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ORIGINAL ARTICLE

Thermal cracking of petroleum residue oil using three level factorial design

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Abstract   Thermal cracking of petroleum residue oil was conducted in a high-pressure batch reactor under various operating conditions, temperature in range 400–480 °C, reaction time 40–100 min and pressure 120–180 kPa in the presence of hydrogen. Statistical design of experiment (DOE), was used to evaluate the effect of important variables in the thermal cracking of residue oil, and to obtain the optimum operating conditions. Based on the three level factorial design, quadratic model was developed to correlate the thermal cracking variables to total conversion and linear models for yields of total distillate fuels, gasoline, kerosene and diesel. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The predicted conversion and yields of total distillate fuels, gasoline, kerosene and diesel were found to agree satisfactory with the experimental values.

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1. Introduction

Since the early 1980s, the demand for heavy oils fuels from petroleum has decreased steadily. The rises of demand for the light fuels particularly gasoline are important to extract much useful materials from crude oil. About 94% of the projected growth in petroleum consumption stems from increased consumption of light products, including gasoline, diesel, kerosene, jet fuel, and liquefied petroleum gas, which are more difficult and costly to produce than heavy products. Refined product prices are expected to increase and determined by crude oil costs, refining process costs, marketing costs, and taxes. The thermal cracking process which subjected heavy fuels to both pressure and intense heat is physically breaking the large molecules into smaller ones to produce additional gasoline and distillate fuels by the use of high temperature without the aid of catalyst. Thermal cracking processes are commonly used to convert petroleum residual oil into distillable products, although thermal cracking processes as used in the early refineries (Alsobaai et al., 2006, 2007a,b; Yang et al., 1998; Speight, 1998).

In assessing the effect of operating conditions on thermal cracking product, the use of an adequate experimental design is particularly important. The primary goal in scientific research is usually to show the statistical significance of an effect that a particular factor exerts on the dependent variables of interest (Hedayat and Pesotan, 2007). A very fundamental part of statistics is concerned with the design of experiments to determine cause-effect relationship, the relationship with

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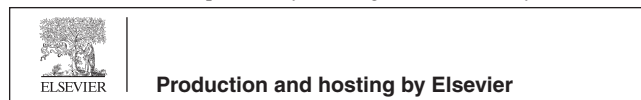
some response of the system is very important. For solving the problem by statistical methods, a plan of experiment must be set up that includes the method of collecting the data, the size of sample and the method of solution of problem (Cochran and Cox, 1957). Response surface methodology (RSM), fractional factorial design, provides a systematic and efficient experimental strategy for studying the parameters effect using statistical methods. It is well suited for the study of main and interaction effects of factors on the products (Adinarayana et al., 2003). The three level factorial design is certainly a possible choice by experimenter who is concerned about curvature in the response function (Montgomery, 2001).

In recent years, RSM has been extensively used. Weska et al. (2007) presented a study consisted of optimization of the deacetylation stage in the production of chitosan using the response surface methodology for the polymer's molecular weight. The study of deacetylation made through a factorial experimental design where temperature and time were varied. The estimate of chitosan's intrinsic viscosity was made by linear regression. Serodio et al. (2007) used the experimental design in the optimization of stir bar sorptive extraction for the determination of polybrominated diphenyl ethers in environmental matrices. Optimization of operating variables in a multistage flash desalination plant using two factorial experiments was performed to ascertain the effect of five factors and their cross-influence on the blow down flow and the production of the unit at different situation (Abdulwahab and Abdo, 2007). Lee et al. (2005) carried out optimization study of conditions for the preparation of flue gas desulphurization absorbent from rice husk ash using standard RSM design (CCD). They reported that the validity of the obtained model was verified using independent experimental runs and was found to agree very well with experimental data. Bacaoui et al. (2001) studied optimization of conditions for the preparation of activated carbon using RSM. Optimum value was determined for the xylene fractions by response surface methodology (Gonzalez et al., 1996). Sanchez et al. (1997) reported an optimization study using RSM for the investigations of esterification of glycerine to glycerol monooleate. Leng et al. (1997) applied experimental design to optimize the operating conditions, such as temperature, time and catalyst properties which show significant factors on the yield of gasoline and aromatic hydrocarbons. Statistical design of experiments in catalytic conversion process of vegetable oils to fuel was also used (Prasad et al., 1986).

In this work, statistical design of experiment (DOE), was used to evaluate the effect of important variables, reaction temperature, contact time and pressure in the thermal cracking of petroleum residue oil. Since the relationship between the independent variables and response was unknown, it was estimated by using regression analysis program (Design-Expert Software).

2. Experimental

2.1. Materials

Petroleum residue oil derived from Yemeni crude oil with density of 0.870 kg/l at 15 °C was used in this investigation. This sample was obtained from Masila Field, Hadhramaut, Yemen. The physical properties and distillate fraction at various temperatures are given in Tables 1 and 2. The high purity gases

nitrogen (99.999%) and hydrogen (99.999%) were obtained from Gas Pantai Timur Sdn. Bhd, Malaysia.

2.2. The experimental set-up

The experiment employed for thermal cracking of petroleum residual oil consisted of a gas metering part whereby the gas flow rates were adjusted to the required levels and a high-pressure batch reactor. The schematic diagram of the experimental set up is shown in Fig. 1. Nitrogen and hydrogen gases were supplied to the system at constant pressure from gas cylinders using pressure regulators. The two streams were combined in a three-way valve. The outlet from the valve was passed to the reactor. All connecting piping in the system was made from 6.35 mm stainless steel tubing joined by stainless steel fittings. The high pressure 300 ml reactor was supplied by M/S Parr instrument company, USA, and is capable of handing pressure up to 14 MPa and a maximum temperature of 500 °C. It is equipped with a gas inlet valve connected to a dip tube, which extends to a point near the bottom of the bomb cylinder. The arrangement allows the introduction of gas below the surface of the liquid sample. A gas release valve is attached to reduce the bomb pressure when it overcharged and also to purge the bomb. A pressure gauge scaled from 0 to 14 MPa with a stainless steel bourdon tube is mounted on the bomb head together with the gas release valve. A type J thermocouple placed in the thermowell and used to read the reaction temperature. The compensation of the motor drive assembly and magnetic drive provides reliable drive for the internal stirrer. The stirrer speed can be controlled up to 2500 rpm by a DC variable speed controller.

A cooling sleeve keeps the magnetic drive at safe temperature level during operations above 100 °C. An internal cooling loop also provides an effective way of controlling temperature overshoot in the reactor. A safety rupture disk of burst rating 14 MPa is attached to the bomb head providing a maximum operating pressure of 10 MPa. The reactor is equipped with high temperature fabric heating mantles housed in sturdy aluminium shells to provide uniform heat distribution to the walls and bottoms of these vessels. The temperature is controlled by a 4840 series PID temperature controller.

About 80 g of atmospheric petroleum residual oil sample are firstly poured into the reactor, and then hydrogen valve is opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor is then heated to reaction temperature in the range 400–480 °C and hydrogen pressure in the range 120–180 kPa. The reaction was carried out for a fixed period of time in the range 40–100 min after the reactor working temperature and pressure are attained. At the end of the run the reactor is cooled down to room temperature and the product was collected for analysis. The reactor was then purged with nitrogen, and the reactor and the stirrer assembly are then washed with dichloromethane. ASTM method D 86 was used to determine the product boiling range distribution and to investigate the yield of the lighter products after thermal cracking reaction. The ASTM distillation unit was supplied by Hotech Instruments Corp.

The conversion and product yields were obtained using the following equations:

$$\% \text{ Conversion} = \frac{(W_F - W_R)}{W_F} \times 100 \qquad (1)$$

Table 1 Physical properties of Yemeni petroleum residue oil.

Property	Quantity	Method of test
Vol.%	47.24	
Specific gravity 15/15 °C	0.9465	ASTM D-1298
Specific gravity API°	18	API = [141.5/(sp15/15 °C)] − 131.5
Carbon No. Ramz BTM wt%	8.2867	ASTM D-524/IP14
Carbon No. Konradson wt%	10	
Betumin ratio %	36	Beumin % = 5 + 3.1 * Konradson No.

Table 2 Distillation fraction of Yemeni petroleum.

No.	Product	Boiling range (°C)		Percentage ratio (vol%)	Percentage ratio (wt%)
		I.B. (°C)	F.B. (°C)		
1	Gasoline	45	180	17.25	13.66
2	Kerosene	180	240	10.58	9.17
3	Diesel	240	320	24.93	22.88
4	Residue	> 320	–	47.24	54.29
Total				100	100
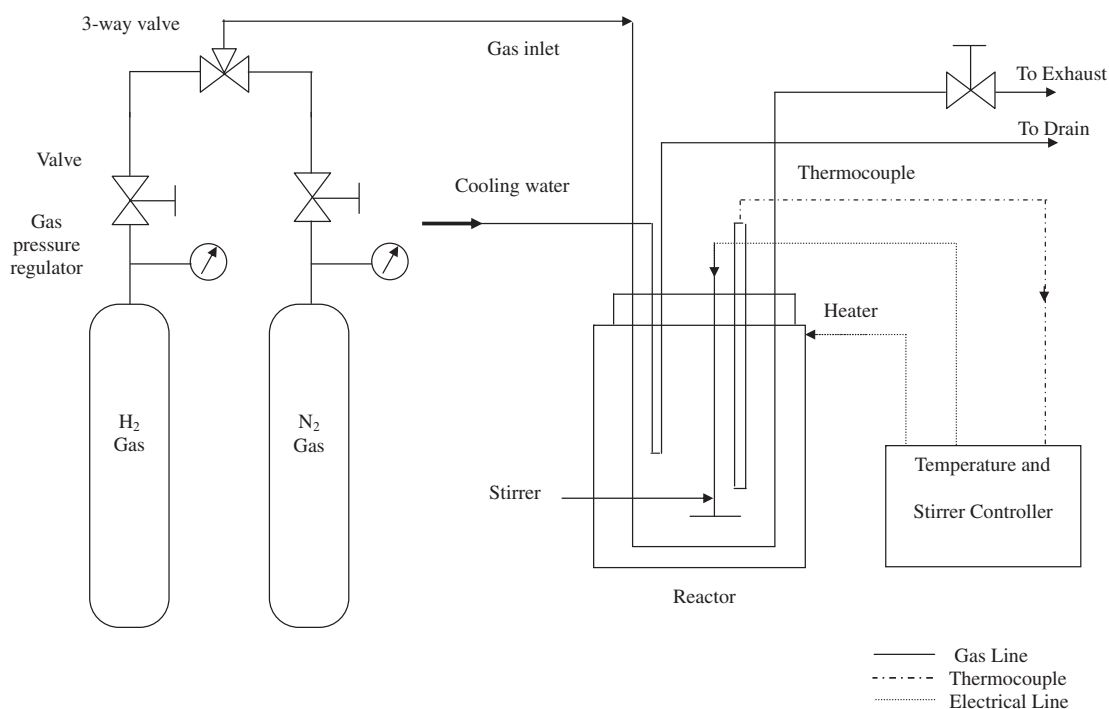
Figure 1 Schematic diagram of experimental set up for thermal cracking of petroleum residual oil.

where W_F, W_R are weight of residual oil feed and weight of residual fraction remained in the liquid product after distillation, respectively.

Yield is defined as a weight of the distillate fraction presented in the liquid product divided by the weight of residual oil feed:

$$Y_I = \frac{W_I}{W_F} \times 100 \qquad (2)$$

where Y_I is the yield of the product (wt%), I is the distillate fraction (gasoline, kerosene, diesel), W_I is weight of the distillate fraction.

2.3. Design of experiment

The response surface methodology (RSM) was used to evaluate the effects of operating conditions in the thermal cracking of residue oil and obtain the values of the total conversion and yields of total distillate fuels, gasoline, kerosene and diesel. RSM is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 2001). The process was studied with 3^3 full factorial design using regression analysis program (Design-Expert Software,

Table 3 The three factors: temperature, time, pressure and their levels.

Factor	Code	Unit	Low level (−1)	Medium level (0)	High level (+1)
Temperature	A	°C	400	440	480
Time	B	min	40	70	100
Pressure	C	kPa	120	150	180

Table 4 The experimental results obtained based on the 3^3 full factorial design.

No.	Temperature (°C)	Time (min)	Pressure (kPa)	X (wt%)	Y (wt%)	Y_1 (wt%)	Y_2 (wt%)	Y_3 wt%
1	440	40	120	71	32	7.9	9.3	14.8
2	400	70	180	68	30	6.9	7.5	15.6
3	400	40	120	52	27	6.2	7.1	13.7
4	440	70	180	81	40	18	13.6	8.4
5	480	100	150	88	44	14.4	16.7	12.9
6	480	100	180	93	48	27	12	9
7	480	100	120	86	43	21.3	13.2	8.5
8	480	40	150	77	36	13.8	13.4	8.8
9	440	70	150	82	42	17.3	16.8	7.9
10	400	40	180	56	28	5.4	7.3	15.3
11	440	40	150	70	31	8	8.9	14.1
12	480	70	150	90	46	22.3	13.3	10.4
13	400	70	120	64	29	8.2	8.8	12
14	480	70	180	89	44	23.1	12.9	8
15	400	100	150	72	31	8.8	8.3	13.9
16	440	70	150	80	39	17	12.9	10.1
17	400	100	120	73	33	7.9	9.2	15.9
18	440	100	120	84	41	17.2	16.6	7.2
19	400	100	180	74	33	10.2	8.1	14.7
20	440	40	180	69	30	8.4	8.8	12.8
21	440	100	180	75	33	9.5	8.9	14.6
22	480	40	180	79	39	14.2	12.9	11.9
23	400	40	150	55	28	7.7	7.6	12.7
24	440	70	150	76	35	10	11.2	13.8
25	440	70	150	78	38	9.9	11	14.1
26	480	40	120	67	34	12.1	12.4	9.5
27	480	70	120	80	40	13.8	12.7	13.5
28	440	70	150	78	37	9.7	11.1	14.2
29	440	70	120	76	36	9.4	11.3	15.3
30	400	70	150	67	30	8.5	9	12.6
31	440	100	150	77	36	9.8	11.2	15
32	440	70	150	75	34	9.5	11	13.5

X = Conversion, Y = yield of total distillate fuels, Y_1 = Gasoline yield, Y_2 = kerosene yield, Y_3 = diesel yield.

version 6.0.3, 2001). The variables identified were the reaction temperature (A), reaction time (B) and pressure (C). The factors named and levels are shown in Table 3.

Design-Expert software fitted four models, linear, two factor interaction (2FI), quadratic and cubic polynomials to the responses and displayed a measure of progress during the calculations. The model hierarchy is described below:

(1) *Linear model*: the significance of adding the linear terms to the mean.
(2) *2FI model*: the significance of adding the two factor interaction terms to the mean and linear terms already in the model.
(3) *Quadratic model*: the significance of adding the quadratic (squared) terms to the mean, linear and 2FI terms already in the model.
(4) *Cubic model*: the significance of adding the cubic terms beyond all other terms.

Linear models are generally used at most studies to assess the dependent and independent factors. In this model, the behaviour of the dependent variable (response) can be expressed as Eq. (3) (Montgomery, 1991):

$$y_i = \beta_0 + \sum_{j=1}^{n} \beta_j X_{ij} + \varepsilon_i \qquad (3)$$

where ε_i is independent random variables, β_0 is the mean of observations, β_j is unknown constant, j is the factor and n is the number of observations.

The non-linear models are important and necessary to consider an experimental design, which would allow one to fit the experimental data to a quadratic model (Cochran and Cox, 1957). The factorial design allow for experimentation of all main effects of the factors at any level and interactions between each pair of factor as well as all three ways interactions between each triplet of factors. To describe the non-linear

Table 5 Analyses of variance (ANOVA) for conversion.

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F value	Prob > F	Comment
Model	2729.05	9	303.23	27.25	<0.0001	Significant
A	1568.00	1	1568.00	140.90	<0.0001	
B	882.00	1	882.00	79.26	<0.0001	
C	53.39	1	53.39	4.80	0.0394	
A^2	20.26	1	20.26	1.82	0.1910	
B^2	97.03	1	97.03	8.72	0.0074	
C^2	1.91	1	1.91	0.17	0.6830	
AB	12.00	1	12.00	1.08	0.3103	
AC	30.08	1	30.08	2.70	0.1144	
BC	18.75	1	18.75	1.68	0.2077	
Residual	244.82	22	11.13			
Lack of fit	211.99	17	12.47	1.90	0.2469	Not significant
Pure error	32.83	5	6.57			

Table 6 Analyses of variance (ANOVA) for total distillate fuels.

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F value	Prob > F	Comment
Model	798.56	3	266.19	36.24	<0.0001	Significant
A	612.50	1	612.50	83.39	<0.0001	
B	180.50	1	180.50	24.57	<0.0001	
C	5.56	1	5.56	0.76	0.3919	
Residual	205.66	28	7.35			
Lack of fit	164.16	23	7.14	0.86	0.6429	Not significant
Pure error	41.50	5	8.30			

Table 7 Analyses of variance (ANOVA) for gasoline yield.

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F value	Prob > F	Comment
Model	591.57	3	197.19	16.15	<0.0001	Significant
A	472.27	1	472.27	38.67	<0.0001	
B	99.88	1	99.88	8.18	0.0079	
C	19.43	1	19.43	1.59	0.2176	
Residual	341.93	28	12.21			
Lack of fit	269.21	23	11.70	0.80	0.6781	Not significant
Pure error	72.71	5	14.54			

model, the general model presented in Eq. (4) is used (Montgomery, 2001):

$$y_i = \beta_0 + \sum_{j=1}^{n} \beta_i X_i + \sum_{j=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{i<j=2}^{n} \beta_{ij} X_i X_j \quad (4)$$

3. Results and discussion

In the statistical study, the variables identified were the reaction temperature, reaction time and pressure. Since the relationship between the independent variables and responses was unknown, it was estimated by using regression analysis program (Design-Expert Software, version 6.0.3, 2001). The process was studied with a 3^3 full factorial design. The experimental results are presented in Table 4.

According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. The quadratic model comes out best for conversion.

This is because it exhibits a low standard deviation (Std. Dev) of 3.34, high (R-squared) values of 0.9177, and a low prediction error sum of squares (PRESS) of 578.91. The predicted R-squared of 0.8053, is in reasonable agreement with the adjusted R-squared of 0.8840. Adequate precision measures the signal to noise ratio and the ratio greater than 4 is desirable. The ratio for conversion was 19.364. These values indicate an adequate signal and model can be used to navigate the design space. Similarly, it was found that the linear models come out best for yields of total distillate fuels, gasoline, kerosene and diesel.

The analyses of variance (ANOVA) for responses are presented in Tables 5–9. For each response, the probability "prob > F" was examined to check if it falls below 0.05 and thus the quadratic model was suggested for conversion and linear models for yields of total distillate fuels, gasoline, kerosene and diesel. The cubic model is aliased because the 3^3 full factorial design matrix provides too few unique design points to determine all of the terms in the cubic model, so this model was not chosen. For the quadratic model of conversion (Table 5), the Model F-value of 27.25 implies that the model is

Table 8 Analyses of variance (ANOVA) for kerosene yield.

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F value	Prob > F	Comment
Model	139.88	3	46.63	13.91	< 0.0001	Significant
A	120.64	1	120.64	35.98	< 0.0001	
B	15.13	1	15.13	4.51	0.0426	
C	4.11	1	4.11	1.23	0.2777	
Residual	93.88	28	3.35			
Lack of fit	67.25	23	2.92	0.55	0.8518	Not significant
Pure error	26.63	5	5.33			

Table 9 Analyses of variance (ANOVA) for diesel yield.

Source of data	Sum of squares	Degree of freedom (DF)	Mean square	F value	Prob > F	Comment
Model	64.05	3	21.35	3.83	0.0205	Significant
A	63.84	1	63.84	11.45	0.0021	
B	0.20	1	0.20	0.036	0.8510	
C	5.556E−004	1	5.556E−004	9.962E−005	0.9921	
Residual	156.15	28	5.58			
Lack of fit	121.41	23	5.28	0.76	0.7078	Not significant
Pure error	34.73	5	6.95			
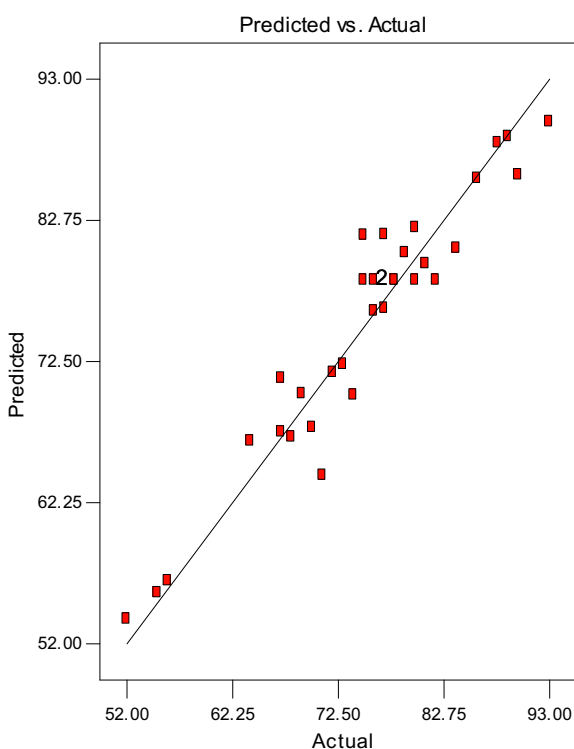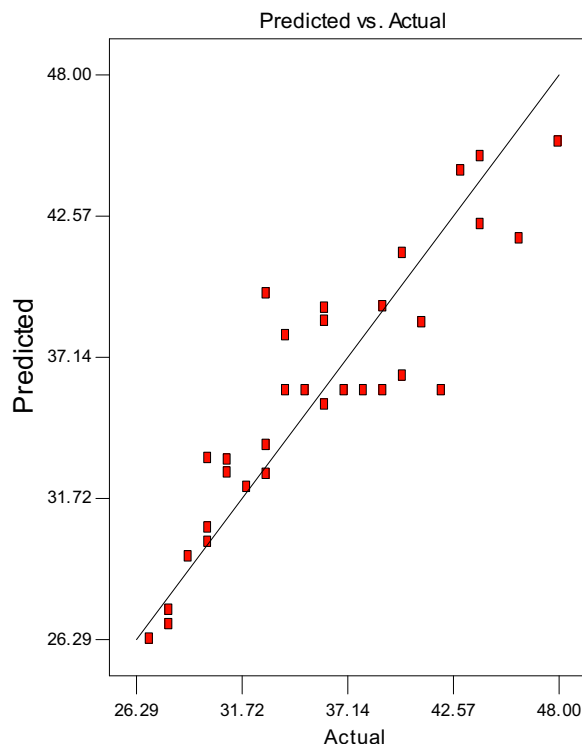
Figure 2 Actual and predicted values obtained from models for: (a) total conversion and (b) total distillate fuels.

significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate that the model terms are significant. Based on the F values (Tables 5–9), contact time, reaction temperature and pressure were found to have significant effects on conversion and yields of total distillate fuels, gasoline, kerosene and diesel. In this case A, B, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The quadratic model for conversion and linear models for yields of total distillate fuels, gasoline, kerosene and diesel are shown in Eqs. (5)–(9), respectively. These model equations are applicable in the range of variables studied.

$$\text{Conversion} = -238.97909 + 1.01929A + 1.38121B - 0.25388C - 4.09200E - 003B^2 \quad (5)$$

$$\text{Total distilled fuels} = -38.48958 + 0.14583A + 0.10556B + 0.018519C \quad (6)$$

$$\text{Gasoline yield} = -54.74144 + 0.12806A + 0.078519B + 0.034630C \quad (7)$$

$$\text{Kerosene yield} = -17.13403 + 0.064722A + 0.030556B - 0.015926C \quad (8)$$

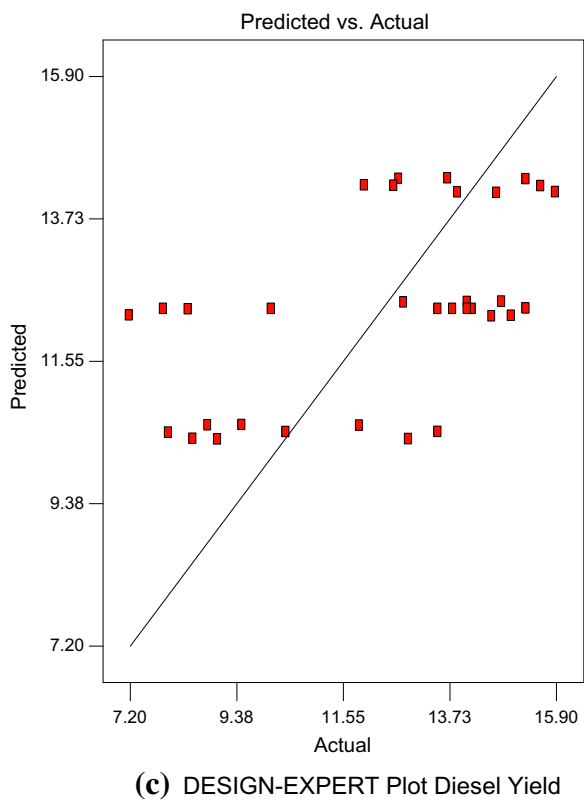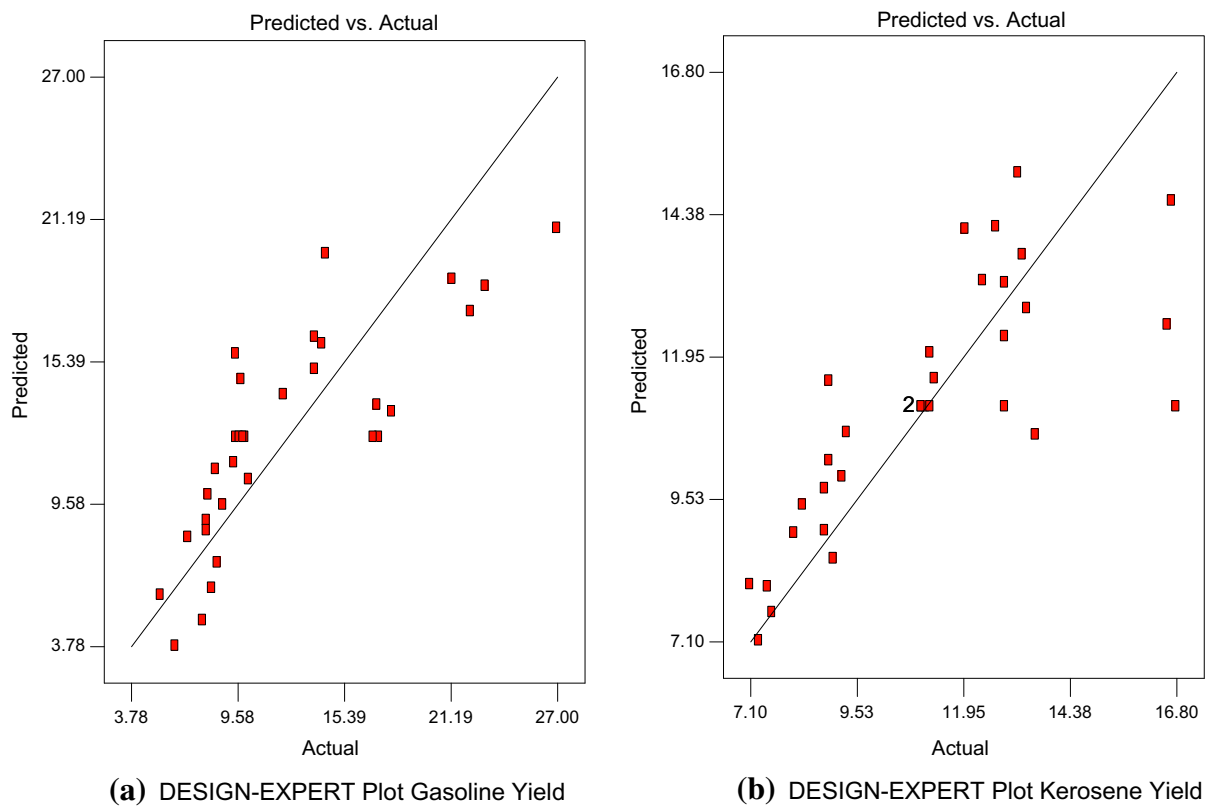$$\text{Diesel yield} = 33.32512 - 0.047083A - 3.51852E - 003B - 1.85185E - 004C \quad (9)$$

Figure 3 Actual and predicted values obtained from models for: (a) gasoline yield, (b) kerosene yield, and (c) diesel yield.

where A, B and C are reaction temperature, contact time and pressure in terms of actual values, respectively. Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect.

Figs. 2 and 3 compared the actual values of responses (conversion and yields of total distillate fuels, gasoline, kerosene and diesel) with the predicted values obtained from models. It can be seen that the predicted values agree well with the experimental values. These show that the models proposed could be used to predict conversion and yields of total distillate fuels, gasoline, kerosene and diesel within the range of temperature, time and pressure employed in this study.

The effects of the operating conditions (contact time, reaction temperature and pressure) on conversion and yields of total distillate fuels, gasoline, kerosene and diesel were found to have significant effects on the response. The conversion and yields of total distillate fuels, gasoline, kerosene and diesel were found to increase with increasing in operating conditions (contact time, reaction temperature and pressure). The highest values of responses were obtained when all the three variables were at the maximum point within the range studied. The region in the important factors that leads to the best possible response was determined using statistical design of experiment (DOE) software. It was found that the optimum operating conditions for thermal cracking of petroleum residue oil are:

(1) reaction temperature of 480 °C;
(2) contact time of 100 min;
(3) pressure of 178 kPa.

4. Conclusions

In this work, experimental design methodology has been shown to be a valuable tool to model a complex process such as thermal cracking of petroleum residue oil. It evaluated the effects of important variables (temperature, contact time and pressure) on total conversion and yields of total distillate fuels, gasoline, kerosene, diesel, and obtained the optimum operating conditions for thermal cracking of petroleum residue oil. Quadratic model was developed to correlate the thermal cracking variables to total conversion and while linear models obtained for yields of total distillate fuels, gasoline, kerosene and diesel. The experimental values obtained for the conversion and yields were found to agree satisfactory with the predicted values. It was found that the optimum operating conditions for thermal cracking of petroleum residue oil are: reaction temperature of 480 °C, contact time of 100 min and pressure of 178 kPa.

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