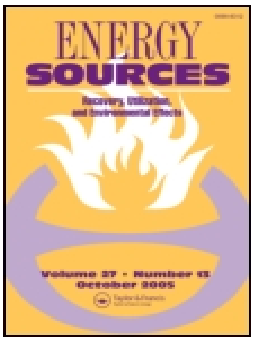

Taylor & Francis
Taylor & Francis Group

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

ISSN: 1556-7036 (Print) 1556-7230 (Online) Journal homepage: http://www.tandfonline.com/loi/ueso20

Response Surface Methodological Approach to Optimize Microwave-assisted Extraction of Cayirhan Lignite

Ö. Sönmez, B. Gözmen, M. Ö. Çakır & T. Cevik

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37:2458–2466, 2015

ISSN: 1556-7036 print/1556-7230 online
DOI: 10.1080/15567036.2012.721053

Response Surface Methodological Approach to Optimize Microwave-assisted Extraction of Cayirhan Lignite

Ö. Sönmez,[1] B. Gözmen,[1] M. Ö. Çakır,[1] and T. Cevik[1]

[1]*Department of Chemistry, Arts and Science Faculty, Mersin University, Mersin, Turkey*

Microwave-assisted extraction of Cayirhan lignite was investigated using N-methyl-2-pyrrolidinone. The response surface methodology was employed to optimize the microwave-assisted extraction conditions. The controllable factors selected in the present investigation included the extraction temperature, extraction time, and solvent-to-coal ratio. The obtained results demonstrated that the extraction temperature was the most important factor, which had a positive influence on the extraction yield. The statistical model predicted that a higher extraction yield of up to 28% would be obtained at the following optimized conditions: an extraction temperature between 217–230°C, a solvent-to-coal ratio of 13.5, and an extraction time of 28–30 min.

Keywords: coal, microwave-assisted extraction, N-methyl-2-pyrrolidinone, optimization, response surface methodology

1. INTRODUCTION

Solvent extraction of coal aims to obtain liquid or solvent soluble molecules from coal. Many extraction methods, such as Soxhlet (Renganathan et al., 1988), supercritical fluid extraction (Vayisoglu et al., 1993; Sangon et al., 2006), pressurized liquid extraction (Butala et al., 2000), and ultrasonic-assisted extraction (Iino et al., 1988), have been performed to the coal. The use of microwaves as a source of energy is rapidly growing. Microwave irradiation (MI) has been used to promote numerous organic reactions under mild conditions (Lidstrom et al., 2001). Compared to thermal heating, the main advantage of the microwave energy is that it can easily penetrate to the particle inside and all particles can get heated simultaneously (Hamid, 1992; Mingos and Baghurst, 1991). The other advantages of MI are low organic-solvent consumption and reduced processing time. In recent years, microwave energy has been used in coal processing and conversions researches, such as pyrolysis (Monsef-Mirzai et al., 1992), desulphurization (Elsamak et al., 2003; Mi et al., 2007), and liquefaction (Simsek et al., 2001; Yagmur and Togrul, 2005). Simsek et al. (2001) investigated the liquefaction of six Turkish coals in tetralin using MI. They found that MI was effective in producing liquid products within a short reaction time and the largest fraction in liquid products was oil. Yagmur and Togrul (2005) investigated the liquefaction of Turkish coals in tetralin by microwave using microwave receptors. Similar conclusions were drawn from the

Address correspondence to Dr. Ö. Sönmez, Department of Chemistry, Arts and Science Faculty, Mersin University, Ciftlikkoy Campus, Mersin 33343, Turkey. E-mail: ozgursonmez@hotmail.com

other studies on liquefaction of Turkish coal by MI (Sonmez and Giray, 2011; Simsek et al., 2002; Agun et al., 2005).

N-methyl-2-pyrrolidinone (NMP) is a good solvent to use for solvent extraction of coal and has been used by numerous researchers (Renganathan, 1988; Iino et al., 1988; Hengfu, 2005; Kim et al., 2008). NMP is a strong polar solvent and it dissociates and disrupts the strong ionic and hydrogen bond in coal (Masaki et al., 2004). As a polar compound, the dielectric constant of NMP is 32.55. Because of the high dielectric constant, NMP absorbs microwave energy strongly and reaches high temperatures in a short time. Therefore, NMP was used as a solvent to extract coal. It was reported that NMP gave more than 60% extraction yield at its boiling temperature of 202°C (Renganathan, 1988). The extraction yield of Pasir sub-bituminous coal using crude methyl-naphthalene oil (CMNO) increased by around 10% from 54.3 to 64.2% when 20% NMP was added to CMNO (Masaki et al., 2004). Kim et al. (2008) reported that the extraction yield increased with the increase in extraction temperature.

Response surface methodology (RSM) is a useful method for developing, improving, and optimizing processes. It is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors (Xie et al., 2010). The main advantage of RSM is the reduced number of experimental trials needed to evaluate the multiple parameters and their interactions. Therefore, it is less laborious and time-consuming than the other approaches required for optimizing a process. The aim of the present study was to optimize the microwave-assisted extraction (MAE) of coal using RSM at moderate conditions. The effects of the extraction time, temperature, and solvent-to-coal ratio were investigated. Next, RSM was employed to optimize the operational conditions targeted at the maximum extraction yield.

2. EXPERIMENTAL

2.1. Coal Sample

Cayirhan Turkish lignite was used in the present experiments. The sample was ground in a ball mill and sized to <60 mesh, dried at 80°C for 12 h in a vacuum, and stored in a desiccator before use. The proximate and ultimate analyses are presented in Table 1. The proximate analyses were determined according to the ASTM standard (ASTM D3172-74). NMP was used as extraction solvent without further purification. Each experiment was repeated three times.

TABLE 1
Analysis of the Coal Sample

Proximate Analysis, wt%, db	
Ash	27.2
Volatile matter	27.0
Fixed carbon	45.8
Elemental analysis (wt%, daf)	
C	58.6
H	4.7
N	1.9
S	6.4
O[a]	28.4

[a]By difference.

TABLE 2
Experimental Design of Extraction Yield of Cayirhan Coal with MAE

Factor Name	*Low Actual Value*	*High Actual Value*
Temperature (°C)	180	230
Time (min)	10	30
Solvent-to-coal ratio (v/m)	5	15

2.2. Extraction

The extraction of coal was carried out in a Mars (CEM) microwave reaction system equipped with a temperature control system and a magnetic stirrer. In brief, coal (2 g) and NMP were charged into a polytetrafluoroethylene (PTFE)-lined extraction vessel. Then the vessel was closed. The contents of the vessel were heated to the desired temperature in 5 min, and held at the desired temperature for a certain time period according to the experimental design. During the extraction, both the temperature and pressure in a single vessel (control vessel) were monitored by temperature and pressure sensors, respectively. Stirring was applied during extraction for homogeneous heating. The maximum oven power was 800 W. MAE was carried out using different extraction times (10, 20, 30 min), extraction temperatures (180, 205, 230°C) and solvent-to-coal ratios (5/1, 10/1, 15/1). After the extraction, the solid residue and the liquid phase were separated by filtration. The residue was washed with fresh hot NMP until the filtrate became almost colorless. Then the residue was washed with deionized water, methanol, and then with acetone, and then dried in vacuum at 80°C for 12 h. The extraction yield was determined from the weight of the residue.

2.3. Optimization of MAE

The D-optimal design of the Design Expert® 8 program was used for the response surface methodology in the experimental design. The D-optimal criterion can be used to select points for a mixture design in a constrained region. The independent variables of temperature, extraction time, and solvent-to-coal ratio were coded with low and high levels in the D-optimal design, as presented in Table 2. Here, the extraction yield of coal was the response.

In the optimization process, the responses can be simply related to the chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is shown as follows:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} {x_j}^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{jj} x_j x_j + e_i, \quad (1)$$

where Y is the response, k is the number of factors, x_i and x_j are the coded variables, β_0 is the constant coefficient, β_j, β_{jj}, and β_{ij} are interaction coefficients of linear, quadratic, and interaction effects, respectively, and e_i is the residual error (Montgomery, 1996; Myers and Montgomery, 2002).

The purpose of using the response surface methodology was to investigate the response over the entire variables' space and identify the region where it reaches its optimum value.

3. RESULTS AND DISCUSSION

A set of three process variables, the operating temperature (T), the extraction time (t), and the solvent-to-coal ratio (S/C) were identified to investigate their influence on the extraction yield

TABLE 3
Results of D-optimal Design Validation Conditions

Run	*T, °C*	*t, min*	*Solvent-to-coal Ratio*	*Extraction Yield, wt%, daf*
1	230	30	15	27.8
2	230	30	10	26.8
3	230	10	5	22.7
4	180	30	15	25.0
5	180	10	5	22.3
6	230	30	5	23.2
7	230	20	15	27.2
8	205	30	10	26.5
9	205	10	15	25.3
10	180	30	5	22.2
11	230	30	5	23.4
12	205	20	5	23.4
13	180	10	15	23.0
14	230	10	15	26.6
15	180	20	10	23.2
16	180	30	5	22.7
17	180	30	15	24.6
18	180	10	5	23.0
19	180	20	10	24.0
20	230	10	10	25.4

(wt%, daf) of Cayirhan lignite using NMP with MAE. The experimental results obtained in the D-optimal design with the real values for the three variables studied are presented in Table 3.

The significance of the independent variables and their interactions were tested by the analysis of variance (ANOVA) and *t*-test statistics in the program for Eq. (1). The quadratic model was found to be statistically significant. Thus, it was chosen for the subsequent data analysis. The results of the quadratic surface response model, as determined by the analysis of variance (ANOVA) for the extraction efficiency, are presented in Table 4.

The quadratic regression model was highly significant as the *F*-test (*F*-value) was found to be 45.56 with a very low probability value (P-value < 0.0001). This indicated that only 0.01% of the model was due to noise (Ghasempur et al., 2007). The quality of fit of the polynomial model was expressed by the coefficient of determination, R^2, and the adjusted coefficient of determination,

TABLE 4
ANOVA Test for the Extraction Yield % with MAE

Parameter	*Sum of Squares*	*Degrees of Freedom*	*Mean* Square	*F-value*	*P-value*
Model	59.19	9	6.58	45.56	<0.0001
x_1: temperature (°C)	15.84	1	15.84	112.13	<0.0001
x_2: time (min)	3.69	1	3.69	26.09	0.0005
x_3: solvent-to-coal	27.45	1	27.45	194.37	<0.0001
$x_1 \times x_3$	6.41	1	6.41	45.36	<0.0001
Residual	1.41	10	0.14		

Note: $R^2 = 0.9767$; $R^2_{adj} = 0.9557$; Adeq Precision = 21.641.

$R^2{}_{adj}$. The obtained values of R^2 and $R^2{}_{adj}$ were 0.9767 and 0.9557, respectively. The goodness of fit of the model was checked by the correlation coefficient (R^2) between the experimental and model predicted values of the response variable, as shown in Figure 1a. A plot of the normal probability of the residuals is shown in Figure 1b. The residuals from the analysis should be normally distributed. This plot is an important diagnostic tool to detect and explain the systematic departures from the assumption (Singh et al., 2011). The trend of the residual to a normal distribution is shown in Figure 1b. Here, the errors are normally distributed and are independent of each other. In addition, the error variance is also homogeneous.

The experimental results were evaluated with RSM of Design-Expert® 8. The approximating functions of the extraction yield percent (Y) in terms of the coded variables obtained with D-optimal design are shown as follows:

$$Y = 25.56 + 1.00x_1 + 0.49x_2 + 1.38x_3 + 0.077x_1x_2 + 0.72x_1x_3 + 0.39x_2x_3 - 0.82{x_1}^2 + 0.30{x_2}^2 - 0.84{x_3}^2. \quad (2)$$

Solvent-to-coal ratio (x_3), extraction temperature (x_1), and the two-variable interaction $x_1 \times x_3$ have been demonstrated to be the crucial factors for the extraction yield of Cayirhan lignite with MAE, while the extraction time (x_2) has no significant influence on the optimization.

The extraction efficiency of coal in the MAE process correlated some important parameters, such as the temperature, MI period, and solvent-to-coal ratio. Figure 2a shows the response surface and the contour plots for the effects of the extraction temperature and solvent-to-coal ratio on the extraction yield at 30 min extraction time. It was observed that the extraction yield increased with an increasing temperature and solvent-to-coal ratio. To achieve a high extraction yield at low temperatures, the solvent-to-coal ratio should be over 13. As shown in Figure 2a, when the solvent-to-coal ratio is increased from 5 to 15 at 205°C, the extraction yield is increased from 23.7 to 27.4%. An increase in the temperature from 180 to 230°C at 11 solvent-to-coal ratio resulted in an increase of the extraction yield from 24.6 to 27%. On the other hand, while solvent-to-coal ratio is 15 at 230°C, the extraction yield is 28.3%. It was observed that the temperature affected the extraction yield of coal and, thus, a high extraction yield was expected at high temperatures. It was reported that NMP resulted in a high extraction yield when the extraction was carried out at high temperatures, such as 200–300°C, although the extraction yield with NMP at room temperature was low (Iino et al., 1988; Takanohashi et al., 2003). At higher temperatures, the solvent molecules had higher kinetic energy. Thus, the diffusion of the solvent vapor into the intermolecular coal structure was faster. As a result, some of the physical forces between the coal molecules were dissociated at higher temperatures (Giri and Sharma, 2000). Consequently, the NMP extraction yield increased with increasing temperature.

The effects of temperature and extraction time on the extraction yield, while keeping the solvent-to-coal ratio at 14, is shown in Figure 2b. Experiments were carried out to study the effect of temperature on the extraction yield at 180, 205, and 230°C. When the extraction was performed at a temperature above 210°C, a maximum yield of 28% was obtained after 20–30 min extraction time. It was observed that the increase in the extraction time had little effect on the extraction yield at a temperature below 200°C.

Experiments were also carried out to study the effect of the solvent-to-coal ratio on the extraction yield at 5, 10, and 15. The effect of the solvent-to-coal ratio and extraction time on the extraction yield at 226°C is shown in Figure 2c. When the solvent-to-coal ratio was under 9, the extraction yield was low and did not change with the extraction time. However, when the solvent-to-coal ratio was 12–13 and the extraction time was after 25 min, the extraction yield of over 28% was obtained.

The experimental results were optimized by Design-Expert software using the approximating function of extraction yield percent in Eq. (1). Desirability is an objective function that ranges from

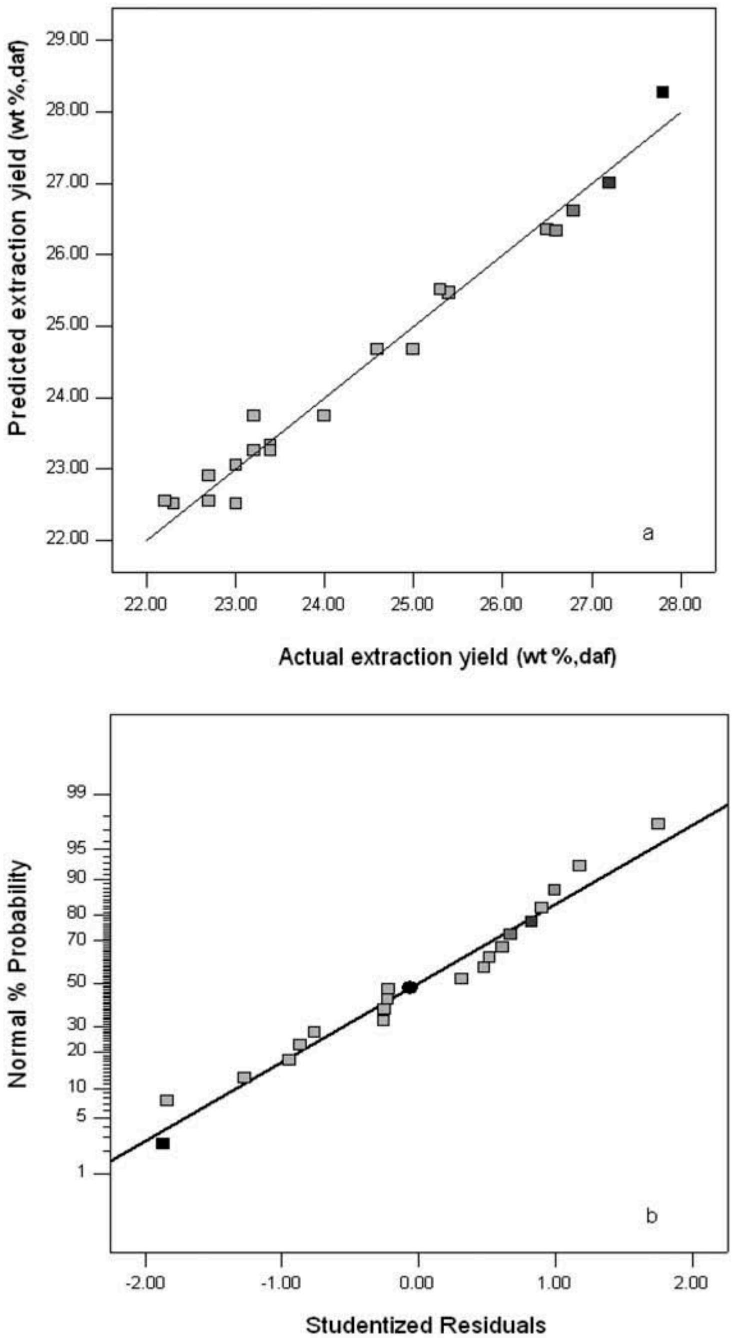

FIGURE 1 (a) Plot of the measured and model predicted values of the response variable and (b) the normal probability plot of the raw residuals.

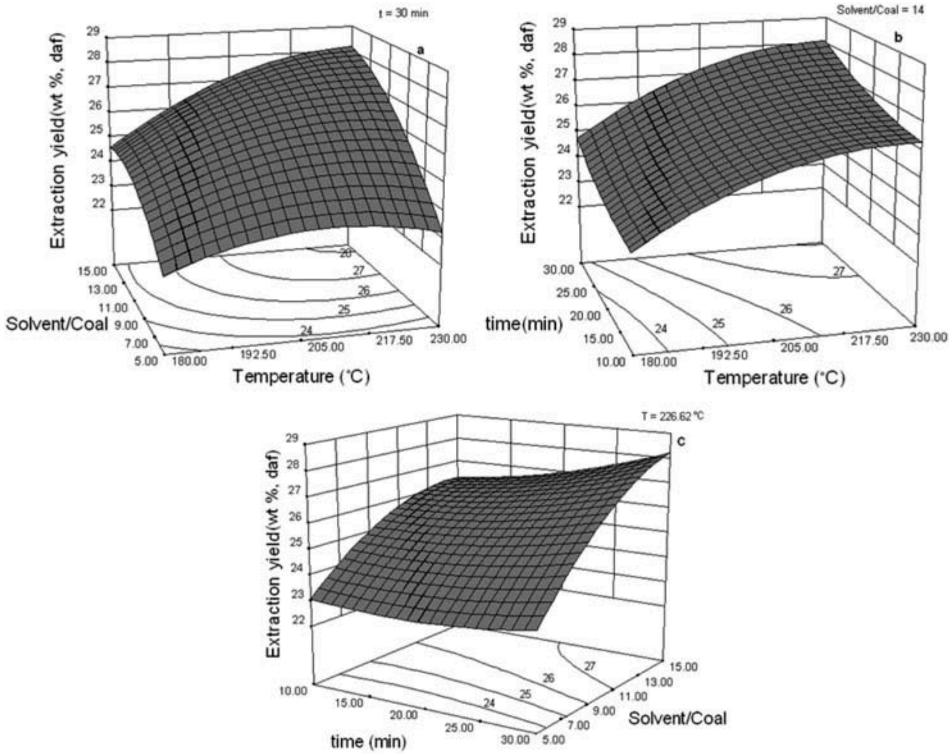

FIGURE 2 Response surface and contour plots of extraction of Cayirhan lignite with temperature, solvent-to-coal ratio, and extraction time.

zero outside of the limits to one at the goal. In this study, temperature was preferred in the range of 210–230°C; extraction time was preferred in the range of 20–30 min, and solvent-to-coal ratio equal to 13.5, whereas extraction yields were maximized. The desirability values to maximize extraction yield percent (between 27 and 28%) depending on the selected goal for the variables are shown in Figure 3. Optimal conditions were chosen with the highest desirability as solvent/coal ratio at 13.5, time between 28–30 min, and temperature between 217–230°C to avoid spending excess solvent.

4. CONCLUSIONS

In the present study, the RSM was applied to optimize the MAE of Cayirhan lignite with NMP. The experimental data obtained were fitted to a quadratic equation using multiple regression analysis and also analyzed by appropriate statistical methods. The 3-D response surface and the contour plots derived from the mathematical models were applied to determine optimal conditions. The optimum MAE conditions were as follows: an extraction temperature between 217–230°C, a solvent-to-coal ratio of 13.5, and an extraction time of 28–30 min. It was concluded that the RSM is a more economical approach, which offers a large amount of information from a small number of experiments. Thus, the present study demonstrates that the number of experiments can be significantly reduced by RSM.

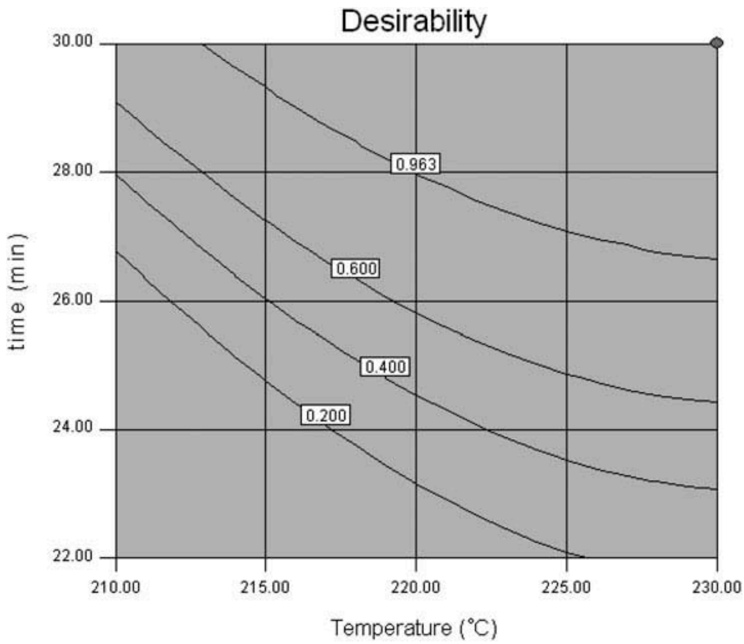

FIGURE 3 The desirability values to maximize extraction yield percent of Cayirhan coal.

ACKNOWLEDGMENT

The authors are grateful to Mersin University Research and Application Center (MEITAM) for providing the facilities for the microwave-assisted extractions experiments.

FUNDING

This work was supported by the Mersin University Research Fund (Contract no: BAB-FEF KB (OS) 2010-4A) and TUBITAK (Scientific and Technical Research Council of Turkey, Project Reference 111M145).

REFERENCES

Agun, N. E., Yagmur, E., Simsek, E. H., and Togrul, T. 2005. The effect of swelling pretreatment on the coal liquefaction in tetralin with microwave energy. *Energy Sources Part A* 27:1105–1115.

Butala, S. J. M., Medina, J. C., Hulse, R. J., Bartholomew, C. H., and Lee, M. L. 2000. Pressured fluid extraction of coal. *Fuel* 79:1657–1664.

Elsamak, G. G., Öztas, N. A., and Yürüm, Y. 2003. Chemical desulfurization of Turkish Cayirhan lignite with HI using microwave and thermal energy. *Fuel* 82:531–537.

Ghasempur, S., Torabi, S. F., Ranaei-Siadat, S .O., Jalali-Heravi, M., Ghaemi, N., and Khajeh, K. 2007. Optimization of peroxidase-catalyzed oxidative coupling process for phenol removal from wastewater using response surface methodology. *Environ. Sci. Technol.* 41:7073–7079.

Giri, C. C., and Sharma, D. K. 2000. Mass-transfer studies of solvent extraction of coals in N-methyl-2-pyrrolidone. *Fuel* 79:577–585.

Hamid, M. 1992. Basic principles of microwave power heating. *Heat Transfer Eng.* 13:73–84.

Hengfu, S. 2005. Effect of coal extracted with NMP on its aggregation. *Fuel* 84:939–941.
Iino, M., Takanohashi, T., Ohsuga, H., and Toda, K. 1988. Extraction of coals with CS_2-N-methyl-2-pyrrolidinone mixed-solvent at room-temperature-effect of coal rank and synergism of the mixed-solvent. *Fuel* 67:1639–1647.
Kim, D. S., Woo, K. J., Jeong, S. K., Rhim, Y. J., and Lee, S. H. 2008. Production of low ash coal by thermal extraction with N-methyl-2-pyrrolidinone. *Korean J. Chem. Eng*. 25:758–763.
Lidstrom, P., Tierney, J., Wathey, B., and Westman, J. 2001. Microwave assisted organic synthesis—A review. *Tetrahedron* 57:9225–9283.
Masaki, K., Yoshida, T., Li, C., Takanohashi, T., and Saito, I. 2004. The effects of pretreatment and the addition of polar compounds on the production of "HyperCoal" from subbituminous coals. *Energy Fuels* 18:995–1000.
Mi, J., Ren, J., Wang, J. C., Bao, W. R., and Xie, K. C. 2007. Ultrasonic and microwave desulfurization of coal in tetrachloroethylene. *Energy Sources Part A* 29:1261–1268.
Mingos, D. M. P., and Baghurst, D. R. 1991. Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chem Soc. Rev*. 20:1–5.
Monsef-Mirzai, P., Ravindran, M., McWhinnie, W. R., and Burchil, P. 1992. The use of microwave heating for the pyrolysis of coal via inorganic receptors of microwave energy. *Fuel* 71:716–717.
Montgomery, D. C. 1996. *Design and Analysis of Experiments*, Fourth Ed. New York: John Wiley & Sons.
Myers, R. H., and Montgomery, D. C. 2002. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, Second Ed. New York: John Wiley & Sons.
Renganathan, K., Zondlo, J. W., Mintz, E. A., Kneisl, P., and Stiller, A. H. 1988. Preparation of an ultra-low ash coal extract under mild conditions. *Fuel Process. Technol*. 18:273–278.
Sangon, S., Ratanavaraha, S., Ngamprasertsith, S., and Prasassarakich, P. 2006. Coal liquefaction using supercritical toluene-tetralin mixture in a semi-continuous reactor. *Fuel Process. Technol*. 87:201–207.
Simsek, E. H., Karaduman, A., and Olcay, A. 2001. Liquefaction of Turkish coals in tetralin with microwaves. *Fuel Process. Technol*. 73:111–125.
Simsek, E. H., Karaduman, A., and Togrul, T. 2002. The effect of moisture on the liquefaction of some Turkish coals in tetralin with microwave energy. *Energy Sources Part A* 24:675–684.
Singh, K. P., Gupta, S., Singh, A. K., and Sinha, S. 2011. Optimizing adsorption of crystal violet dye from water by magnetic nanocomposite using response surface modelling approach. *J. Hazard. Mater*. 186:1462–1473.
Sonmez, O., and Giray, E. S. 2011. Producing ashless coal extracts by microwave irradiation. *Fuel* 90:2125–2131.
Takanohashi, T., Xiao, F., Yoshida, T., and Saito, I. 2003. Difference in extraction yields between CS2/NMP and NMP for Upper Freeport coal. *Energy Fuels* 17:255–256.
Vayisoglu, E. S., Erbatur, O., Bartle, K. D., Erbatur, N. G., Harput, B., Snape, C. E., and Garcia, R. 1993. Supercritical toluene extraction of maceral concentrates obtained from Turkish coals. *Fuel Process. Technol*. 36:25–32.
Xie, J. H., Xie, M. Y., Shen, M. Y., Nie, S. P., Li, C., and Wang, Y. X. 2010. Optimisation of microwave-assisted extraction of polysaccharides from *Cyclocarya paliurus* (Batal.) lljinskaja using response surface methodology. *J. Sci. Food Agric*. 90:1353–1360.
Yagmur, E., and Togrul, T. 2005. Part 1. The effect of microwave receptors on the liquefaction of Turkish coals by microwave energy in a hydrogen doner solvent. *Energy Fuels* 19:2480–2487.