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Research article

Optimization of solvent extraction process of some Turkish coals using response surface methodology and production of ash-free coal

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ABSTRACT: In order to produce ash-free coal (AFC) from three Turkish coals, solvent extraction of coals using 1-methylnaphthalene (1-MN) at different temperatures were conducted. The extraction yield of coals was found dependent on coal, temperature, and solvent type. When there was usage of 1-MN as solvent, the extraction yield was low. However, on addition of N-methyl-2-pyryrolidone (NMP) or quinoline (QN) into 1-MN, the extraction yield increased. Following the extractions, we obtained AFC with less than 0.65% ash content for the three coals used in this study. The response surface methodology (RSM) was employed to investigate the solvent extraction conditions. The factors investigated were extraction temperature and additional polar solvent ratio. The obtained results demonstrated that either excess amount of polar solvent into 1-MN should be added at low temperatures or extraction should be done at high temperatures using less polar solvent to obtain an increase in extraction efficiency. The sensitivity and validity of results obtained by RSM were confirmed through validation experiments. The results of validation experiments showed a good agreement between the experimental and predicted values (relative error <1.2) and that indicated the robustness of the models. © 2016 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: coal; ash-free coal; solvent extraction; response surface methodology; 1-methylnaphthalene

INTRODUCTION

Turkey's energy demand is increasing year after year mainly because of population growth and industrialization. Turkey abounds with low-rank coals, especially lignites, which are unsuitable for fuel use because of high content of moisture, mineral matter, and organic oxygen, resulting in low calorific value and causing high pollution from their burning. On the other hand, the abundance of valuable organic components, including aromatic and aliphatic chemicals, makes lignites attractive raw materials for the production of value-added products.[1,2] Therefore, it is essential to develop alternative processing technologies for effective utilization of lignites. There have been many attempts made to find effective approaches to the efficient use of lignites. One of the efficient methods of using coal is to produce ash-free coal (AFC), namely 'hypercoal,' from low-rank coal. The process of hypercoal has been developed in Japan and the aim of this process is to develop AFC with the content of the inorganic component as low as 0.02%.[3,4] To obtain hypercoal, coal is extracted with high boiling point organic solvent, such as N-methyl-2-pyryrolidone (NMP), 1-methylnaphthalene (1-MN), quinoline (QN), tetralin, and corbol oil. Several works have concentrated on the preparation of ash free-coals using solvent extraction techniques. Yoshida *et al.*[4] reported that they obtained extraction yields higher than 60% for several types of bituminous coals at 360 °C with the nonpolar solvents 1-MN and light cycle oil (LCO), while they could attain an extraction yield of around 80% with polar solvents NMP and crude methylnaphthalene oil (CMNO). Miura *et al.*[5] carried out thermal extraction of Illinois No. 6 coal and obtained nearly a 70% extraction yield with tetralin. Li *et al.*[6] studied solvent extraction with organic solvents, such as nonpolar 1-MN and polar NMP, for various ranks of coal. Extraction yield was 28–61% with 1-MN and reached about 90% when there was usage of NMP. Kim *et al.*[7] used NMP to produce low ash coal from low-rank coals. They reported that the extraction yield increased with the increase in extraction temperature, and the ash content of extracted coal decreased below 0.4% at 400 °C.

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Usually, polar solvents are more effective than nonpolar solvents for solvent extraction of low-rank coals. To increase the solvent extraction yield of low-rank coals in nonpolar solvents, there is addition of a small amount of polar component into nonpolar solvents. Kashimura *et al.*[8] reported that addition of a polar component that contained CMNO, such as indole and QN derivates, into 1-MN greatly increased the extraction yield. Yoshida *et al.*[9] investigated the effect of addition of some polar solvents into nonpolar solvents. They found that the extraction yield increases linearly with the increase of polar solvents. Masaki *et al.*[10] found that when 20% NMP was added to CMNO, the extraction yield of sub-bituminous coal increased by 10%.

To obtain value-added products from coal by solvent extraction, the coal must be extracted effectively. Various parameters, such as extraction temperature, extraction pressure, extraction time, coal-to-solvent ratio, and particle size, significantly affect solvent extraction of coal. Response surface methodology (RSM) is a useful method for developing, improving, and optimizing processes and is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors.[11] One of the advantages of RSM is that it reduces the number of experiments, which results in the use of less material and reagents. Therefore, it is less laborious and time-consuming than the other approaches required for optimizing a process. Although the application of RSM is in varied areas, there are few publications on the optimization of solvent extraction of coal using RSM. Ghani *et al.*[12] employed the RSM for the optimization of liquefaction of Mukah Balingian low-rank Malaysian coal. They found that the predicted optimum conditions of liquefaction temperature and solvent mixed ratio were at 450 °C and 70:30 tetralin-to-water ratio, respectively, with coal conversion of 70.6%.

The main objectives of present work were to optimize the influence of temperature and additional polar solvent ratio on the solvent extraction of coal using RSM and to produce AFC extracts. While there was usage of 1-MN as extraction solvent, QN and NMP were used as polar additives.

EXPERIMENTAL SECTION

Materials

We used three coals of different ranks for this investigation: Çayırhan lignite from mid-Anatolia, Tunçbilek lignite from west Anatolia, and bituminous Üzülmez coal from the Western Black Sea region. The samples were ground in a ball mill and sized to <60 mesh, dried at 80 °C for 12 h in vacuum, and stored in a desiccator before use. Table 1 presents the proximate and ultimate analyses. Determination of the proximate and ultimate analyses were according to the ASTM standards (ASTM D3172-74 and ASTM 5373). All solvents used were commercial pure chemical reagents without further purification.

Solvent extraction experiment

The extractions were carried out in a Mars (CEM) microwave reaction system equipped with a temperature control system and a magnetic stirrer. There was usage of 1-MN as extraction solvents and two polar solvents (NMP and QN) as additives. In brief, coal (2 g) and solvent 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, temperature and pressure sensors monitored both the temperature and pressure in a single vessel (control vessel), respectively. There was application of stirring during extraction for homogeneous heating. After the extraction, the solid residue and the liquid phase were separated by filtration. The residue was washed with fresh hot 1-MN until the filtrate became almost colorless. Then, the residue was washed several times with toluene and acetone, and then dried in vacuum at 80 °C for 12 h. Each experiment was repeated three times. The extraction yield was defined as follows:

$$\textit{Extraction Yield}\ (wt\%,\ daf) = \left[\left(1-\frac{\mathrm{M}_r}{\mathrm{M}_\mathrm{c}}\right)\Big/\left(1-\frac{\mathrm{A}_c}{100}\right)\right]\times 100 \qquad (1)$$

where, Mc (g), Mr (g), and Ac (wt%, db) are the initial mass of the coal, the mass of the residue, and the ash content of the initial coal, respectively.

Table 1. Analysis of the coal samples.

Proximate analysis (wt%, db)	Tunçbilek	Çayırhan	Üzülmez
Ash	20.9	27.2	6.2
Volatile matter fixed	35.4	27.0	28.9
carbon	43.7	45.8	64.9
Elemental analysis (wt%, daf)			
C	82.2	67.6	91.8
H	4.7	4.6	3.9
N	3.8	2.2	1.3
S	2.4	9.1	0.7
O[a]	6.9	16.5	2.3

[a] By difference.

AFC production

The liquid extracts were concentrated by distillation and addition of an excess of n-hexane precipitated the solids extracts. The precipitate was washed with n-hexane and dried in vacuum at 80 °C for 12 h. When NMP was used as an additive, the precipitate was washed with a water/acetone mixed solvent (4:1 by volume) to remove NMP after washing with n-hexane. The precipitate was termed as AFC. Calculation of the AFC yield was as follows:

$$AFC\ \ Yield, (wt\%,\ \ daf) = \left[\frac{\mathrm{M_{AFC}}}{\mathrm{M_C}\ (1 - \mathrm{A_C}\times 0.01)}\right]\times 100 \tag{2}$$

where, M_{AFC} (g) and M_c (g) are the mass of AFC and raw coal, respectively. Ac (wt%, db) is ash percentage in raw coal. The ash content in the solid extract was determined by the proximate analysis (ASTM 3174).

FTIR measurement

The FTIR spectra were carried out using Perkin-Elmer Spectrum 100 with an attenuated total reflectance (ATR) attachment. Each sample was scanned 32 times for a wave number range from 500 to 4000 $\mathrm{cm^{-1}}$ and at a spectral resolution of 4 $\mathrm{cm^{-1}}$.

Central composite design for coal extraction efficiency

RSM is a collection of mathematical and statistical techniques. RSM offers statistical design of experiment parameters that lead to peak process performance.[13] RSM produces precise maps based on mathematical models, which is derived from Eqn. (3). This second-order polynomial equation gives a relationship between the independent operating variables and the responses:

$$\begin{aligned} \mathrm{Y(Extraction\ \ Yield\ \ \%)} &= \beta_0 + \sum_{i=1}^{k} \beta_i x_i \\ &+ \sum_{i=1}^{k} \beta_{ii} x_i^2 \\ &+ \sum_{i=1}\sum_{j=1} \beta_{ij} x_i x_j + \varepsilon \end{aligned} \tag{3}$$

where, Y is the response (dependent variables), that is, experimental results, $x_{(i,j)}$ are several independent variables (factors), which influence the response, β_0 is the constant coefficient, β_i, β_{ii}, and β_{ij} are the coefficients for linear, quadratic, and interaction effects, and ε is the error.

The most known second-order design is central composite rotatable design (CCD). The number of the experiment was obtained according to $N = k^2 + 2k + C_p$, where k is the factor number and C_p is the number of central points.[14]

In this design, all factor levels have to be adjusted at five levels (−α, −1, 0, +1, −α). The alpha (α), 1, and 0 levels correspond to axial, factorial, and central points, respectively. The alpha (α) value varies from 1 to square root of the number of factors ($\sqrt{k}$), which produces a spherical geometry.[13] In the present study, the CCD design was employed for determining the optimum conditions of microwave extraction for three Turkish coals using two solvent mixtures (1-MN/NMP and 1-MN/QN). The independent variables (factors) used in this study were temperature (X_1) and the additional polar solvent ratio (NMP or QN) into the 1-MN (X_2). For two factors, the recommended number of experiments is 13.[14] Tables 2 and 3 give the levels of the two parameters investigated in this study and experimental results, respectively. Table 3 gives the extraction yield results together for the two solvents (NMP/QN), which were added into 1-MN.

RESULTS AND DISCUSSION

Statistical analysis

To ensure the statistical significance of the quadratic model employed for explaining the experimental data at a 95% confidence level, the model was tested by analysis of variance (ANOVA) results by using Desert Expert 9.0 software. The results of experiments, carried out in experimental conditions as given in Table 2, showed that the suitable quadratic model for the three Turkish coals when NMP was into 1-MN solvent and presented their corresponding fit quadratic model equations is as follows:

$$\begin{aligned} &Y(Extraction\ \ yield\ \ \%\ for\ \ \text{Çay ırhan}) \\ &\quad = 19.36 + 2.44X_1\ + 2.43X_2 + 0.075X_1X_2 \\ &\qquad -0.78X_1^2 - 1.40\ \ X_2^2 \end{aligned} \tag{4}$$

Table 2. Experimental ranges and levels of the independent variables.

Variables	Factors	Range and levels				
		−α (−1.414)	−1	0	+1	+α (+1.414)
Temperature (°C)	X_1	184	200	240	280	297
NMP or QN %	X_2	4	10	25	40	46

Table 3. Experimental design matrix because of CCD and results.

Run	Temperature (°C)	NMP/QN, %	Extraction yield, % (daf)		
			Çayırhan	Tunçbilek	Üzülmez
1	200	10	12.5/10.2	10.8/9.8	13.3/10.5
2	280	10	16.6/12.3	14.5/10.1	32.2/23.5
3	200	40	17.2/13.2	17.1/12.0	30.7/21.3
4	280	40	21.6/19.3	16.9/17.6	42,5/33.8
5	183	25	14.1/11.1	13.9/10.2	17.9/12.2
6	297	25	21.9/16.8	17.6/14.6	38.3/27.2
7	240	4	13.3/12.1	9.5/9.2	20.8/20.2
8	240	46	20.2/18.3	17.7/15.1	37.1/31.2
9	240	25	19.7/13.7	17.7/12.4	34.1/26.7
10	240	25	17.6/13.6	16.0/12.2	34.1/24.3
11	240	25	20.1/13.3	16.0/12.2	34.4/25.9
12	240	25	19.2/13.7	17.2/12.6	34.7/25.6
13	240	25	20.2/13.7	16.9/12.5	34.2/25.1

$$Y(\textit{Extraction\ \ yield\ \ \%\ for\ \ Tun\ çbilek}) = 16.76 + 1.09X_1\ + 2.54X_2 - 0.98X_1X_2 - 0.47X_1^2 - 1.54\ \ X_2^2 \tag{5}$$

$$Y(\textit{Extraction\ \ yield\ \ \%\ for\ \ Üz\ \}00FClmez}) = 34.30 + 7.44X_1\ + 6.34X_2 - 1.78X_1X_2 - 2.81X_1^2 - 2.39\ \ X_2^2 \tag{6}$$

When quinolin was added to 1-MN, fitted models were obtained as quadratic for Çayırhan and Üzülmez coals, and linear 2 factor interaction (2FI) for Tunçbilek coal.

$$Y(\textit{Extraction\ \ yield\ \ \%\ for\ \ Çay\ ırhan}) = 13.60 + 2.03X_1\ + 2.35X_2 + 1.00X_1X_2 - 0.031X_1^2 + 0.59\ \ X_2^2 \tag{7}$$

$$Y(\textit{Extraction\ \ yield\ \ \%\ for\ \ Tun\ çbilek}) = 12.35 + 1.52X_1\ + 2.26X_2 + 1.33X_1X_2 \tag{8}$$

$$Y(\textit{Extraction\ \ yield\ \ \%\ for\ \ Üz\ \}00FClmez}) = 25.52 + 5.84X_1\ + 4.58X_2 - 0.13X_1X_2 - 3.02X_1^2 - 0.016\ \ X_2^2 \tag{9}$$

Tables 4 and 5 give the ANOVA results for each model equation (Eqns (4–9). Obtained F-value for all models with a very low probability value (p-value), which was greater than the critical value of F ($F_{\alpha,df,n-(df+1)} = F_{0.05,5,7} = 3.97$) using $\alpha = 0.05$, confirming the adequacy of the model fits.[15] Pareto charts are extremely useful for analyzing which variables have the greatest cumulative effect on a given system. The single, synergistic, or antagonistic effects of each factor

Table 4. Analysis of variance regression model for solvent extraction of Turkish coals with 1-MN/NMP.

Coal	Source	Degrees of freedom	Sum of squares	Mean square	F-value	p-value
Çayirhan	Model	5	111.28	22.26	27.76	0.0002
	X_1:T	1	47.68	47.68	59.46	0.0001
	X_2: NMP%	1	47.33	47.33	59.52	0.0001
	Residual	7	5.61	0.80		
	Lack of fit	3	1.12	0.37	0.33	0.8036
	Pure error	4	4.49	1.12		
Tunçbilek	Model	5	81.88	16.38	30.81	0.0001
	X_1:T	1	9.53	9.53	17.93	0.0039
	X_2: NMP%	1	51.49	51.49	96.87	<0.0001
	Residual	7	3.72	0.53		
	Lack of fit	3	1.47	0.49	0.87	0.5268
	Pure error	4	2.25	0.56		
Üzülmez	Model	5	861.77	172.35	199.96	<0.0001
	X_1:T	1	443.27	443.27	514.27	<0.0001
	X_2: NMP%	1	321.97	321.97	87.43	<0.0001
	Residual	7	6.03	0.86		
	Lack of fit	3	5.77	1.92	29.61	0.0034
	Pure error	4	10.26	0.065		

Table 5. Analysis of variance regression model for solvent extraction of Turkish coals with 1-MN/QN.

Coal	Source	Degrees of freedom	Sum of squares	Mean square	F-value	p-value
Çayirhan	Model	5	83.62	16.72	69.96	<0.0001
	X_1:T	1	33.05	33.05	138.27	<0.0001
	X_2: QN %	1	44.03	44.03	184.19	<0.0001
	Residual	7	1.67	0.24		
	Lack of fit	3	1.55	0.52	17.26	0.0094
	Pure error	4	0.12	0.030		
Tunçbilek	Model	5	66.09	22.03	428.50	<0.0001
	X_1:T	1	18.37	18.37	357.31	<0.0001
	X_2: QN %	1	40.70	40.70	791.61	<0.0001
	Residual	7	0.46	0.051		
	Lack of fit	3	0.33	0.067	2.09	0.2472
	Pure error	4	0.13	0.032		
Üzülmez	Model	5	505.08	101.02	72.84	<0.0001
	X_1:T	1	272.77	272.77	196.68	<0.0001
	X_2: QN %	1	167.96	167.96	121.11	<0.0001
	Residual	7	9.71	1.39		
	Lack of fit	3	6.50	2.17	2.70	0.1806
	Pure error	4	3.21	0.80		

(temperature (T) and solvent % (NMP/QN)) were examined on extraction yields of three coal samples. This chart for NMP indicated that the both factors affected positively and almost equally on extraction yield of Çayırhan coal. While the percentage of added solvent was a major factor for Tunçbilek, it seems to be temperature for Üzülmez. Only for Çayırhan coal, two factors showed a positive synergistic effect (Fig. 1).

The percentage of added QN into 1-MN in extraction was the most important factor for Tunçbilek and Çayırhan coals; temperature seems to be a more prominent factor for Üzülmez coal. The synergistic effect of the two factors (TxQN%) seem fairly large positive value for Tunçbilek and Çayırhan. Figure 2 shows the relation between experimental and predicted extraction yields for the three coal samples, in case of the addition of NMP or QN into 1-MN. Predicted values were obtained by calculating quadratic or 2FI models, which were derived by using the approximation function (Eqns (4–11). Determination coefficient (R^2) value indicates how much variability the mathematical model can predict in the observed response values.[16] Also, Radj2 represents the amount of variation that can be explained by the model. Figure 2 presents the R^2 values for each model. The obtained R^2 values in the range of 96–99% indicated that the models could not explain only 1–4% of the total variation.[16] Figures 3 and 4 present the corresponding response 3D surface plots obtained from Eqns (4–9).

Interactive effect of temperature and additional polar solvents into 1-MN on extraction yield

Figures 3 and 4 show the effect of both temperature and the amount of polar solvents on the extraction yield for three coal samples. In this part of the experiment, solvent-to-coal ratio as 15 and the extraction time as 20 min were kept. As seen from Figs 3 and 4, extraction yield increases with increasing temperature. However, additional solvents, NMP and QN, show different effects on the extraction yield. Table 6 shows the

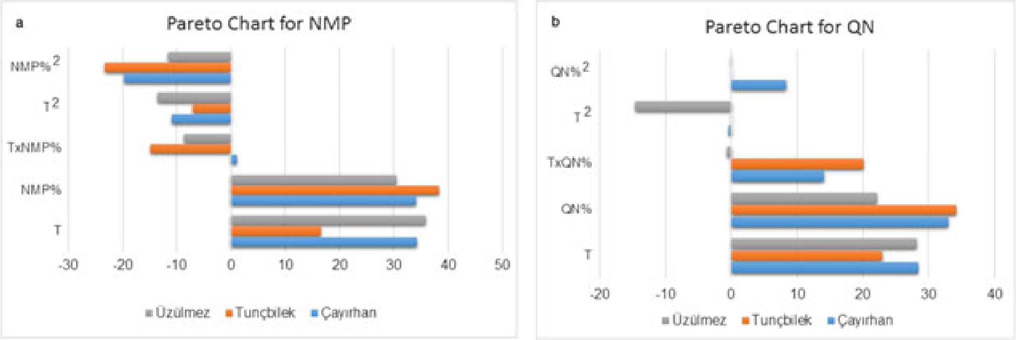

Figure 1. Pareto chart analysis when NMP (a) and QN (b) were added into 1-MN.

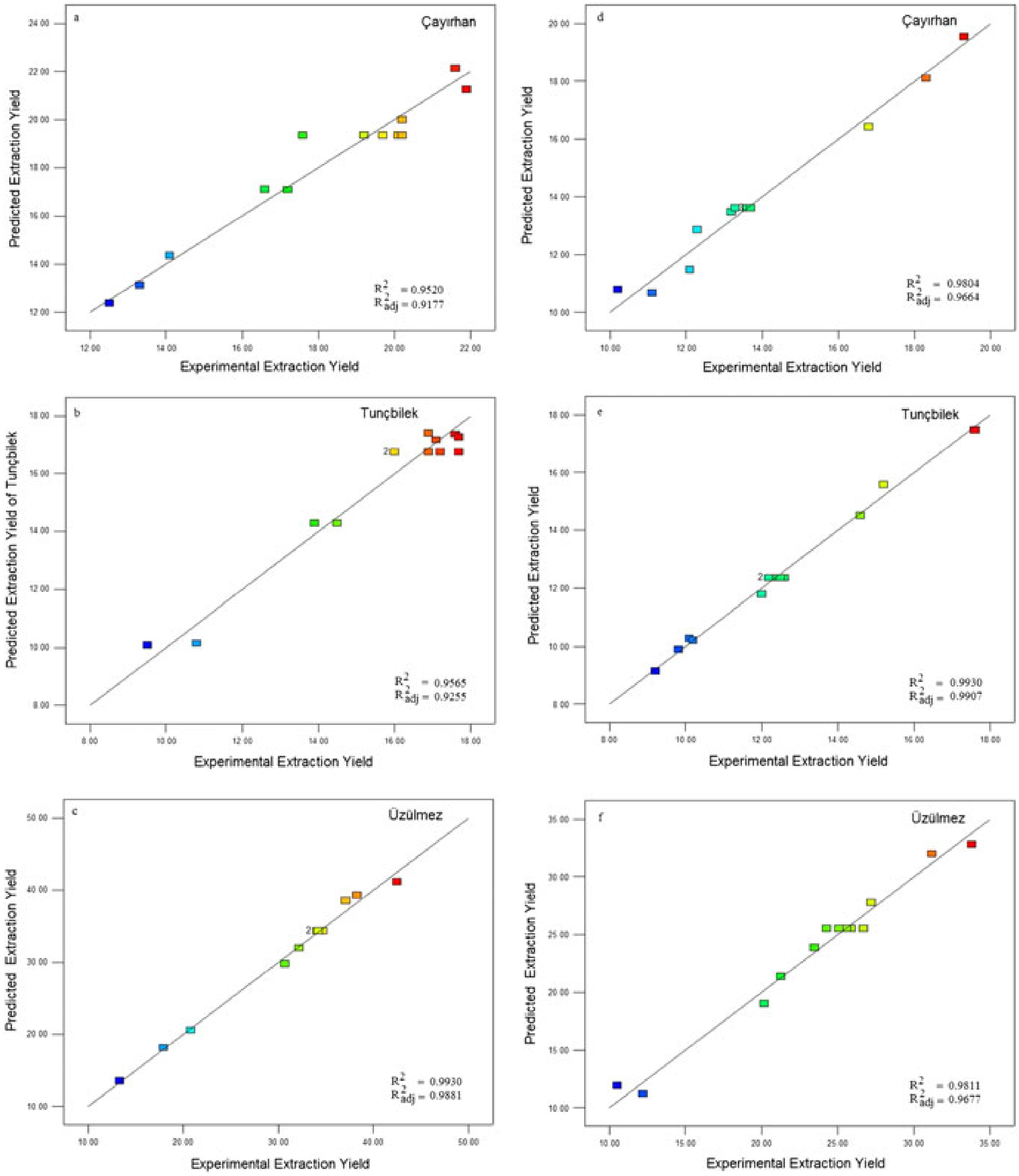

Figure 2. Predicted *vs* experimental plot for the extraction yield of coals by 1-MN/NMP (a–c) and 1-MN/QN (d–f) solvent mixtures.

extraction yields at higher (280 °C) and lower (200 °C) temperatures with lower (10%) and higher (%40) volumes of NMP and QN. It can be seen that the extractions performed at the highest temperature, with the lowest amount of polar solvents, and the extractions performed at the lowest temperature, with the highest amount of polar solvents, give similar extraction yields. For example, at a higher temperature of 280 °C and lower amount of NMP (10%), the extraction yields of Çayırhan, Tunçbilek, and Üzülmez coals are 17.1, 14.4, and 32%, respectively. On the other hand, at a lower temperature of 200 °C and higher amount of NMP (40%), the extraction yields of Çayırhan, Tunçbilek, and Üzülmez coals are 17.1, 17.2, and 29.8%, respectively. Similar results were obtained when there was usage of QN as the polar solvent. These results show that high extraction yields may be obtained with increasing the amount of polar solvents at lower extraction temperature. The lowest extraction yields were obtained at lower temperature and by using lower amount of polar solvents, and the highest extraction yields were obtained at higher temperature and by using higher amount of polar solvents. For maximum extraction yield for Çayırhan and Tunçbilek coals, temperature should be around 240–280 °C, while the amount of NMP% should be above 30%. To obtain

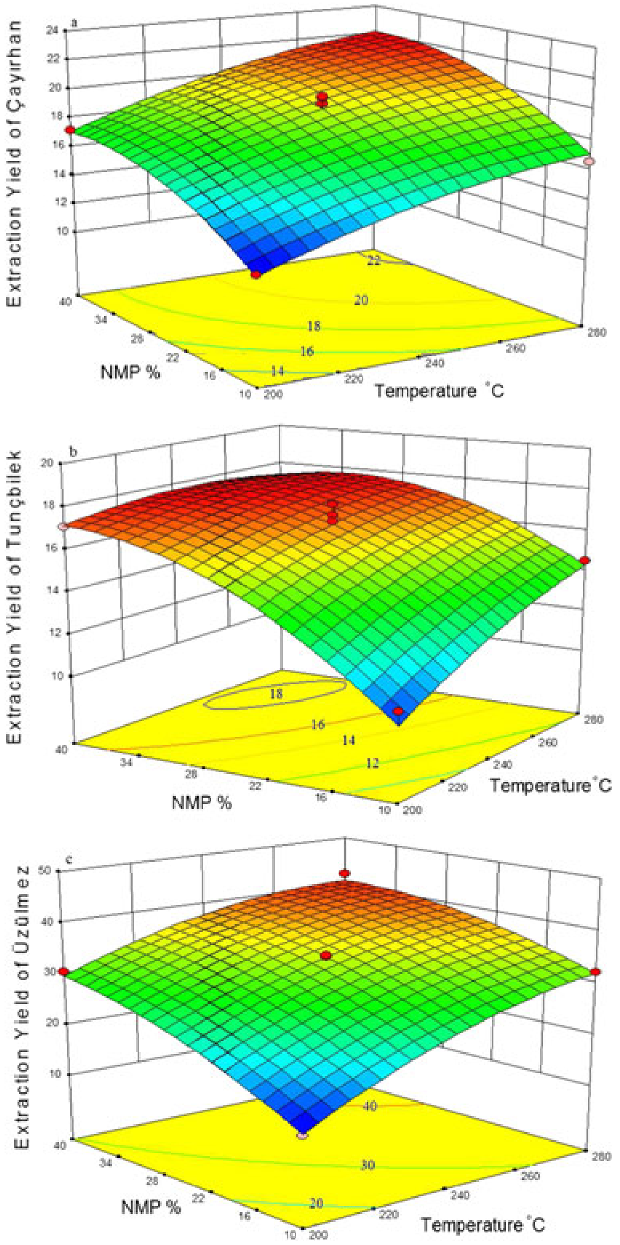

Figure 3. 3-D surface plots for interactive effects of temperature and NMP% on extraction yield of Çayırhan (a), Tunçbilek (b), and Üzülmez (c) coals.

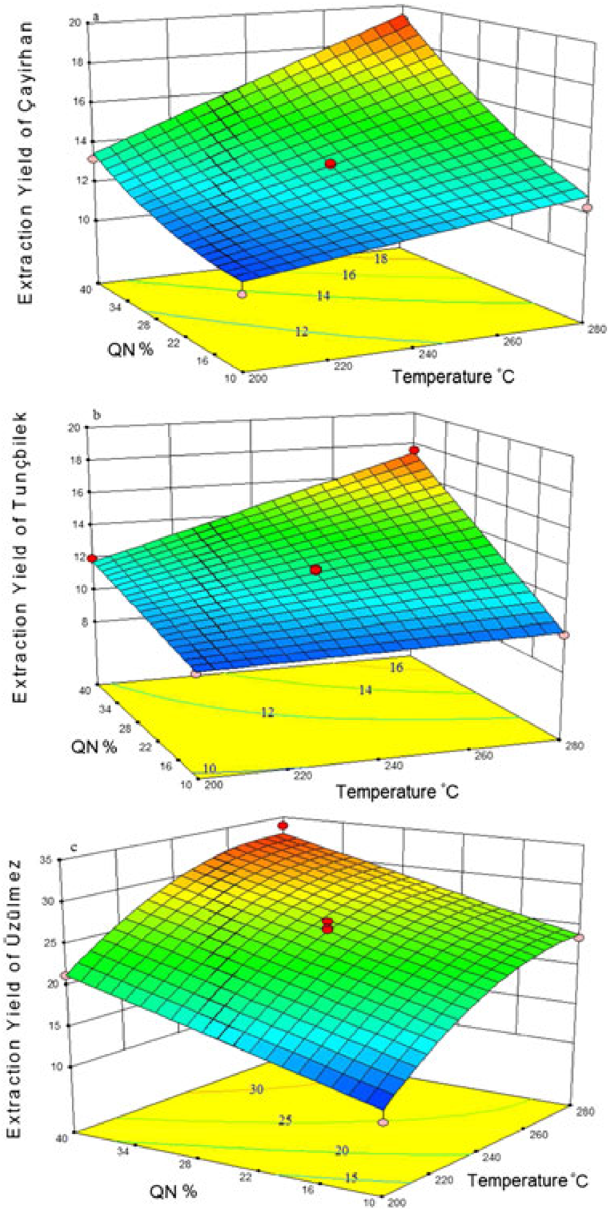

Figure 4. 3-D surface plots for interactive effects of temperature and QN% on extraction yield of Çayırhan (a), Tunçbilek (b), and Üzülmez (c) coals.

maximum extraction yield for Üzülmez coal, temperature should be in the range of 260–280 °C, and the amount of NMP% should be above 35%. On the contrary, when QN is used as polar solvent, the amount of QN% should be in the range of 35–40% for all coal samples. However, temperature should be around 250–280 °C for Çayırhan and Üzülmez coals, and 270–280 °C for Tunçbilek coal.

Model validation

The experimental verification test showed the sensitivity and validity of results obtained by RSM. Validation of the models that were proposed for extraction yield of three Turkish coals was performed in randomly selected experimental conditions. Table 7 gives the experimental conditions along with the model predicted and experimental results. While the majority of the experimental values were within the limits of predicted values, some of them were obtained close to this limit. The predicted extractions yields were in close agreement with validation experiment result, and this indicated that RSM models were accurate in designing and optimizing the extraction of coal.

Effect of temperature on the extraction yield

Temperature is an important factor for the solvent extraction of coal. At this stage of study, we examined

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Table 6. Extraction yields of coals at higher and lower temperatures with lower and higher volumes of additional solvent.

Coal	Temperature	Volume of additional solvent (%)	Extraction yield (wt%, daf) NMP	QN
Çayırhan	280	10	17.1	12.9
	200	40	17.1	13.5
	200	10	12.4	10.9
	280	40	22.1	19.5
Tunçbilek	280	10	14.4	10.3
	200	40	17.2	11.8
	200	10	10.2	9.9
	280	40	17.4	17.5
Üzülmez	280	10	32.0	23.9
	200	40	29.8	21.4
	200	10	13.5	11.9
	280	40	41.1	32.9

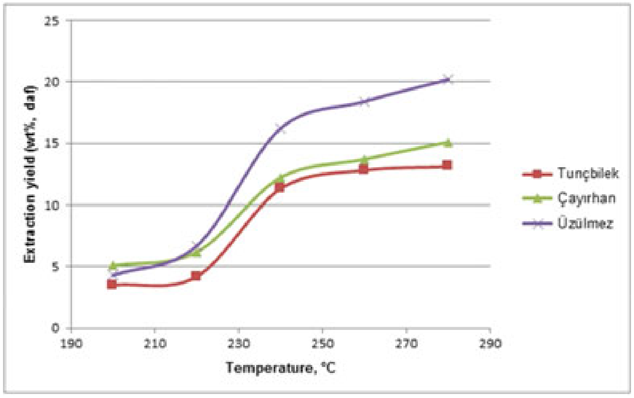

Figure 5. Variation of extraction yield by the extraction temperature.

the effect of extraction temperature on the extraction of coal in 1-MN. To understand the effect of temperature on extraction yield without adding polar solvents, extraction of coals was studied at different temperatures ranging from 200 to 280 °C using 1-MN alone with 20 min of holding time. The interactions between organic part of coal and an organic solvent drive the solvent extraction. During the extraction, with the relaxation of organic part of coal, the dissolution of coal in organic solvent takes places.[17] Relaxation of coal molecule proceeds in two ways, which are solvent-induced relaxation and thermal-induced relaxation.[4,9,17] Polar solvents, such as NMP, disrupt noncovalent interactions (hydrogen bonds, π–π interactions, van der Waals interactions) with solvent-induced relaxation even at low temperatures. However, nonpolar solvents, such as 1-MN, only induce a thermal relaxation of coal structure through breaking of noncovalent bonds.[18] Figure 5 shows variations of extraction yield by the extraction temperature. It can be observed that with the temperature rising from 200 °C to 280 °C, the extraction yields increase. Because 1-MN cannot disrupt the noncovalent interactions at low temperatures, the extraction yields of coals are low. With the increasing temperature, the extraction yields are increased. The high extraction yields obtained at high temperatures may be the outcome by the releasing noncovalent bonds by the thermal-induced relaxation. When the extraction temperature is 200 °C and 220 °C, the extraction yields of the three coal samples are almost the same. The extraction yields of Tunçbilek, Çayırhan, and Üzülmez coals at 220 °C are 4.2%, 6.2%, and 6.7%, respectively. After 240 °C, the extraction yields of Üzülmez sample are higher than that of the other two coal samples. This may be because of differences in the solvent-interacting sites between low-rank coals and bituminous coals.[19] The high extraction yield of Üzülmez sample maybe the result of the π–π interactions between the naphthalene ring of 1-MN and condensed aromatic rings in Üzülmez coal.[20]

Effect of polar solvents on extraction yield

To understand the effect of additive polar solvents on extraction yield at a given temperature, the extraction of coals were studied at 240 °C with holding time of 20 min. It was reported that the addition of polar solvents into a nonpolar solvent enhanced the extraction yield.[8,10] The extraction yields of coal

Table 7. Model validation set and corresponding values of the response variable.

Coal	Added solvent	T, °C	Experimental yield (wt%, daf)	Predicted yield (wt%, daf)
Çayırhan	35% NMP	270	22.2	21.8 ± 0.90
Çayırhan	35% QN	270	16.6	17.4 ± 0.49
Üzülmez	30% QN	260	26.1	29.2 ± 1.18
Üzülmez	40% QN	260	30.9	32.2 ± 1.18
Üzülmez	40% QN	240	28.5	30.1 ± 1.18
Üzülmez	20% NMP	260	36.2	35.2 ± 0.93
Tunçbilek	40% QN	240	14.0	14.6 ± 0.21
Tunçbilek	20% NMP	260	15.8	16.3 ± 0.73
Tunçbilek	40% NMP	260	16.4	17.7 ± 0.73

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samples are low, when 1-MN was used alone as the solvent. As seen in Figs 3 and 4, when NMP or QN was added in to 1-MN, the extraction yield greatly increased. Figure 6 shows variations of extraction yield by addition of polar solvents into 1-MN at 240 °C. For 25 vol% addition of polar solvents, the extraction yield increased by 1–18%. When 25 vol% NMP was added into 1-MN, the extraction yield was increased from 11.3% to 16.9% (the difference is 5.6%) for Tunçbilek coal, from 12.2% to 19.1% (the difference is 6.9%) for Çayırhan coal, and from 16.2% to 34.4% (the difference is 18.2%) for Üzülmez coal. On the other hand, when 25 vol% QN was added into 1-MN, the extraction yield was increased from 11.3% to 12.4% (the difference is 1.1%) for Tunçbilek coal, from 12.2% to 13.7% (the difference is 1.5%) for Çayırhan coal, and from 16.2% to 24.5% (the difference is 8.3%) for Üzülmez coal. As mentioned above, 1-MN is not strong enough to break noncovalent interactions in coal, so the extraction yield is low. However, the extraction yield increased with the addition of polar solvents. Polar solvents dissociate and disrupt the strong cross-links in the coal, so they give additional solvent-induced relaxation to the thermal-induced relaxation resulting in higher extraction yield.[10,21] Among the compounds added, it was found that NMP was more effective at extraction of coal than QN. NMP contains a pyrrlodine ring interacting strongly with aromatic rings, especially polycondensed aromatic compounds.[21,22] NMP also destroys the charge-transfer interactions and π–π interactions between aromatic groups in coal..[23,24] Therefore, NMP is more effective than QN.

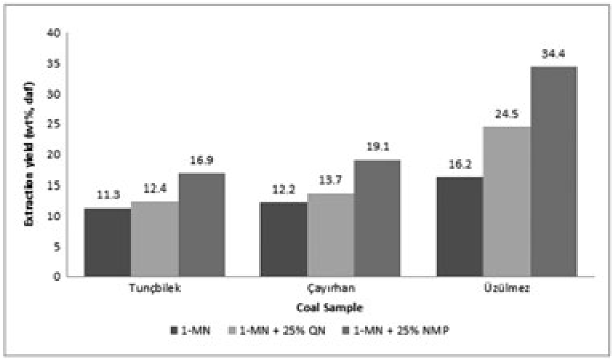

Figure 6. Extraction yields of coal samples in 1-MN with addition of polar solvent at 240 °C.

Ash contents of AFC

Table 8 shows the ash contents of AFC. As seen from Table 8, the extraction yields and AFC yields are different from each other. While the difference between extraction yields and AFC yields was low for Üzülmez and Tuncbilek coals, it was observed a remarkable difference for Çayırhan coal. This might be because of the high oxygen content of Çayırhan coal. When the coals are with high oxygen content, it makes coal more reactive, and thus there is production of more gaseous products during the thermal solvent extraction.[18,25] Besides, during the preparation of AFC, some components may dissolve in hexane added to produce AFC precipitation.[4–18] Therefore, this may cause the lower AFC yields than extraction yields for three coal samples.

With addition of polar solvents into 1-MN, the extraction yields and AFC yield were increased. However, the ash contents of AFC tended to increase by adding polar solvents, except in the case of Çayırhan coal. These results show that some ash materials could also be extracted using polar solvents. Yoshida *et al.*[9] suggested that polar solvents extracted some ash materials in coals of lower rank. It was reported that some organically associated species such as Al, Ca, and Fe remained in the extracts.[26] Similar results were observed during the production of AFC by solvent extraction with polar solvents.[21,25,27] The FTIR spectra of raw, residue, and solid extract were recorded, and Fig. 7 shows a typical FTIR spectrum. The FTIR spectrum shows a pair of peaks within the range of 1000–1100 and 3600–3700 cm^{-1}. These peaks indicate the presence of mineral matter.[4] In particular, the band close to 1020 cm^{-1} originates from the group Si–O–(ash).[28] However, these bands disappeared in the FTIR spectrum of solid extract.

Table 8. Ash contents of AFC with extraction yields and AFC yields.

Coal	Solvent	Extraction yield, (wt%,daf)	AFC yield, (wt%,daf)	Ash in AFC (wt%,db)
Çayırhan	1-MN	12.20	6.50	0.65
	1-MN + %25 QN	13.70	6.40	0.55
	1-MN + %25 NMP	19.10	10.80	0.50
Tunçbilek	1-MN	11.30	10.70	0.10
	1-MN + %25 QN	12.40	10.50	0.29
	1-MN + %25 NMP	16.90	13.60	0.31
Üzülmez	1-MN	16.20	16.00	0.06
	1-MN + %25 QN	24.50	23.90	0.09
	1-MN + %25 NMP	34.40	33.30	0.11

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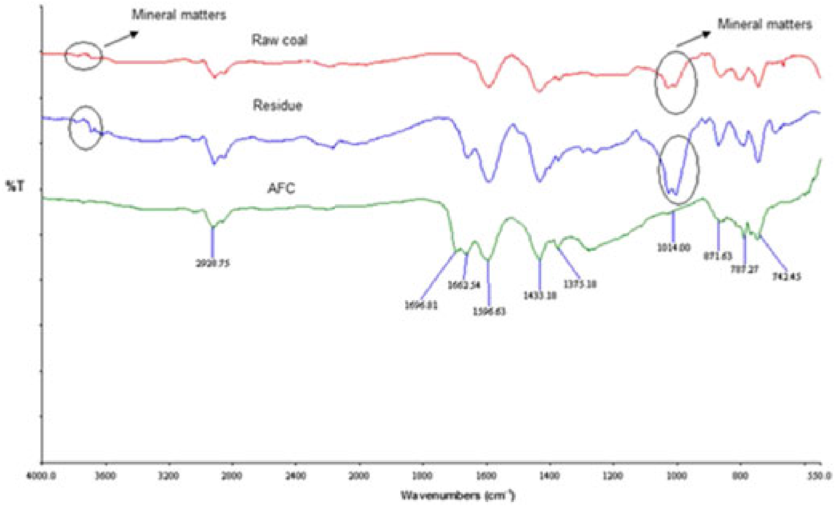

Figure 7. A typical FTIR of raw coal, residue, and AFC.

Meanwhile, the FTIR spectrum of residue shows bands belonging to minerals.

CONCLUSIONS

Solvent extractions were carried out on three Turkish coals to produce AFC. 1-MN and its NMP and QN mixtures were used as extraction solvents. RSM was applied to investigate the effect of two important extraction variables, that is, extraction temperature and additional polar solvents ratio. We obtained the following conclusions:

The extraction yield of coals was found dependent on coal type, temperature, and solvent. In all coal samples used, the extraction yield increased with the increase of extraction temperature. When extractions were performed below 240 °C, 1-MN was not very effective. However, a dramatic increase of extraction yield was obtained after 240 °C because of releasing noncovalent bonds in coal by the thermal-induced relaxation. Üzülmez coal, which is bituminous coal, showed higher extraction yields than Çayırhan, and Tunçbilek coals, which are lignites, because of the π–π interactions between the naphthalene ring of 1-MN and condensed aromatics rings in bituminous Üzülmez coal. On addition of NMP or QN into 1-MN, the extraction yield increased because of additional solvent-induced relaxation to the thermal-induced relaxation, resulting in increase in the extraction yield. Nevertheless, NMP was more effective at extraction of coal than QN. It has been ascertained that under extraction conditions, ash contents of AFC vary in rates between 0.65 and 0.06%. While the ash contents of AFC obtained from Çayırhan coal ranged between 0.65 and 0.50, the ash contents of AFC obtained from Tunçbilek and Üzülmez coals were 0.10–0.31 and 0.60–0.11%, respectively.

RSM was applied to investigate the effect of extraction temperature and additional polar solvent ratio on the extraction yield. The RSM results showed that extraction yield increased with increasing temperature and additional polar solvents. From the RSM results, the maximum extraction yields of Çayırhan, Tunçbilek, and Üzülmez coals were 22.1, 17.9, and 41.1% between 275 and 280 °C by adding 35–40 vol% NMP, respectively. The validation experiments were performed to test sensitivity and validity of results obtained by RSM, and a good agreement between the experimental and predicted values (relative error <1.2) was found. The present study demonstrates that the number of experiments can be significantly reduced by RSM, so RSM is a more economical approach, which offers a large amount of information from a small number of experiments.

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