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Desulfurization of Crude Oil by Laboratory Developed Multipumping Flow Injection Analysis System with Optimization by Response Surface Methodology

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ABSTRACT

Sour crude oil is the crude oil that contains a high level of sulfur impurity. It can be toxic and corrosive. Before this lower-quality crude can be processed into other crude oil derivatives, the sulfur content must be reduced, raising the processing cost. A homemade semi-automated multipumping flow analysis system was constructed, consisting of several parts available on the local markets and at low economic costs to decrease the sulfur content of crude oil samples collected. The central composite design (CCD) and response surface methodology (RSM) have been used for modeling and optimization. The effects of the operational parameters, including polar and nonpolar solvent types, solvent flow rates (10–40 ml/min), mixing coil lengths (120–200 min), temperature (30–60 °C), and solvent entry time to the system (0–60 sec) were studied. Experimental and theoretical applications were made to determine the optimal sulfur content, which came out to be 1.438 and 1.395 wt.%, respectively. This system evaluated the effectiveness of the sulfur removal content for actual heavy crude oil by experimentally and theoretically to be 65.73 and 66.75% respectively. The semi-automated system was applied successfully to reduce the sulfur content in a highly sensitive and accurate way.

Keywords: multipumping flow system, desulfurization, response surface, optimal conditions.

INTRODUCTION

Sulfur removal is an important step in the refinement of petroleum. The sulfur content of crude oil is often expressed in weight percent (wt.%) or parts per million by weight (ppm) [Vetere et al., 2017]. Most sour crudes contain sulfur levels between 1.0 and 2.0 weight percent, although some have values beyond 4 weight percent. Examples of sulfur compounds are mercaptans, thiophenes, cyclic and noncyclic sulfides, thiols, sulfoxides, and sulfones [Corilo et al., 2016]. Because sulfur may cause corrosion in refinery equipment and deactivate the catalysts that facilitate desirable chemical reactions in some refining processes, as well as result in adverse car emissions of sulfur compounds, the sulfur content of crude oil is important for a variety of reasons. Among all the hetero elements in crude oil, sulfur has the most significant effects on refining [Abdulrazzaq et al., 2020; Huang et al., 2012]. Most sulfur compounds are created either through bacterial sulfate reduction or by releasing elemental sulfur from the sulfate when unsaturated organic matter reacts with H_2S. Thermal maturation may drastically alter the sulfur content of petroleum, increasing the relative abundance of highly condensed aromatic sulfur compounds [Demirbas et al., 2014]. Thermochemical interactions between sulfate and hydrocarbons at high temperatures are another significant route for sulfur addition. In the refining of petroleum, certain sulfur compounds that have comparatively poor chemical stability readily break down into smaller sulfur compounds [Al-Yasiri et al., 2016; Awadh et al., 2015]. The principal goal of this work was to build a semi-automated system and utilize it to reduce the sulfur content of Iraqi crude oil by using different parameters at different levels, whereas a central composite design was used to optimize the applied variables during the desulfurization process.

EXPERIMENTAL

Feedstock

In the experimental investigation, the samples of crude oil from the Nasiriyah oil Laboratory (ThiQar, Iraq) were used, where the crude oil characteristics show that it is a heavy type, as indicated in Table 1.

Chemicals

During analytical application with a multi-pumping flow analysis system, high purity solvents were used in the flow injection system, and a di-n-Butyl Sulfide (DBS) high-purity standard was used for sulfur content analysis by an X-ray fluorescence analyzer. The chemical materials used in the conducted study are listed in Table 2.

Table 1. Untreated crude oil test characterizations

It.	Characteristics	Standard methods	Result
1	Density	ASTM D-5002	0.8927
2	Specific gravity @ 60 F°	=	0.8936
3	API gravity	=	26.85
4	Water content, vol.%	ASTM D-4928	0.007
5	Sediment by extraction, wt.%	ASTM D-473	0.025
6	Water & sediment, vol.%	ASTM D-4007	0.032
7	Salt content, ppm	ASTM D-3230	36.7
8	Sulfur content, wt.%	ASTM D-4294	4.1967
9	Asphaltene content, wt.%	D-3297	2.4873
10	Reid vapor pressure @100 F°-Psi	ASTM D-6377	5.87
11	Refractive index	ASTM D-1218	1.51458
12	Kinematic viscosity, cSt 1 @ 70 °F (21.1 °C) 2 @100 °F (37.8 °C) 3 @ 120 °F (48.9 °C) 4 @140 °F (60.0 °C)	ASTM D-445	 5.169 3.792 2.940 2.312

Experimental design

To minimize the number of tests, the experimental parameters were optimized using a central composite design (CCD) as part of an investigation into the performance of the semi-automated system. To carry out the experimental design, data analysis, model fitting, and graph plotting, Design Expert version 13 software was used [Ebrahimi et al., 2014]. Table 5 displays the specifics of the central composite design with total sulfur weight percentage (actual and predicted).

Desulfurization procedures

A schematic diagram of the lab-made system established in the laboratory of the chemistry department, college of science, ThiQar University used in this study is shown in Figure 1. Two Miniperistaltic pumps were used to draw the crude oil and solvent at different flow rates by controlling their flow rates through the Arduino Uno and the motor driver, which is connected to the computer. All the parameters used in the study are listed in Table 3.

The crude oil meets the solvent at a Y junction, and then the mixture goes to the copper mixing coil, which was spirally coiled. The mixing coil is placed in a water bath for heating at different temperatures. After the mixture comes out of the mixing coil, the solvent is separated from the crude oil with a separating funnel or rotary

Table 2. Chemicals employed in the semi-automated flow injection system

Seq.	Name	Purity, %	Supplier
1	n- Hexane	99.5	CDH
2	n- Heptane	99.5	CDH
3	Acetone	99.5	CDH
4	Acetonitrile	99,0	CDH
5	Ethanol	99.5	CDH
6	di-n-Butyl Sulfide	98,0	CDH

Table 3. Parameters and their levels used in the system

Parameter	Symbol	Values				
		Level 1	Level 2	Level 3	Level 4	Level 5
Solvent type	A	n-Hexane	n-Heptane	Acetone	Acetonitrile	Ethanol
Flow rate, ml/min	B	10	17.5	25	32.5	40
Coil length, cm	C	120	140	160	180	200
Temperature, ^{o}C	D	30	37.5	45	52.5	60
Time, sec.	E	0	15	30	45	60

Table 4. Components of the semi-automated flow injection system

Component	Work	Origin
Peristaltic pump	Pulling liquids	China
Arduino Uno	Microcontroller	China
Driver motor L298N	Microcontroller	China
Power supply	DC electrical source	China
Mixing Coil	Mixing liquids	Lab-made
Water bath	Heating of mixing Coil	Korea
Rotary evaporator	Solvent extraction	Korea
ED-X-ray fluorescence	Sulfur measurement	Japan

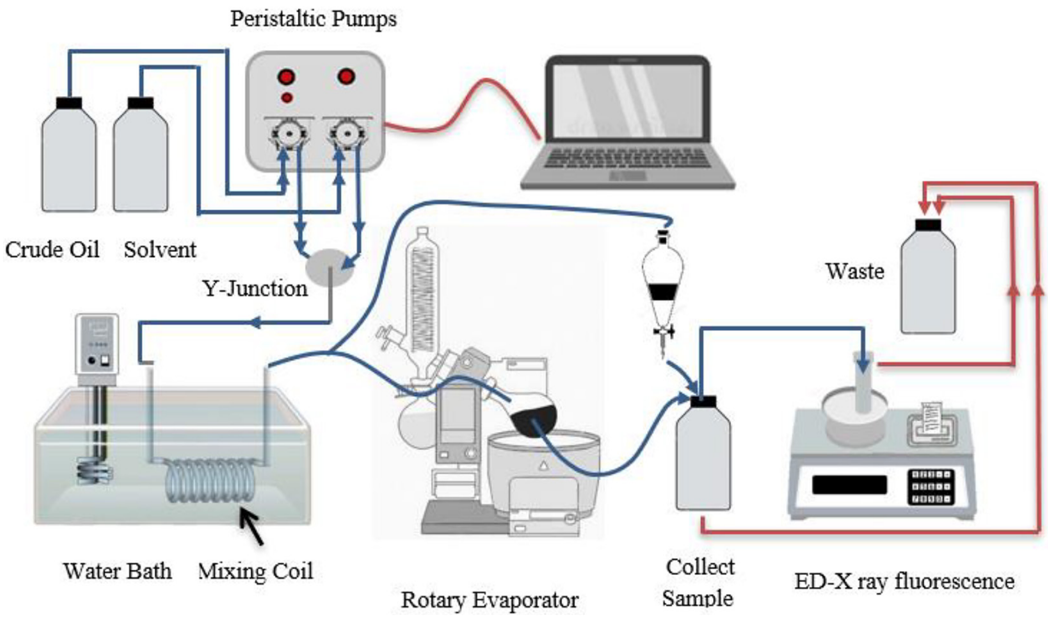

Fig. 1. 2D Graphic of semi-automated flow injection system – X-ray system

evaporator to separate solvent, and the separated crude oil will be taken manually to the X-ray sulfur analyzer. The components of the semi-automated system are listed in Table 4.

Sulfur content analysis method

The sulfur content (%) of treated and untreated heavy crude oil samples was evaluated using an X-ray fluorescence analyzer (Horiba Company, USA) in accordance with ASTM D-4294, and the sulfur reduction percentage was calculated using the formula (1):

$$\text{Sulfur removal} = (Cre/Cin) \cdot 100\% \quad (1)$$

where: *Cre* – the content of sulfur removed from the crude oil during the desulfurization process,
Cin – the initial content of sulfur in crude oil before starting the process of desulfurization.

RESULTS AND DISCUSSION

Crude oil analysis

The actual crude oil sample that was used in this experiment was examined in the lab at Nasiriyah Oil Laboratory. The crude oil used was heavy crude oil due to its 0.8936 specific gravity and 26.85 API according to ASTM D-3297 with a high sulfur content of 4.1967 wt.% based on ASTM D-4294. The results of total sulfur (actual and predicted) are presented in Table 5.

Interpreting the process graphs

The difference between the actual value and the predicted value in data analysis is a key factor in the model interpretation, which is clear from the normal distribution of the data (included in Fig. 2), The results are more accurate if the

Table 5. The experiments of five variables by central composite design and response results

Run no.	Operating parameters					Actual sulfur	Sulfur removal, %
	Solvent type	Flowrate, ml/min	Coil length, cm	Temp., ºC	Time, Sec.		
1	n-Heptane	17.5	180	37.5	15	3.037	27.63
2	n-Heptane	17.5	140	52.5	15	3.414	18.65
3	n-Heptane	32.5	140	52.5	45	2.201	47.55
4	n-Heptane	17.5	140	37.5	15	3.996	4.78
5	n-Heptane	17.5	180	37.5	45	3.755	10.52
6	n-Heptane	17.5	180	52.5	45	3.237	22.87
7	n-Heptane	32.5	140	52.5	15	2.186	47.91
8	n-Heptane	17.5	140	37.5	45	3.386	19.32
9	n-Heptane	17.5	140	52.5	45	3.237	22.87
10	n-Heptane	17.5	180	52.5	15	3.153	24.87
11	n-Heptane	32.5	140	37.5	45	3.083	26.54
12	n-Heptane	32.5	180	52.5	45	2.788	33.57
13	n-Heptane	32.5	140	37.5	15	2.914	30.56
14	n-Heptane	32.5	180	52.5	15	1.771	57.80
15	n-Heptane	32.5	180	37.5	15	1.538	63.35
16	n-Heptane	32.5	180	37.5	45	2.093	50.13
17	Acetone	25	160	45	30	2.843	32.26
18	Acetone	25	160	60	30	2.586	38.38
19	Acetone	40	160	45	30	1.943	53.70
20	Acetone	25	160	30	30	1.975	52.94
21	Acetone	25	120	45	30	2.152	48.72
22	Acetone	25	160	45	60	2.033	51.56
23	Acetone	10	160	45	30	2.707	35.50
24	Acetone	25	200	45	30	1.884	55.11
25	Acetone	25	160	45	0	2.002	52.30
26	n-Hexane	25	160	45	30	2.201	47.55
27	Ethanol	25	160	45	30	1.438	65.73
28	Acetonitrile	32.5	140	52.5	45	2.691	35.88
29	Acetonitrile	17.5	160	37.5	45	3.033	27.73
30	Acetonitrile	32.5	160	52.5	45	2.539	39.50
31	Acetonitrile	32.5	140	37.5	45	2.838	32.38
32	Acetonitrile	32.5	140	37.5	15	2.723	35.12
33	Acetonitrile	32.5	140	52.5	15	2.718	35.23
34	Acetonitrile	17.5	140	37.5	15	3.204	23.65
35	Acetonitrile	32.5	160	37.5	45	2.891	31.11
36	Acetonitrile	32.5	160	37.5	15	2.752	34.42
37	Acetonitrile	32.5	160	52.5	15	2.873	31.54
38	Acetonitrile	17.5	160	37.5	15	3.493	16.77
39	Acetonitrile	17.5	140	52.5	45	3.755	10.52
40	Acetonitrile	17.5	140	52.5	15	3.433	18.20
41	Acetonitrile	17.5	160	52.5	15	3.352	20.13
42	Acetonitrile	17.5	140	37.5	45	3.437	18.10
43	Acetonitrile	17.5	180	52.5	45	2.631	37.31

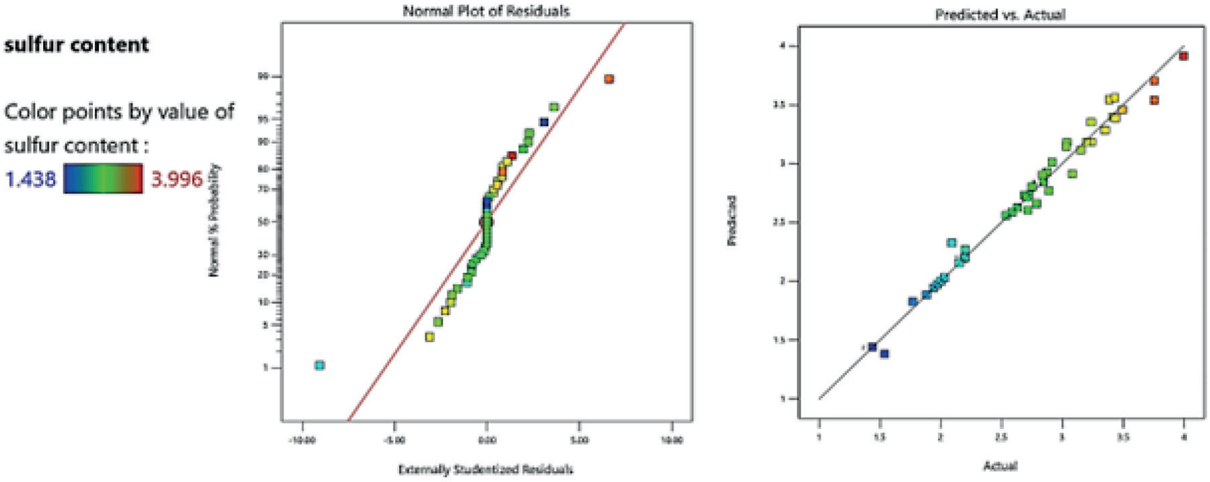

Fig. 2. Residual plot and actual vs. predicted value of sulfur content of the sulfur removal process

practical and predicted results are near to the italic line. The residuals must be randomly and naturally distributed for a model to be excellent. external residuals in Figure 2 are roughly ordinarily distributed and exhibit no discernible pattern.

Effect of two operating parameters

Effect of flow rate and coil length

As flow rate and mixing coil length were increased within the experimental range while maintaining other parameters constant. Figure 3a illustrates that the desulfurization process increased within a positive relationship. As it can be seen, raising the flow rate from 10 to 40 ml/min increases the quantity of solvent entering the system, and that will increase the amount of solvent that mixes with crude oil, leading to an improvement in system efficiency [Gunady et al., 2021]. Moreover, the long mixing coil (160 to 200 cm) gives a high mixing efficiency between the crude oil and the solvent. According to Table 6, these two parameters have a significant effect with a confidence level less than 0.05.

Effect of flow rate and temperature

The combined impact of temperature and flow rate of the solvent on the reduction of sulfur content while maintaining other parameters constant is shown in Fig. 3b. The graph shows that the combined effects of the flow rate of the solvent and temperature on the desulfurization process have a positive relationship. In actual experiments, it was found that when the flow rate was increased from 10 to 40 ml/min, the desulfurization process increased due to the higher amount of solvent that would be mixed with the crude oil sample [Tavan et al., 2021]. The effect of temperature also has a positive effect on reducing the sulfur content. As it is shown in Table 6, these two parameters have no significant effect on the sulfur removal process.

Effect of flow rate and time

Figure 3c indicates that the desulfurization process has a positive relationship with both the flow rate and the time, as the process efficiency increased along with these two factors while maintaining other parameters constant. The desulfurization process increased along with the flow rate to 10-40 ml/min of the solvent [Peralta et al., 2012]. Figure 3c of the response surface plots shows the effect of these two parameters together. These two parameters have not significantly effect, as seen in Table 6.

Effect of coil length and temperature

The effect of mixing coil length and temperature on the desulfurization process at a fixed flow rate and time is shown in Figure 3d. It can be observed that the desulfurization process changed slightly as the temperature was changed from 30 to 60 °C [Kondyli et al., 2021]. It was also observed that the desulfurization process increased when the coil length was increased up to 200 cm. Table 6 demonstrates that these two parameters have no significant effect.

Effect of coil length and time

The desulfurization process increased with coil length and time parameters while maintaining other parameters constant shown in Fig. 3e.

Table 6. ANOVA results for the desulfurization process

Specification	Term Df	Error Df	F-value	P-value	
Whole plot	4	16.00	90.15	< 0.0001	significant
A-A	4	16.00	90.15	< 0.0001	
Subplot	22	16.00	11.54	< 0.0001	significant
B-B	1	16.00	55.14	< 0.0001	
C-C	1	16.00	4.52	0.0494	
D-D	1	16.00	0.4258	0.5233	
E-E	1	16.00	1.59	0.2250	
BC	1	16.00	5.85	0.0278	
BD	1	16.00	0.4439	0.5147	
BE	1	16.00	0.7984	0.3848	
CD	1	16.00	4.05	0.0613	
CE	1	16.00	12.08	0.0031	
DE	1	16.00	1.84	0.1943	
B^2	1	16.00	20.82	0.0003	
C^2	1	16.00	52.82	< 0.0001	
D^2	1	16.00	24.55	0.0001	
E^2	1	16.00	52.88	< 0.0001	
R^2	0.9818	Adj. R-Squared		0.9324	
Std. Dev	0.1452	Mean	2.72	C.V%	5.33%

Note: Df – degree of freedom, F – probability distribution, P – probability.

The length of the mixing coil of 160 to 200 cm provides an additional period to mix the solvent with the crude oil which increases the process efficiency [Aghaei et al., 2020]. Moreover, the time parameter increases the efficiency of the sulfur removal process positively. According to Table 6, these two parameters have a significant effect with a confidence level less than 0.05.

Effect of temperature and time

According to Figure 3f, the desulfurization process is enhanced by raising the temperature with time parameters while maintaining other parameters constant. When the temperature was raised up to 60 ºC, the desulfurization process very slightly increased. Moreover, the removal process was very slight when increasing the time [Tang et al., 2015]. These two parameters have no significant effect, as seen in Table 6.

The analysis of variance (ANOVA)

In the intended experimental investigation, an ANOVA test was utilized to determine the significance of each variable [Zarei et al., 2010; Nagham et al., 2019]. The ANOVA table shows the analysis of variance for the factors involved in the experiment, where the presence of significance for the model is noted, because the calculated value of the F-test amounted to 90.15 and its P-value was less than 0.001 which is less than the level of significance of 5%. Table 6 provides the coefficient of determination (R^2) that was used to evaluate how well the model fits the data. R^2 was near one, which is acceptable. The R^2 and adjusted R^2 values were 0.9818 and 0.9324, respectively. The fact that the R^2 is close to the adjusted R^2 indicates that the model is significant [Mook et al., 2013]. Because of its low standard deviation (Std. Dev =0.1452), the quadratic model was the best option. A significantly low coefficient of variation (CV= 5.33%) indicates that the model is accurate and reliable [Mottaghi et al., 2021].

Interpreting of regression analysis

In terms of coded factors in the case of ethanol solvent, the final equation of the effectiveness was as in formula 2:

$$Y = -14.00560 + 0.156669B + 0.141905C + 0.100019D + 0.028818E + 0.000013B \cdot C + 0.000036\, B \cdot D + 0.000628B \cdot E + 0.000354C \cdot D + 0.000100C \cdot E - 0.000189D \cdot E - 0.002302B^2 - 0.000516C^2 - 0.002500D^2 - 0.000917E^2 \quad (2)$$

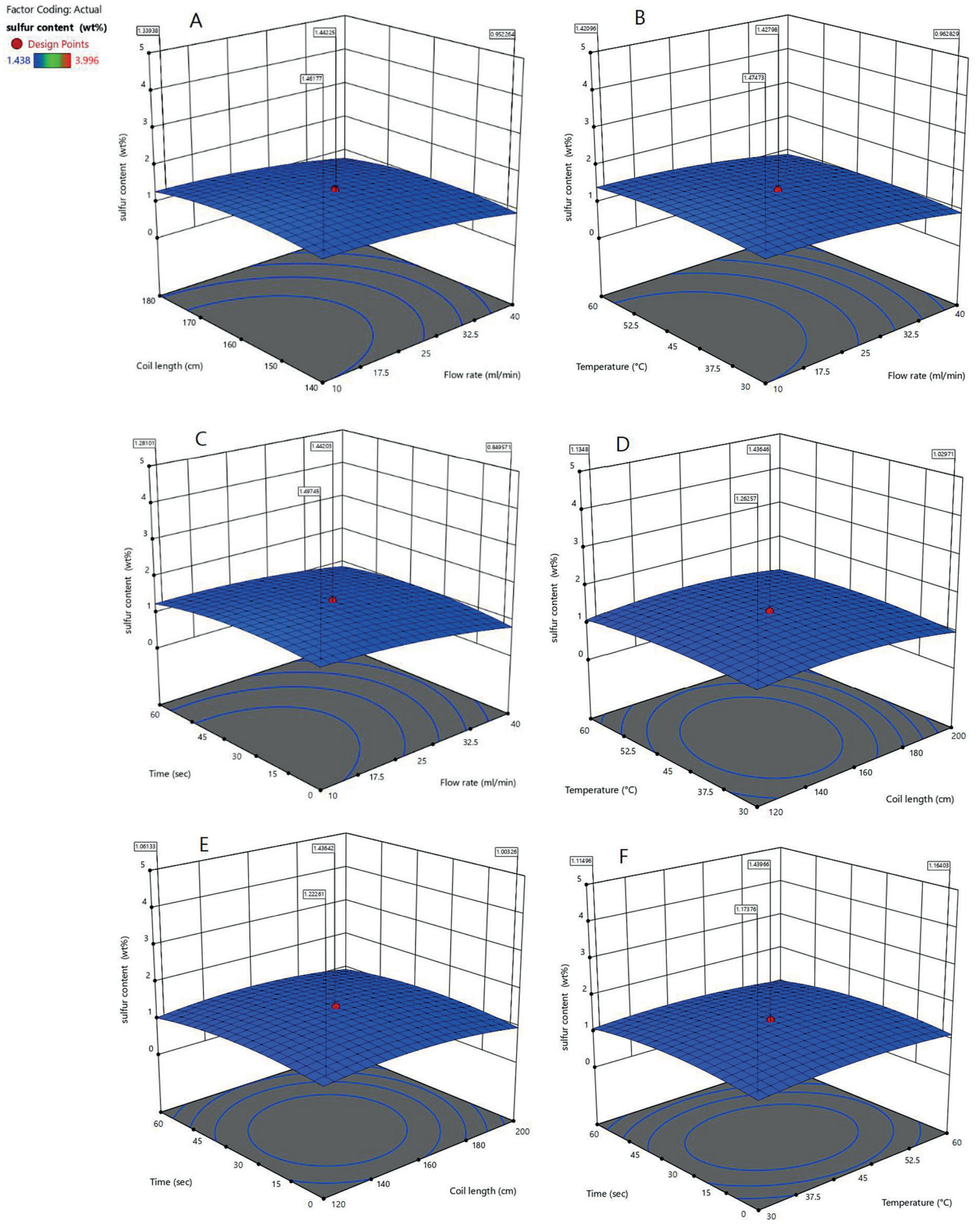

Fig. 3. Response surface plots showing the two parameters effect on the sulfur removal process

where: *Y* – sulfur content; *B* – flow rate; *C* – mixing coil length; *D* – temperature, *E* – time; while two variables indicate an interaction effect. According to equation 2, parameter B (flow rate) has the greatest influence on extraction efficiency, followed by parameters *C*, *D* and *E*.

System optimization

Effect of solvent type

The solvent extraction technique was shown to be particularly successful in removing sulfur from heavy crude oil [Saha et al., 2021]. In this study, 43 experiments were conducted, combined with other variables to observe the extraction performance of five different solvents used in the study. It is known that sulfur atoms take part in hydrogen bonding (H-bonds), and it is believed that these sulfur-containing H-bonds have a significant impact on extraction procedures [Chand et al., 2020]. The ethanol solvent is characterized by high polarity, Therefore, its ability to dissolve the sulfur compounds present in crude oil and its ability to separate easily from the non-polar compounds found in crude oil. The ethanol solvent has Dipole Moment (μ)= 1.66, Dielectric Constant (ε)= 24.6, and Polarity Index(p)= 5.2 [Chen et al., 2019]. These indicators seem that ethanol is not higher polar than acetone and acetonitrile, but what distinguishes ethanol is that it contains a hydrogen atom directly connected to an oxygen atom, which can form hydrogen bonds with the sulfur compounds found in crude oil, this leads to increase the extraction process by ethanol solvent, as indicated in Figure 4a. Ethanol has a significant effect since the p-value is less than 0.05.

Effect of flow rate

The effects of solvent to oil volume ratio (S/O) (or flow rate) have been investigated on the extraction efficiency of the crude oil at the optimum conditions, which have been studied to select the best (S/O) ratio [Hamidi et al., 2016]. Figure 4b shows that ethanol, as an extracting agent can extract sulfur compounds. The analysis showed that low solvent flow leads to low extraction efficiency. The total desulfurization process is between 10 to 40 ml/min of the flow rate. The desulfurization efficiency increases along with increasing the solvent ratio, because the sulfur compounds are dissolved by ethanol, which has a highly significant effect according to Figure 4b. Another possible reason is that the high flow rate leads to what is known as turbulent flow according to Reynolds law in fluid mechanics. The turbulence results from the differences in the fluid's speed and direction, which may sometimes intersect or even move counter to the overall direction of the flow (eddy currents) [Gunady et al., 2021]. The higher flow rate leads to an increase in the rate of collisions between the fluids and the tube walls, as well as between the fluids themselves, which leads to a rise in the mixing and extraction process. Efficiently extraction using a solvent (ethanol) was obtained using (1:1) (S/O) volume ratios of solvent to crude oil. The desulfurization process by flow rate parameter had a significant effect since the p-value was less than 0.05.

Effect of coil length

As the length of the mixing coil increases from 120 to 180 and 200 cm, the desulfurization process increases. The longer coil length allows for a high mixing efficiency between the crude oil and the solvent (in other words, the crude oil and solvent stay for a longer period), which allows the solvent to extract sulfur compounds more effectively [Abd Al-Khodor et al., 2020]. Another possible reason that may be related to the mixing coil is its geometry. The mixing coil is wrapped in a helical shape; this allows the solvents to disperse in the crude oil in both axial and radial ways which in turn led to an increase in the efficiency of the mixing and extraction process. The effect of mixing coil length is shown in Figure 4c. The desulfurization process by mixing coil length parameter has a significant influence since the p-value is less than 0.05.

Effect of temperature

Figure 4d indicates that the desulfurization process increases slightly with increasing temperature (from 30 to 60 °C). Similar results have been reported in previous studies [Ahmed et al., 2015]. This increase in the desulfurization process was not a significant effect, because it is more than 5%.

Effect of time

The effect of time on the process of reducing sulfur content in crude oil is shown in Figure 4e. The time parameter used represents the time of the solvent entering the system, where the first level is zero seconds, which means its entry at the same time as the crude oil enters the system, and the last level is 60 seconds, which means that the solvent enters the system after 60 seconds of entering the crude oil. Figure 4e shows that the shorter the time, the more efficient the process of extracting sulfur from crude oil, and this can be explained by increasing the time and quantity of solvent mixing process with the crude oil, which in turn increases the efficiency of the extraction process.

Optimizing the parameters will aid in determining the optimum factors, resulting in optimal performance. Five parameters were analyzed in the conducted investigation to determine the values that have the lowest sulfur concentration as

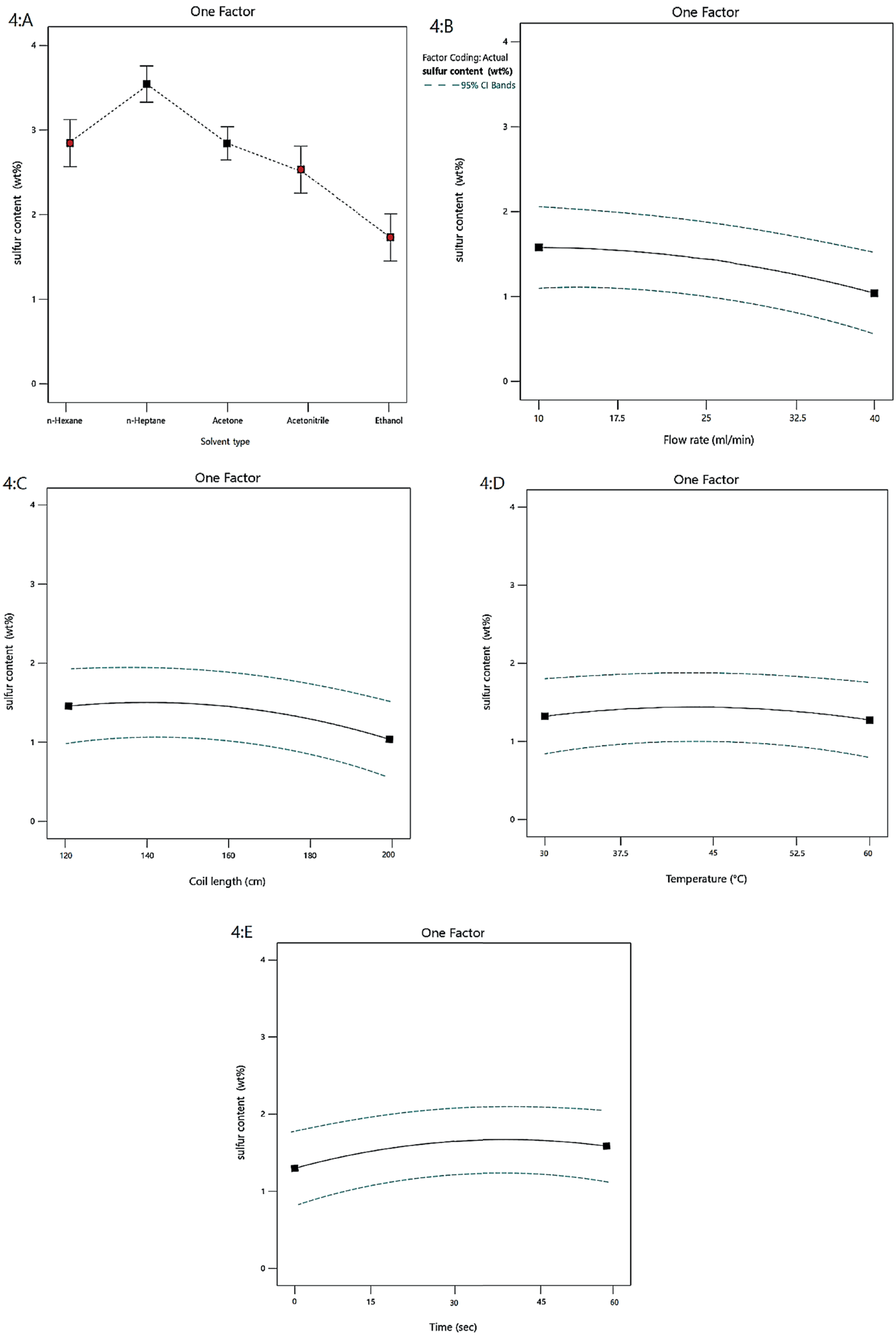

Fig. 4. One-factor effect on the sulfur removal process

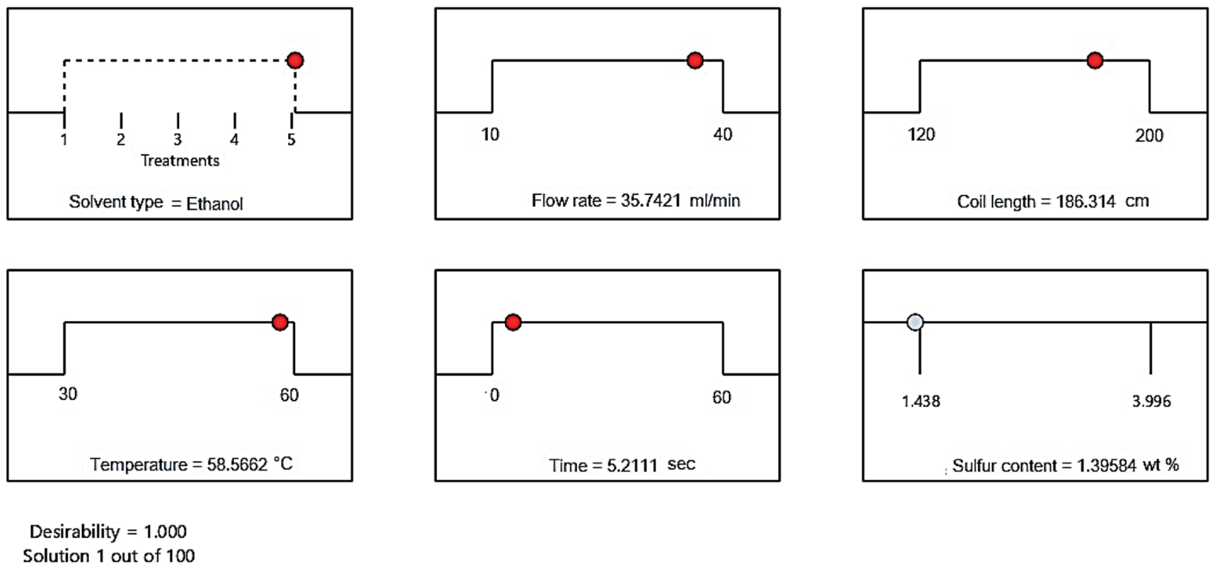

Fig. 5. Scheme of desirability for sulfur removal process parameters

Table 7. Comparison of this study to other studies

No.	Method	Fuels type	Sulfur removal	Ref.
1	Combinations of oxidation-extraction, and oxidation-adsorption	Crude oil	43% and 58%	33
2	Process of caustic desulfurization	Heavy crude oil	56.89%	34
3	Liquid extraction with aqueous ionic liquids	Jet fuel oil, diesel oil, and heavy residue	60%, 71%, and 67%,	26
4	Bio-desulfurization	Diesel and heavy crude oil	76.1%	35
5	Ionic liquid and ultrasound for oxidation desulfurization process	Heavy crude oil and diesel	95%, and 65%	36
6	Supercritical liquid desulfurization	Bitumen and heavy oil	60%	37
7	Desulfurization via oxidation-extraction	Sample A and sample B, of heavy crude oil	Sample A (29%) and sample B (73%)	38
8	Oxidation-extraction desulfurization	Crude oil	35.11%	39
9	Electrochemical extractive	Crude diesel	65%	40
10	Millifluidic flow Injection system	Heavy crude oil	65.73%	This study

a result of the flow injection system design. The obtained optimum operating conditions, as shown in Figure 5, in which ethanol solvent, 36 ml/min of flow rate, 186 cm of mixing coil length, 59 °C of temperature, and 5 sec of time were the best conditions. These values are considered economically and practically beneficial when compared with other studies.

Comparative study

The purpose of this research was to evaluate and validate a system designed to reduce the sulfur content in heavy crude oil. In this study, a method was devised to reduce the sulfur content in real heavy crude oil. Furthermore, the procedure offers the benefits of simple design, simple use, and low cost. This improves the procedure in this study when compared to others (as stated in Table 7), which include time-consuming procedures, costly chemicals, and equipment.

CONCLUSIONS

A semi-automated flow system built in a lab using a few readily available, straightforward, and inexpensive parts is crucial. In the lab, the proposed system was controlled by a microcontroller (Arduino Uno and motor driver) that was working with the software that was developed by authors. The percentage of sulfur content before working on the designed system was 4.1967 wt.% and after applying the parameters mentioned in the previous parts, the practical and theoretical percentages of sulfur became 1.438 and 1.395 wt.%, respectively. On the other hand, this process is considered economically inexpensive due to the recovery of the used solvent.

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