CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917259

Optimization of diesel fuel desulfurization by adsorption on activated carbon

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Diesel fuel was desulfurized by adsorption on a commercial activated carbon in a batch adsorber. Response surface methodology was applied for optimizing the adsorption process of organic sulfur compounds. The four factor Box-Behnken design with five center points and two responses was performed and aimed at developing second order polynominal models and to generate the optimum conditions. The objective was to find how output sulfur concentration and sorption capacity are related to the input sulfur concentration, adsorbent mass, time and temperature in order to get a clear picture and lead points for further column research. Adsorptive desulfurization of diesel fuel is a viable alternative to the conventional hydrodesulfurization process which is used on a large scale in petroleum refining industry but in most cases can not achieve the ultra low sulfur content of below 10 mg/kg. Additionally, several separate experiments were conducted at the determined optimum conditions and good agreement between experimental data and the values calculated using the models was obtained.

Key words: desulfurization, diesel fuel, adsorption, activated carbon

1. Introduction

The surge in public concerns about the environment is causing the increase in number and stringency of legislative actions world-wide. The petroleum refining industry, perceived as one of the largest sources of pollution, both direct and indirect via motor exhaust fumes, is on the front line of the battle for achieving environmentally friendly and sustainable operation. The pressure is mounting on the refineries to produce cleaner products while at the same time to minimize or completely eliminate the negative impact on the environment.
Several trends are emerging towards achieving these goals and one is the lowering of sulfur content in transportation fuels to below 10 mg/kg. This value is currently maximum allowable sulfur content in diesel fuel in the EU while in the US it is less than 15 mg/kg. Reducing the sulfur level in diesel to less than 50 mg/kg by conventional hydrodesulfurization process is difficult due to the presence of refractory sulfur compounds such as alkyl dibenzothiophenes (DBTs) with one or two alkyl groups at 4- and/or 6-positions (Muzic et al., 2008, Alhamed and Bamufleh, 2009).
Adsorption is one of the methods which can be used to achieve ultra-low sulfur content in diesel fuel. It is considered the most effective method for the removal of the trace amounts of residual sulfur in fuels after HDS treatment. (Xue et al., 2006). The idea behind this approach is to selectively separate less than 1 wt.% of fuel mass using

Please cite this article as: Muzic M., Sertic-Bionda K., Adzamic A., Gomzi Z. and Podolski S., (2009), Optimization of diesel fuel desulfurization by adsorption on activated carbon, Chemical Engineering Transactions, 17, 1549-1554 DOI: 10.3303/CET0917259

selective adsorption for removing sulphuric compounds and leave the 99 wt.% of non-sulfur-containing fuel mass untouched (Ma et al., 2002).
In this work desulfurization of diesel fuel was carried out in a batch adsorber system and the process was optimized applying Response Surface Methodology (RSM).

2. Materials and Methods

2.1 Adsorbents and diesel fuel

The adsorbent was Chemviron Carbon SOLCARB^{TM} C3 activated carbon whose initial characteristics were: particle size, 1.0-2.0 mm, bulk density, 0.48 g cm^{-3}, surface area, 936 m^2 g^{-1}, pore volume, 0.53 cm^3 g^{-1}. Activated carbon was grinded and sieved to the particle size between 0.40-0.80 mm. Typical physical and chemical properties of diesel fuels that were used are presented in Tab. 1.

Table 1. Physical and chemical properties of a typical diesel fuel.

Property		Value
Cetane number		51,0
Cetane index		46,0
Density at15°C, kg m^{-3}		820,0
Polycyclic aromatic hyadrocarbons, wt.%		2,1
Total sulfur, mg kg^{-1}		27.2
Ignition point , °C		>55
Kinematic viscosity at 40°C, mm^2 s^{-1}		3.98
Distilation:	vol.% distiled until 250 °C	<40
	vol.% distiled until 300 °C	75
	end of distilation, °C	342

2.2 Adsorption experiments

Adsorptive desulfurization experiments were carried out using semiautomatic laboratory apparatus LAM A1 (Fig. 1) developed for batch adsorption. Process was conducted under ambient pressure in stainless steel adsorbers with continuous stirring at 300 rpm. Total capacity of adsorbers is 250 cm^3 and volume of diesel fuel used was 50 cm^3. The LAM A1 apparatus is controlled via personal computer (PC).

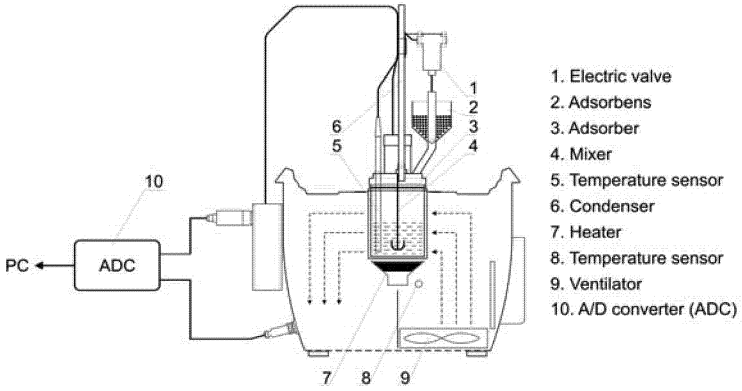


Figure 1. *LAM A1 batch adsorption apparatus.*

Activated carbon samples were dried for 4 hours at 110 °C, after which they were transferred to desiccator for storage. Removal of activated carbon particles from treated

diesel fuel was carried out by filtration through Filtrak filter paper no. 391 using Buchner funnel and vacuum pump. Total sulfur content was measured using wave dispersive x-ray fluorescent spectrometer according to standard method ISO 20884.

2.3 Response Surface Methodology

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. Most applications of RSM are sequential in nature. That is, at first some ideas are generated concerning which factors or variables are likely to be important in the response surface study (Myers and Mongomery, 2002). For this purpose we used the results of our previous study, Muzic et al., 2008. There are many reasons for using RSM for research of which the most important is the need to conduct experiments efficiently by a proper choice of design, in order to determine operating conditions according to the optimal response based on a set of controllable variables (Thang et al., 2008). In this work we used four parameters: input concentration (X_1: C_0, mg kg^{-1}), adsorbent mass (X_2: m_{C3}, g), time (X_3: t, min), temperature (T, °C), Box-Behnken design (BBD) with 5 center points (Tables 2 and 3). The BBD is an efficient group of designs with three evenly spaced levels for fitting second-order response surfaces.

Table 2. Actual and coded values of factors.

Factor	Value	Level		
		Lower	Center	Higher
Input sulfur concentration, mg kg^{-1}	Actual(C_0)	16,0	27,2	38,4
	Coded(X_1)	–1	0	+1
Adsorbent mass, g	Actual(m_{C3})	2.00	3.00	4.00
	Coded(X_2)	–1	0	+1
Time, min	Actual(t)	20	60	100
	Coded(X_3)	–1	0	+1
Temperature, °C	Actual(T)	30	50	70
	Coded(X_4)	–1	0	+1

Table 3. Four factor BBD with 5 center points.

Std. no.	X_1	X_2	X_3	X_4	C_{exp}, mg kg^{-1}	q_{exp}, g mg^{-1}	Std. no.	X_1	X_2	X_3	X_4	C_{exp}, mg kg^{-1}	q_{exp}, g mg^{-1}
1	–1	–1	0	0	11.3	0,0964	16	0	+1	+1	0	12,5	0,1507
2	+1	–1	0	0	24.2	0,2911	17	–1	0	–1	0	10.2	0,0793
3	–1	+1	0	0	7.2	0,0902	18	+1	0	–1	0	21.9	0,2255
4	+1	+1	0	0	19.6	0,1927	19	–1	0	+1	0	7.9	0,1107
5	0	0	–1	–1	17.8	0,1285	20	+1	0	+1	0	19.9	0,2528
6	0	0	+1	–1	16.4	0,1476	21	0	–1	0	–1	19.4	0,1599
7	0	0	–1	+1	17.5	0,1326	22	0	+1	0	–1	15.2	0,1230
8	0	0	+1	+1	16.3	0,1490	23	0	–1	0	+1	19.4	0,1599
9	–1	0	0	–1	11.3	0,0642	24	0	+1	0	+1	15.1	0,1240
10	+1	0	0	–1	22.7	0,2146	25	0	0	0	0	15.3	0,1626
11	–1	0	0	+1	11.2	0,0656	26	0	0	0	0	15.2	0,1640
12	+1	0	0	+1	22.9	0,2118	27	0	0	0	0	15.3	0,1626
13	0	–1	–1	0	18.5	0,1784	28	0	0	0	0	15.2	0,1640
14	0	+1	–1	0	15.1	0,1240	29	0	0	0	0	15.2	0,1640
15	0	–1	+1	0	16.8	0,2132							

3. Results and Discussion

Experimental data from Tab. 3 was statistically analyzed using Design-Expert© software. The levels of factors were determined and the second order polynomial model equations (1a) and (2a) in coded form, and equations (1b) and (2b) with actual values, were developed to describe relations of output sulfur concentration (Y_C, C) and sorption capacity (Y_q, q) to the four process parameters: input sulfur concentration, adsorbent mass, time and temperature. The analysis of variance (ANOVA) was carried out (Tab. 4) and the results were used for validating the models and the model coefficients.

$$Y_C = 15{,}24 + 6{,}01X_1 - 2{,}08X_2 - 0{,}93X_3 - 0{,}033X_4 - 0{,}095X_1^2 + \\ + 0{,}41X_2^2 - 0{,}033X_3^2 + 1{,}77X_4^2 - 0{,}12X_1X_2 \quad (1a)$$

$$C_{cal} = 21{,}50 + 0{,}61C_0 - 4{,}20m_{C3} - 0{,}02t - 0{,}44T - 7{,}57*10^{-4}C_0^2 + \\ + 0{,}41m_{C3}^2 - 2{,}03*10^{-5}t^2 + 4{,}42*10^{-3}T^2 - 0{,}01C_0m_{C3} \quad (1b)$$

$$Y_q = 0{,}160 + 0{,}074X_1 - 0{,}025X_2 + 0{,}013X_3 + 4{,}271*10^{-4}X_4 + \\ + 0.002X_1^2 + 0.003X_2^2 + 0{,}001X_3^2 - 0{,}025X_4^2 - 0.023X_1X_2 \quad (2a)$$

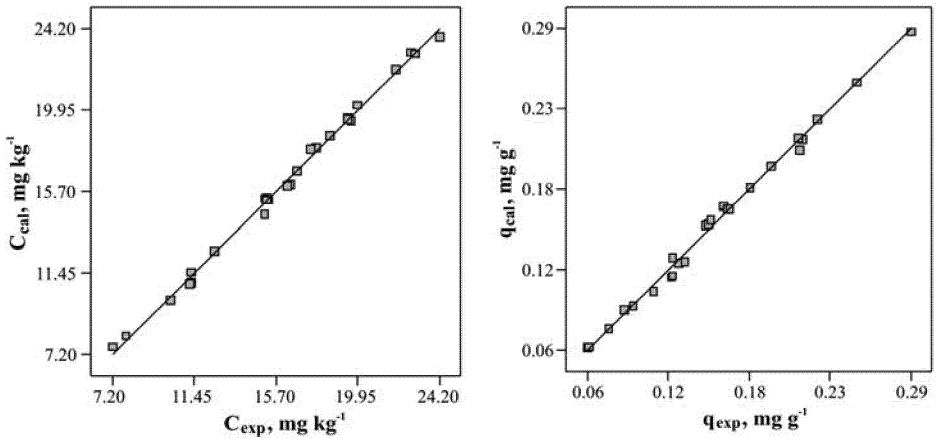
$$q_{cal} = -0{,}2519 + 0{,}0121C_0 + 0{,}0157m_{C3} + 0{,}0002t + 0{,}0063T + \\ + 12507*10^{-5}C_0^2 + 0{,}0026m_{C3}^2 + 7{,}6697*10^{-7}t^2 - 6{,}3023*10^{-5}T^2 - \\ - 0{,}0021C_0m_{C3} \quad (2b)$$

Table 4. ANOVA

	Output sulfur concentration				Sorption capacity			
Source	SS	DF	F-value	P-value	SS	DF	F-value	P-value
X_1	433,20	1	4498,94	< 0,0001	0,065	1	2945,87	< 0,0001
X_2	51,67	1	536,59	< 0,0001	$7{,}212*10^{-3}$	1	327,57	< 0,0001
X_3	10,45	1	108,56	< 0,0001	$2{,}023*10^{-3}$	1	91,88	< 0,0001
X_4	0,01	1	0,14	0,7139	$2{,}189*10^{-6}$	1	0,10	0,7560
X_1^2	0,06	1	0,61	0,4452	$1{,}596*10^{-5}$	1	0,73	0,4051
X_2^2	1,06	1	11,05	0,0036	$4{,}509*10^{-5}$	1	2,05	0,1686
X_3^2	0,01	1	0,07	0,7925	$9{,}768*10^{-6}$	1	0,44	0,5134
X_4^2	20,26	1	210,45	< 0,0001	$4{,}122*10^{-3}$	1	187,24	< 0,0001
X_1X_2	0,06	1	0,65	0,4304	$2{,}128*10^{-3}$	1	96,64	< 0,0001
Model	517,74	9	597,44	< 0,0001	0,081	9	408,87	< 0,0001
Total	519,57	28			0,081	28		
Residual	1,83	19			$4{,}183*10^{-4}$	19		

The confirmation of the models significance is done by calculation of F-values which are 597,44 and 408,87, respectively. There is only 0,01% chance that models F-values this large could occur due to noise. The P-values lower then 0,0500 indicate that in the case of output sulfur concentration response model terms X_1, X_2, X_3 and X_4^2 are significant while the same can be seen for soprtion capacity response with the addition of X_1X_2 interaction model term. The other model terms with P-values larger then 0,0500 are retaind to ensure that the hyerarchy and consistency of the models are supported. The models variabilty is also tested by calculation of corelation coeficients, the R^2 values, which are 0,9965 and 0,9949, respectively. These R^2 values which are very close to 1 mean that developed empirical models can adequately account for nearly all the variability in the system.

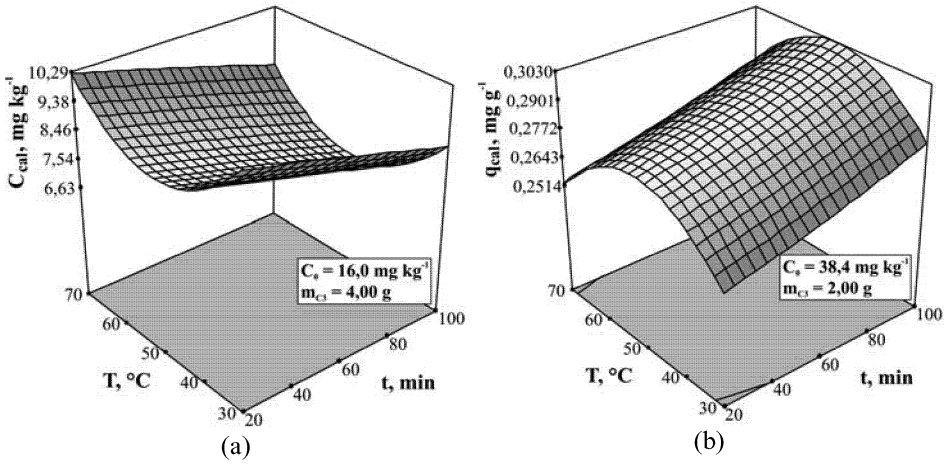
The testing of the models validity is further more carried out by by fitting predicted (C_{cal}, q_{cal}) against measured values (C_{exp}, q_{exp}) of output sulfur concentration and sorption capacity (Figs. 2a) and 2b)).



(a) (b)

Figure 2. *Predicted vs. measured values of (a) output sulfur concentration and (b) sorption capacity.*

The points on Figs. (2a) and (2b) are not diverging very much from the straight line which means that the calculated data fits very well with the experimental results. This is a confirmation that the models can adequately describe the behavior of the investigated system, i.e. the adsorptive desuflurization of diesel fuel. The optimal operating conditions can be determined by navigating the response surfaces as described by the developed models (Figs. 3(a) and 3(b)).



(a) (b)

Figure 3. *Response surface plots of (a) output sulfur concentration and (b) sorption capacity vs. temperature and time.*

The optimum with regard to the lowest calculated output sulfur concentration of 6,63 mg kg^{-1} was determined to be at 50 °C and 100 minutes with input sulfur concentration

of 16,0 mg kg^{-1} and adsorbent mass of 4,00 g. The optimal sorption capacity ($q_{opt,cal}$) of 0,3030 mg g^{-1} was determined to be at 50 °C and 100 minutes as well, but for input sulfur concentration of 38,4 mg kg^{-1} and adsorbent mass of 2,00 g. Since the fore mentioned process parameter combinations were not a part of the experimental design shown in Tab. 3, three separate experiments for each of those process parameter combinations were performed in order to check accuracy and further validate the models. The experimental results for optimal output sulfur concentration were 6,6, 6,6 and 6,5 mg kg^{-1} and for optimal sorption capacity were 0,3034, 0,2973 and 0,3014 mg g^{-1}, respecitvely. It is evident that very good agreement with the calculated values was achieved. The fact that optimal output sulfur concentration and sorption capacity are achieved for different values of the input sulfur concentration and adsorbent mass is in line with the results of our previous work, Muzic et al., 2008, as well as the work of Bakr et al., 1997.

4. Conclusions

Response surface methodology was used to model and optimize batch adsorption process for desulfurization of diesel fuel. Box-Behnken experimental design with four process parameters: input concentration, adsorbent mass, time, temperature, and five centre points was carried out and two runs resulted with sulfur content lower then 10 mg kg^{-1}, i.e. with 7,2 and 7,9 mg kg^{-1}, respectively. The statistical analysis of experimental data yielded second-order model equations for the two responses, output sulfur concentration and sorption capacity. The models were validated by analysis of variance and graphically, and their significance was determined as well as their very good ability to describe the behaviour of the system. This was reaffirmed after additional experiments were carried out at the conditions which were predicted by the model to be optimal regarding both responses. The experimental results were in very good agreement with calculated values. Since the main purpose of diesel fuel desulfurization is the achievement of the lowest possible sulfur content, the overall process optimum in this case is reached at 50 °C and 100 minutes with input sulfur concentration of 16,0 mg kg^{-1} and adsorbent mass of 4,00 g when sulfur concentrations of around 6,6 mg kg^{-1} are attained.

5. References

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