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A Modeling Optimization of Photocatalytic Liquefaction of Turkish Lignites using Response Surface Methodology

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In this study, the application of response surface methodology for modelling the influence of some operating variables such as reaction time, UV irradiation power and photocatalyst (TiO_2 and $ZnCl_2$) on the performance of liquid yields. The regression analysis, statistical significance and response surface were done using Design Expert Software for predicting the responses in all experimental regions. Mathematical Models demonstrate the functionality of different parameters to the three operating variables and their interactions based on the ANOVA analysis. Predicted values were found to be in good agreement with experimental values. Using numerical optimization, the optimum conditions for manufacturing of photocatalytic liquefaction of Turkish lignites, which were based on response surface and contour plots, were found as follows: reaction time of 7.12 days, UV irradiation power of 141 W and $ZnCl_2$ photocatalyst.

1. Introduction

The study of natural macromolecules which could substitute petroleum as energy and chemical feedstocks has been widely stimulated in the last decades, particularly those involving coal, shale oil and biomass. Among them, coal has received special attention due to its large proven reserves as well as the similarity between the products obtained by its processing and crude oil (Lancas (1990)). Coal (lignite and bituminous coal) is the most important natural energy source available in abundance in Turkey and used widely as fuel for thermal power plants (TPPs) producing electricity. Lignite coal is the largest energy source produced in Turkey. Turkish lignites the use of these coals for domestic purposes and in power generation causes serious environmental problems (Yılmaz (2008)). Coal liquefaction is one of the potential solutions to these problems. As one of the clean coal technologies, liquefaction has been attracting a resurgent interest. The liquefaction of coal to convert into alternative transportation fuels or clean liquid fuel has been paid more and more attentions. Liquefaction of coal aims to obtain liquid or solvent-soluble molecules by treating coal under various conditions (Schobert and Song, (2002)). Coals may be liquefied by UV irradiation at ambient temperature and pressure. Although different catalysts are used to enhance liquid product yields and selectivity in the thermally activated liquefaction reactions, their use in the process photochemical liquefaction/dissolution are very rare. Oyedun et al., (2012) proposed the optimisation of the operating parameters in multi-stage pyrolysis in order to limit the increase in completion time and also reduce the overall energy. Šíma and Hasal, (2013) studied photocatalytic degradation of textile dyes in a TiO_2/UV System.

In assessing the effect of treatments on quality attributes, the use of an adequate experimental design is particularly important (Karacan and Toğrul, (2007)). Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It usually contains three stages: (i) design and experiments, (ii) response surface modelling through regression, (iii) optimization. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions (Karacan et al (2007)). Although the optimization of experimental conditions using RSM was widely applied in a large area of chemical processes, there is not the application in photocatalytic liquefaction of Turkish lignite. In this study, the

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application of response surface methodology for modelling the influence of some operating variables such as reaction time, UV irradiation power and photocatalyst (TiO_2 and $ZnCl_2$) on the performance of liquid yields. The regression analysis, statistical significance and response surface were done using Design Expert Software for predicting the responses in all experimental regions. Mathematical Models demonstrate the functionality of different parameters to the three operating variables and their interactions based on the ANOVA analysis. Predicted values were found to be in good agreement with experimental values.

2. Materials and Methods

2.1 Experimental section

In this study, two lignites obtained from the Beypazarı and Tunçbilek mining basins, which differ considerably in mineral matter, were used. The lignite samples were ground in a porcelain ball mill and sieved to -0.3 mm. The sieved samples were stored in plastic containers under a nitrogen atmosphere. All experiments were carried out with air-dried samples. The main characteristics of the lignites samples are given in Table 1. Photochemical dissolution of lignite samples was carried out in a 500 mL quartz flask equipped with a magnetic stirrer at UV cabin, which has six high-pressure 30 W mercury lamps (Philips UV-C). The self-designed batch irradiation set-up are given elsewhere (Karacan and. Toğrul,(2007)). The flask was first charged with a mixture of 75 g of tetralin as the solvent and 15 g of ground, air-dried lignite in the non-catalytic conditions. The catalytic dissolution experiments were performed using an impregnation method with TiO_2 and $ZnCl_2$ (Merck) as the catalyst. In the impregnation, the first stage consists of mixing by stirring the 15 g lignite samples with a solution consisting of 100 g of water and 0.75 g of a chemical reagent. Mixing was performed at 85 °C and lasted for 3 h. After mixing, the coal slurry was subjected to vacuum drying at 100 °C for 24 h. The amount of loaded catalyst was 0.75 g, so the catalyst concentration of the air-dried lignites was 5 % wt. As stated in the non-catalytic experiments, the flask was first charged with a mixture of 75 g of tetralin and 15 g of impregnated lignite samples. Then the mixture of lignite-tetralin was exposed to UV irradiation in the 60-180 W of irradiation power and the range of 1-10 days. Experiments were also carried out in the dark (the 0 W of irradiation power) under identical conditions.

2.2 Experimental design

The design of experiment (DOE) method is used to design the experiments in such a way to analyze the effect of parameters while using a minimum number of experiments and also to evaluate the interaction between the effective operating parameters. The response surface methodology (RSM) is a technique accompanied by DOE methods used for modelling and analysis of problems where a desired output variable (response) is influenced by several independent variables. The RSM was developed initially by Box and Wilson in 1951 to support the improvement of manufacturing processes in the chemical industry (Hill and Hunter, (1966)). The first step in the RSM practice is to find the functional relationship between the response variables and the independent variables to generate the response surface for analysis purposes. This response surface can be maximized or minimized to find the optimum experimental conditions for a process even if these optimum conditions are not located in the range of variables experimented. Usually, first- or second-order polynomials are used to estimate this relationship, and the coefficients of the model are found using least-squares fit with the experimental data. Because the interactions between variables are important for this study, the central composite design (CCD) method of

Table 1: Analysis of the lignite samples

	Beypazarı	Tunçbilek
Proximate analysis (wt%)		
Moisture	13.00	2.88
Ash	25.55	49.69
Volatile matter	29.19	24.85
Fixed carbon[a]	32.26	22.58
Ultimate analysis (wt% daf)		
C	69.56	69.89
H	4.50	5.14
N	1.25	2.82
S	4.98	2.02
O[a]	19.71	20.13

Table 2: The experiment range and levels of independent variables

Variables	Range and levels		
	-1	0	+1
Reaction time (days)	1	5	10
Power (W)	60	120	180
Catagoric	TiO_2	UV	$ZnCl_2$

experimental design, which is the most common design to fit second-order polynomials, is used here to be able to predict the non-linear interactions between parameters. In this method, three types of experimental runs including factorial runs (2k), axial runs (2k), and centre runs (nc) should be performed, where k is the number of variables (Lazic (2004)). Two factors in the design are the number of replication of the centre point and the distance of the axial runs from the centre (a). In the face-cantered CCD design, a is equal to 1 and locates the axial points on the centres of the faces of a cube (located at (±1, 0, 0), (0, ±1, 0) and (0, 0, ±1)). A value of nc = 2 is often sufficient to give a good variance across the experimental range, but more can be used to increase the accuracy of the results. Six replications of the central run, suggested by the Design Expert_ software (2005), are performed at the midpoints of all the operating ranges to estimate the residual error. Considering two effective parameters and three replications of the centre points, the number of experiments required for this study can be calculated as:

$$N = 2^k + 2k + n_c = 2^2 + 2(2) + 3 = 11 \quad (1)$$

If categorical factors are added, the central composite design will be duplicated for every combination of the categorical factor levels. In this work, there is a categorical factor with 3 levels, in this state, the number of experiments are 33. The list of experimental points calculated for this study using the Design Expert_ software and their corresponding response parameters are shown in Table 2. Each response is used to develop an empirical model that correlates the response to the three operating variables using a second-order polynomial given by:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_{ii}^2 \quad (2)$$

where Y is the predicted response, b_0 the intercept, b_i the linear coefficients ,b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients, and x_i, x_j are the normalized values of the response variables.

Statistical tests are performed to evaluate the precision of the empirical second-order polynomial correlation. Although these correlations are only valid for the range of operating conditions and the experimental setup tested here, they are useful for studying the relative influence of the effective variables and making rough predictions of the systems performance. Because the operating variables have different scales, the variables are normalized to the interval [-1, 1] before the polynomial regression is applied.

3. Results and Discussion

In the present work, the relationship between response (total liquid yields and oil yield) and two independent factors (reaction time and irradiation power) and categorical factor with 3 levels (ZnCI2, TiO2, UV) were studied. The experimental results at each point were obtained based on the designed variables as suggested in Table 3 for Tunçbilek lignite. The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert 7.0.11 software from State-Ease Inc. The quadratic model expressed by Eq(1), where the variables take their coded values, represents total liquid yields (Y_1), oil yield (Y_2) as a function of reaction time (A), irridation power (B) and photocatalyst (C). The final model in terms of actual value is given in Eqs(3) and (4).

$$Y_1 = 41.42 + 2.13A + 2.72B - 0.95C[1] + 1.32[C2] - 0.16AB + 1.86AC[1] + 2.33AC[2] - 1.03BC[1] + 0.079BC[2] - 11.94A^2 - 0.22B^2 \quad (3)$$

$$Y_2 = 32.75 + 1.98A + 1.09B - 0.19C[1] - 0.53[C2] - 0.065AB + 1.77AC[1] + 0.45AC[2] - 0.46BC[1] + 2.04BC[2] - 10.61A^2 - 0.48B^2 \quad (4)$$

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The results obtained were then analyzed by analysis of variance (ANOVA) to assess the goodness

of fit. The significant quadratic models and the corresponding significant model term for all responses are tabulated in Tables 4 and 5.

Table 3: List of designed experiments to study the effects of two operating factors (reaction time and irradiation power), categorical factor with 3 levels (ZnCl2, TiO2, UV) and experimental responses (total liquid yields and oils) for Tunçbilek lignite

Run No.	Reaction Time (Day)	Irradiation Power (W)	Photocatalyst	Total Liquid Yields	Oil Yield
1	1.00	60.00	ZnCl2	28.45	23.15
2	1.00	180.00	TiO2	25.34	17.47
3	5.00	120.00	UV	42.59	30.63
4	5.00	180.00	ZnCl2	45.23	33.27
5	10.00	120.00	UV	34.81	22.89
6	1.00	180.00	TiO2	27.53	20.64
7	5.00	180.00	TiO2	43.25	33.27
8	1.00	120.00	UV	25.24	18.87
9	5.00	120.00	TiO2	41.35	31.88
10	1.00	120.00	ZnCl2	32.75	20.45
11	5.00	180.00	TiO2	43.25	33.14
12	10.00	180.00	UV	37.50	27.70
13	5.00	120.00	UV	42.59	30.63
14	10.00	180.00	TiO2	29.99	24.17
15	5.00	60.00	TiO2	35.76	26.65
16	10.00	60.00	UV	32.79	22.01
17	10.00	120.00	TiO2	33.85	25.63
18	5.00	60.00	UV	36.29	25.87
19	5.00	120.00	UV	42.59	30.63
20	5.00	120.00	ZnCl2	38.50	35.32
21	5.00	120.00	ZnCl2	38.50	35.32
22	1.00	60.00	UV	25.54	18.87
23	5.00	60.00	ZnCl2	36.25	33.42
24	10.00	180.00	ZnCl2	30.92	19.43
25	1.00	120.00	TiO2	23.69	21.50
26	5.00	120.00	TiO2	41.35	31.88
27	10.00	120.00	ZnCl2	27.35	23.45
28	1.00	180.00	TiO2	25.34	17.47
29	5.00	180.00	UV	46.42	37.20
30	10.00	60.00	TiO2	31.25	27.43
31	10.00	60.00	ZnCl2	24.65	21.50
32	1.00	180.00	ZnCl2	34.66	21.60
33	5.00	180.00	ZnCl2	45.23	33.27

Table 4: ANOVA for the regression model and respective model Y1

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	Remarks
Model	1,516.04	11	137.82	37.03	0.0001	Significant
A	33.87	1	33.87	9.10	0.0066	Significant
B	141.75	1	141.75	38.08	0.0001	Significant
C	31.49	2	15.75	4.23	0.0286	Significant
AB	0.27	1	0.27	0.074	0.7885	Not Significant
AC	155.87	2	77.93	20.94	0.0001	Significant
BC	11.79	2	5.89	1.58	0.2288	Not Significant
A^2	1,091.75	1	1,091.75	293.29	0.0001	Significant
B^2	0.36	1	0.36	0.096	0.7600	Not Significant
Residual	78.17	21	3.72			
Lack of Fit	78.17	14	5.58			

Table 5: ANOVA for the regression model and respective model Y_2

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	Remarks
Model	1,044.20	11	94.93	19.67	0.0001	Significant
A	30.91	1	30.91	6.40	0.0194	Significant
B	17.92	1	17.92	3.71	0.0676	Not Significant
C	9.77	2	4.89	1.01	0.3805	Not Significant
AB	0.045	1	0.045	0.009	0.9237	Not Significant
AC	46.45	2	23.22	4.81	0.0190	Significant
BC	43.03	2	21.52	4.46	0.0244	Significant
A^2	862.22	1	862.22	178.64	0.0001	Significant
B^2	1.67	1	1.67	0.35	0.5630	Not Significant
Residual	101.36	21	4.83			
Lack of Fit	101.35	1	47.24	5,996.89	0.0001	Significant

From Table 4, it was observed that the linear term of reaction time (*A*), irridation power (*B*) and photocatalyst (C) has a large significant effect on the liquid yields due to the high *F*-value. The quadratic term of reaction time (A^2) with an *F*-value of 293.29 is more significant than the irridation power (B^2) with an *F*-value of 0.096. Furthermore, the effect of interaction between reaction time and photocatalyst (AC) also affect the total liquid yields significantly (F value 155.87).

From Table 5, it was observed that the linear term of reaction time (*A*) and irridation power (*B*) has a large significant effect on the liquid yields due to the high *F*-value of 19.67 and 6.64, respectively. The quadratic term of reaction time (A^2) with an *F*-value of 178.64 is more significant than the irridation power (B^2) with an *F*-value of 0.35. However, the interaction between reaction time and irridation power (AB), the effect of interaction between irridation power and photocatalyst (BC) also affect the oil yield significantly (*F*-values 4.81 and 4.46). The models presented high determination coefficients (R^2) and low the coefficient of variation (CV).These values were obtained as follows: R^2 = 0.95 and CV = 5.53 for Y_1; R^2 = 0.91 and CV = 8.27 for Y_2. The closer the R^2 is to 1, the better the model fits the experimental data, the less the difference between the predicted and observed values.

Figures 1 and 2 show the contour plot and responses for the effect of reaction time and irridation power on the Total liquid yields on during liquefaction of Tunçbilek lignite. It was observed that the total liquid yields increased with the increase of reaction time and irridation power. It was found that the optimum total liquid yield of 39.99 was achieved at reaction time of 7.12 days, UV irradiation power of 141 W and $ZnCl_2$ photocatalyst.

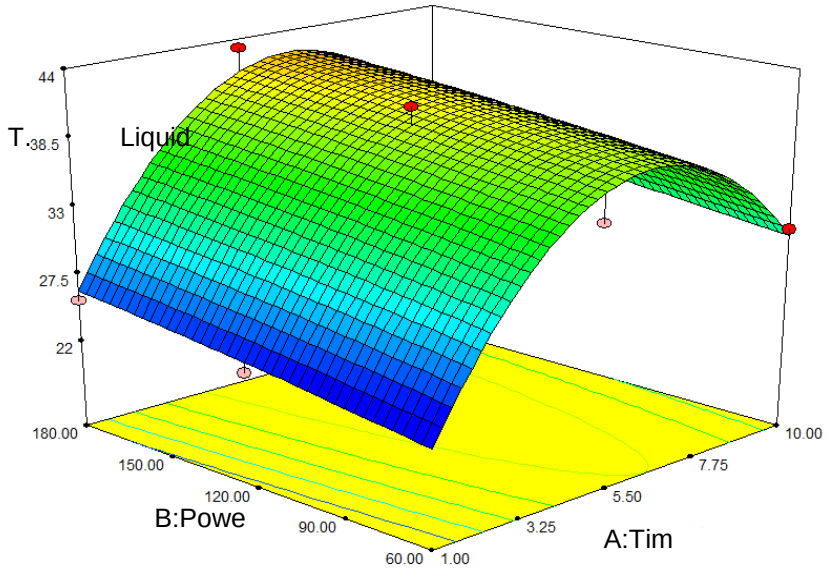

Figure 1: Response Surface plots showing the effects of reaction time and irridation power

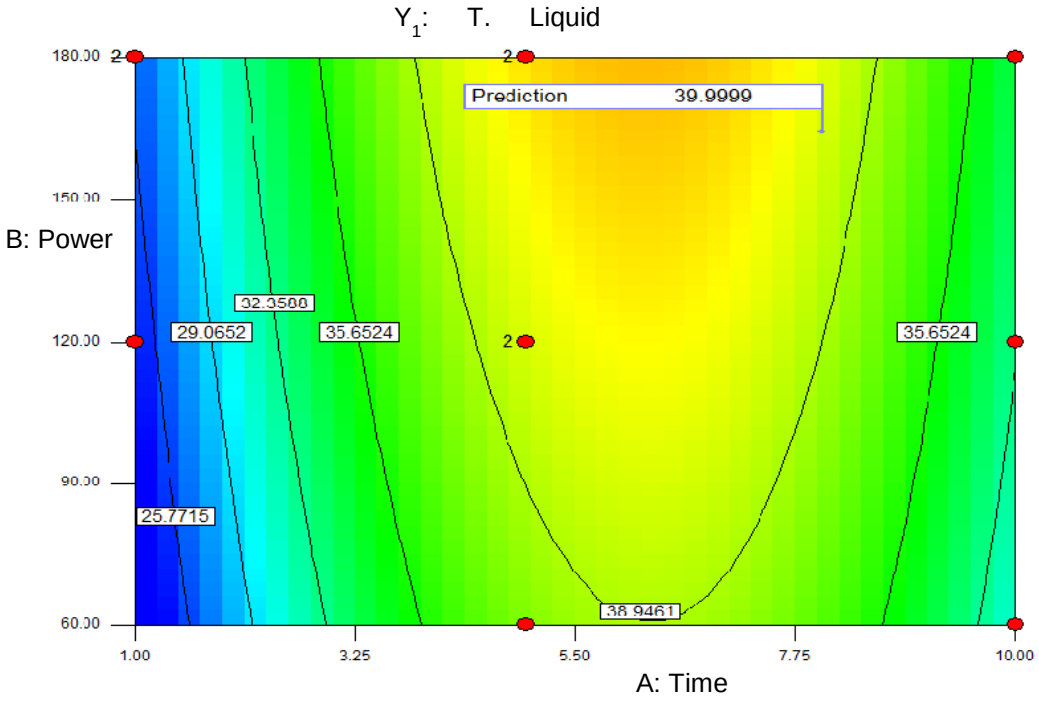

Figure 2: Contour plot showing the effects of reaction time and irridation power

The RSM based on central composite design (CCD) was employed for the optimization of liquefaction of Tunçbilek lignite. The R^2 values of all parameters show a good fit of the models with experimental data. Based on the two models obtained, numerical optimization was conducted. Optimum conditions were confirmed and fitted the experimental data well.

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