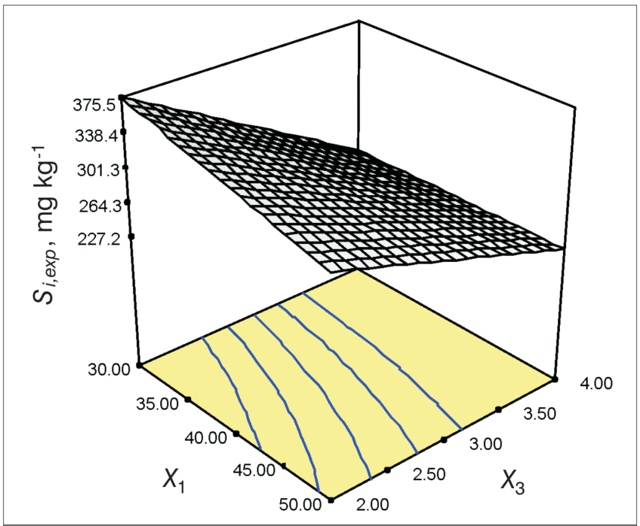

Fig. 8. Response surface and contour plot of sulfur content, $S_{i,exp}$, vs. X_1 and X_3

Sl. 8. Ovisnost modelom procijenjenih vrijednosti sadržaja sumpora, $S_{i,exp}$, o X_1 i X_3

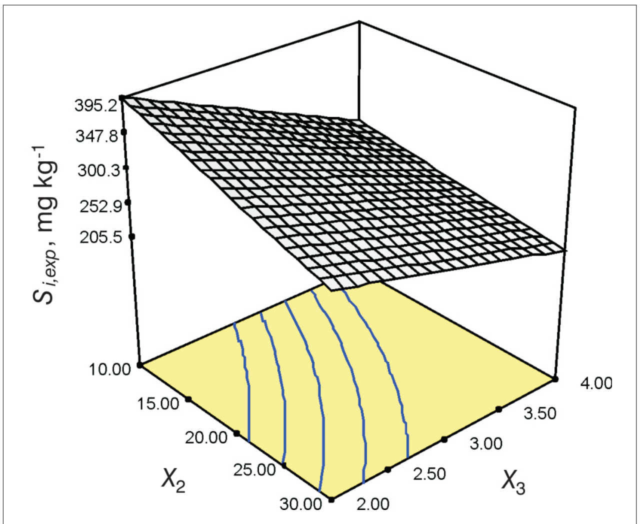

Fig. 9. Response surface and contour plot of sulfur content, $S_{i,exp}$, vs. X_2 and X_3

Sl. 9. Ovisnost modelom procijenjenih vrijednosti sadržaja sumpora, $S_{i,exp}$, o X_2 i X_3

for model and coefficient validation were calculated (Table 3). Statistical analysis showed that all 3 parameters are significant for process response, which can be seen from F-test values below 0.05 for all parameters and their interactions, while F-value of 146.56 implies that the model is significant; with only a 0.01% chance that value this large could occur due to noise. With multiple regression analysis of the obtained data, performed with Design-Expert software tool, mathematical description of extractive desulfurization batch process was expressed with statistical model obtained from coded values ($S_{i,exp}$) and technological model obtained from real values ($S_{i,cal}$).

$S_{i,exp}$ = 286.56 - 14.81 X_1 - 36.06 X_2 - 58.81 X_3 + 15.81 $X_1 X_2$ + 15.31 $X_1 X_3$ + 13.81 $X_2 X_3$ - 20.81 $X_1 X_2 X_3$

$S_{i,cal}$ = 1487.00 - 21.72 T - 39.05 t - 314.18 O/S + 0.78 $T t$ + 5.69 T O/S + 9.70 t O/S -0.20 $T t$ O/S

From the presented calculated values and obtained models, it can be seen that most significant parameter for researched extractive desulfurization was solvent / FCC gasoline ratio, thereafter time, then temperature. Effects of parameters interactions were less expressed, but still significant. Most significant was time-temperature interaction. R^2 values of the models were 0.99 showing excellent variability of the model. Ability of the model to predict extractive desulfurization with sulfolane is presented in Fig. 6. where calculated versus observed values of sulfur content in raffinate are compared. It shows that points that represent observed values diverge very little form the line that represent calculated values, which means that model can be used for predicting sulfur content in raffinate after extractive batch process with sulfolane.

Effects of process parameters on sulfur content in raffinate are presented in Figs. 7-9 in the form of response surfaces with certain space angle, which represents graphical interpretation of obtained mathematical model. It should be mentioned that analysis of the presented response surfaces were made by variation of two parameters, while the third was kept constant in central point which were X_1 = 40, X_2 = 20 and X_3 = 3. From presented response surfaces and contour plots it can be seen that maximum desulfurization efficiency was obtained at high levels of temperature and solvent / FCC gasoline ratio; that time in researched range of values had small impact; and finally that the minimum sulfur content in raffinate of 196 mg kg^{-1} was obtained at values X_1 = 50, X_2 = 30 and X_3 = 4.

CONCLUSIONS

In this research two extraction solvents (sulfolane and furfural) for extractive desulfurization process from FCC gasoline were compared. Impacts of temperature, time, sulfolane / FCC gasoline ratio and extraction times on desulfurization efficiency were investigated. Obtained results show that lower sulfur content in samples after liquid extraction with sulfolane was achieved at temperatures of 50 °C and sulfolane / FCC ratio above 2. This was also verified with statistical analysis of the extractive desulfurization with sulfolane by 2^3 full factorial design. Results of statistical analysis show that the most significant parameter for researched extractive desulfurization was sulfolane / FCC gasoline ratio, then time and temperature, while effects of parameters interactions were less expressed, but still significant. Minimum sulfur content in FCC gasoline sample, after extractive desulfurization process, was 196 mg kg^{-1} and was obtained at temperature of 50 °C and solvent ratio of 4 at process duration of 30 minutes. Mathematical model that can be used for predicting sulfur content in raffinate after extractive batch process with sulfolane was statistically developed and proven with analysis of variance. The lowest sulfur content achieved with extractive desulfurization process with sulfolane was 83 mg kg^{-1} at temperature of 50 °C after 6 extraction times, indicating that 89.1 mass.% of sulfur was extracted from original sample of FCC gasoline.

SYMBOLS

$S_{i, exp}$	(mg kg^{-1})	experimental total sulfur content in raffinate
$S_{i, cal}$	(mg kg^{-1})	calculated total sulfur content in raffinate
T	(°C)	temperature
t	(min)	time
O/S	(-)	solvent / FCC gasoline ratio by volume
X_1	(-)	coded temperature
X_2	(-)	coded time
X_3	(-)	coded solvent / FCC gasoline ratio by volume
R_2	(-)	correlation coefficient

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