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Upgrading the atmospheric distillation residue of Al- Samawah refinery utilizing thermal cracking process

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ABSTRACT

Thermal cracking of heavy oil residues has gained the attention of oil refineries due to the increasing need for light oil fractions, as well as its lower value compared to light oil fractions. In this paper, the thermal cracking process of the residual crude oil that product from atmospheric distillation towers in the Samawah Refinery was studied in order to convert the heavy oil into a lighter oil. API gravity and conversion ratio for the result from the cracking process has been adopted as indicators of the accuracy and efficiency of the thermal cracking process for AR (atmospheric residue), where the API gravity for AR is equal to 15.5 .The response surface methodology (RSM) was adopted in the design of experiments to reach the best variables of operational conditions , which were in a range of temperatures (350-450 degrees Celsius) and time (30-60 minutes), through which we obtain the best results for the conversion ratio and API gravity for the liquid resulting from the thermal cracking process of AR, where the conversion ratio was 53.4% and API gravity equals 34.4 with a time of 45 minutes and temperature 386 ^{0}C.

1. Introduction

Petroleum or crude oil is a liquid composed of various hydrocarbons that may also contain various mineral compounds such as sulfur, oxygen, and hydrogen [1]. Heavy oil residue is obtained as a product of the distillation process, and the higher the density of the refined oil, the greater the residue produced and was heavier[2]. Crude oil is distilled by entering it into an atmospheric distillation tower, which operates at 350 degrees Celsius, where the light components such as gasoline and diesel are separated and the heavy part of the crude oil remains to collect at the bottom of the distillation tower, which is called atmospheric residue[3].

The proportion of heavy residues resulting from the atmospheric distillation of crude oil is about 50% and varies according to the different specifications of the crude oil that used[4]. Atmospheric residue is also treated by entering it into the vacuum distillation unit, which works almost at the same temperature of atmospheric distillation, but under vacuum pressure, where the lighter distillates such as VGO are extracted and the residue of distillation process is produced from the bottom of the tower and is called the vacuum residue [2]. Dealing with heavy petroleum residues has always been one of the difficult problems that oil refineries are exposed to, so it has become important to find ways, such as thermal cracking, to convert

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Nomenclaturethe			
API	American Petroleum Institute	DOF	Degree Of Freedom
CCD	Central–Composite Design	D	Desirability function
X1	Temperature (^{0}C)	Seq. SS	Sum Of Square
X2	Time (min)	Adj. SS	Adjusted Sum of Square
SG	Specific gravity	Adj. MS	Adjusted Mean of Square
Bo	The intercept regression constant.	adj. R2	Adjusted Coefficient of Multiple Correlation
Bi	The linear regression effect.	pred. R2	Predicted Multiple Correlation Coefficient
Bii	The quadratic regression effect.	N	Number of runs
Bij	The interaction regression effect.	q	Number of processing parameters
CI	Confidence interval	Y	Represents the dependent variable (RE)

these heavy wastes into lighter ones, especially with the increase in demand for light derivatives and the expansion of their uses, whether as fuel or in various industries[5]. The properties of the feedstock that used, such as the asphalt content, directly effect on the production of thermal cracking [6] Thermal cracking of hydrocarbons with higher asphalt content and higher molecular weight gives greater coke formation[4]. The efficiency of the thermal cracking process, in addition to the characteristics of the feedstock that used, also depends on the optimal selection of the appropriate operating conditions such as temperature, pressure, reaction time [5]

Thermal cracking of organic compounds occurs by raising the temperature, wherein a break occurs in the (C-C) and (C-H) bonds, resulting in shorter hydrocarbon chains [7]. The breaking of the hydrocarbon chains (C-C) and (C-H) occurs in the thermal cracking of petroleum residues at temperatures higher than (350-370) ^{0}C [8]. In thermal cracking, hydrocarbon chains crack to produce free radicals, which lead to the formation of shorter chains with lower molecular weights, but these reactions may also lead to the production of molecules with a higher molecular weight than the raw materials before cracking. Chain reactions of free radicals are accepted as a mechanism for thermal cracking of hydrocarbons [9]. Generally, there are two types of reactions that occur during thermal cracking:

1. Primary reactions: in which long hydrocarbon chains are converted to shorter ones.

$$CH_3CH_2CH_2CH_3 \rightarrow CH_4 + CH_3CH = CH_2$$

$$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_3 + CH_2 = CH_2$$

2. Secondary reactions: in which the formed free radicals react to produce longer chains of the molecules from which they are formed[1]

$$CH_2 = CH_2 + CH_2 = CH_2 \rightarrow CH_3CH_2CH = CH_2$$
$$or$$
$$R.CH = CH_2 + R^1.CH = CH_2 \rightarrow cracked\ residum + coke + other\ product$$

It is possible to increase the efficiency of the thermal cracking process and reduce the production of coke formation by using hydrogen under high pressure, but this process requires large costs [10] Increasing the temperatures of the thermal cracking process for oils reduces the time required for conversion, but may lead to counterproductive results and lead to a decrease in the quality of production and its desirable specifications [11]. Kaminski et al. studied the effect of temperature and time on AR with temperatures (420,400) ^{0}C and time (1,2) hr., and he showed that the best results were at 420 ^{0}C and two hour time, through which he was able to obtain a result 85 % by weight and API gravity to 34 [12]. Alsobaai discussed Thermal cracking of petroleum residue oil in a high-pressure batch reactor under various operating conditions, temperature in range 400–480 ^{0}C, reaction time 40–100 min and pressure 120–180 kPa in the presence of hydrogen. It was found that the optimum operating conditions for thermal cracking of petroleum residue oil are: reaction temperature of 480 ^{0}C, contact time of 100 min and pressure of 178 kPa [13]. Syamsuddin et al. studied thermal cracking of atmospheric petroleum residue oil in a high pressure batch reactor at (340 ^{0}C, 3 hr.), reaction time. The results revealed that thermal cracking gave product conversion and yield. The conversion was 51.43 wt. % from thermal reaction [14]. Krishna et al. used a reactor unit to research Aghajhari heavy residual oil. They made the experiments in temperature range of (427–500 °C) and flow rates in domain (2.04 – 2.91 lit/hr.) and at a pressure of (17 kg/cm$^{2)}$ [15].

The novelty of this work lies in the study of the use of thermal cracking to obtain light products from the atmospheric residue (AR) produced from the distillation units in the Samawah Refinery. The response surface methodology (RSM) was used to design experiments and analyze the results to know the impact of operational conditions on production specifications.

2. Materials and methods

2.1 Materials

The material that we used as a feedstock for the thermal cracking unit is the atmospheric residue (AR) that got from Samawah refinery.
The properties of (AR) are listed in the table (1)

Table 1. The AR properties

API	Density	Flash point	Pour point	Viscosity	W&s
15.5	0.9686	91	3	284.5	0.06

2.2 Method

Thermal cracking of AR was performed in a 1 liter stainless steel autoclave batch reactor as shown in Fig. (1). First, 200 g of oil sample was added to the reactor, then the autoclave was closed and housed in the thermal cracker and the reactor was then purged by nitrogen to drive out any oxygen before heating. Then the electric furnace is turned on to gradually raise the temperature until it reaches the required temperature, at which the time of experiment has begun. After the experiment time was over, the furnace was stopped; the reactor was withdrawn from the cracker and cooled in water until it reached room temperature. Then the weight of the resulting liquid and the weight of the remainder in the reactor after the end of the experiment were calculated, and then the conversion ratio was calculated according to the following equation:

CONV. %=wt. of liquid product \wt. of sample (1)

The liquid produced was also calculated API gravity according to the following equation:

API gravity = (141.5 / SG) - 131.5 (2)

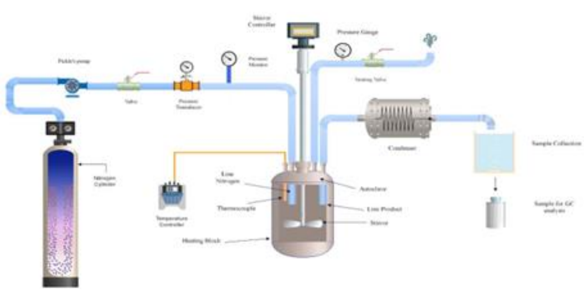

Figure 1. Apparatus.

2.3 Design of experiments

To plan the tests and estimate the influence of production factors on the researched responses, and to determine the combined effect of factors and their nonlinear relationships with responses, a statiatical technical method of (RSM) , (CCD) and statistical program (Minitab -18) were used. The mathematical relationship between responses and production factors is calculated by their fit in a quadratic polynomial equation (Eq. 3), the highest regression coefficient estimation of the (R^2) and the results of the analysis of variance (ANOVA) are indicators of the quality of the obtained model [16, 17]:

$$Y=B_0+\sum B_i\ x_i+\sum B_{ii}\ x_i^2+\sum B_{ij}\, x_i\, x_j \quad (3)$$

Y indicates to the searched responses.
X1,X2 ,to Xq are the conditions that used in the operational process.
(q) Is referring to the total number of the conditions that used in the operational process.
The intercept regression constant is represented by (Bo).
The linear regression effect is represented by (Bi).
The quadratic regression effect is represented by (Bii).
The interaction regression effect is represented by (Bij).
The random error is represented by (ε).
According to earlier research, the operational variables ranges (temperature and reaction time) were chosen to explore as many different behaviors of the searched responses as possible. The operative variables for this investigation were temperature (X1) and reaction time (X2), which were investigated in accordance with their respective ranges of (350-450 ^{0}C) and (30-60 min), respectively. All experiments were set so that the pressure inside the reactor was equal to atmospheric pressure and the mixing speed was 500 rpm. Using the following equation (Eq. 4), by using CCD the total number of test (N) it was estimated.

$$N=q^2+2q+n \quad (4)$$

A total of (11) runs with (4) factors, (4) focal points and (5) central points (n: number of repetitions) were given by design experts to improve the searched responses, i.e. the conversion ratio and API gravity. The ranges of process and levels for the condition of process are shown in table 2 while the experimental design by using RSM, CCD in Minitab program -18 is displayed in table 3

rotability [$\alpha=(2^q)^{0.25}$]equals±1.414 .

(Y) is refer to the response of conversion and API ,and estimated in equ.(1&2)

Table 2. Process variables and their impact on the conversion and API gravity

Process parameters	**range in central composite design (CCD)**		
Coded levels	**Low(-1)**	**Middle(0)**	**High(+1)**
X1- Temp.(^{0}c)	**350**	**400**	**450**
X2- Time (min)	**30**	**45**	**60**

3. Results and Discussion

The estimated values and actual tests predicted results for conversion and API gravity are given in table 4. The observed conversion and API gravity values vary between (3.6-72) % and (29.8-38.4) which are agrees with the expected results.

Table 3. Design of experiments

Run	**Blocks**	**Coded value** X_1	X_2	**X1**	**X2**
1	1	-1	1	365	34
2	1	-1	-1	365	56
3	1	1	1	435	34
4	1	1	-1	435	56
5	1	0	-1.414	400	30
6	1	0	1.414	400	60
7	1	1.414	0	350	45
8	1	-1.414	0	450	45
9	1	0	0	400	45
10	1	0	0	400	45
11	1	0	0	400	45

Table 4. Results of the studied variables

Operational variables			Actual values		Predicted values	
Run	X1: Temp^{0}c	X2: time (min)	CONV.%	API gravity	CONV.%	API gravity
1	365	34	8	37	14.0	36.8
2	365	56	17	36.5	69.9	30.6
3	435	34	68	30	24.2	36.1
4	435	56	70	30	72.0	30.4
5	400	30	57.25	33.5	3.6	38.4
6	400	60	67	32.6	70.0	29.8
7	350	45	0	38.1	52.8	33.8
8	450	45	72	30.5	61.4	32.6
9	400	45	65	32.9	65.6	33.1
10	400	45	65.5	33.1	65.6	33.1
11	400	45	66	33.5	65.6	33.1

3.1. Mathematical correlation of the searched responses

According to the values that estimated in actual tests, the mathematical correlation (Equ. 5-6) and displayed in table (5) were developed in items of coded and real factors explain the interactions between the process parameters to conversion and API gravity.

Table 5. The regression coefficient

	S	R-sq	R-sq(adj)	R-sq(pred)
Conv.	6.56685	97.02%	94.04%	78.66%
API gravity	0.554087	97.99%	95.97%	86.39%

CONV.= -2462 + 11.24 X1 + 5.50 X2 - 0.01287 X1*X1- 0.0377 X2*X2 - 0.00455 X1*X2 ……………………………………………….(5)

API = 133.0 - 0.406 X1 - 0.047 X2 + 0.000382 X1*X1 - 0.00114 X*X2 + 0.000325 X1*X2 ……………………………………………….(6)

3.2. Analysis of variance (ANOVA)

The results of experimental samples alone may not give a true analysis of the data, so it has become important to use analysis of variance (ANOVA) software to accurately calculate process quality . [18,19]. Table 6 gives the analysis of variance for conversion and API gravity, the value (p) less than (0.05) denote that the model items are acceptable in conversion and API gravity model. The regression model is classified as significant in the conversion model but in the API gravity model is insignificant when their values is (0.09). In this research the values of (F) are (32.54) for conversion and (48.86) for API gravity. Which denote that the calculated models are acceptable. In addition, the great values of the regression coefficients for the two responses indicate that these models are acceptable and are in suitable agreement with the modified R^2 values. As a result of that, the correlations of conversion and API gravity will be as follows (Eq. (5) and (6)) after excluding effects that having (P-Value) greater than 0.05 (underline values in Table 6) by using the estimated result of ANOVA analysis, it can be concluded that these models revealed the effective statue of the cracking process and it can be performed to crack the AR.

TABLE 6. ANOVA results for conversion and API gravity (underline numbers mean insignificant effect).

Source	Degree of Freedom	Sum of squares	Mean square	F-Value	P-Value
CONV.%					
model	5	7015.55	1403.11	32.54	0.001
X1	1	5464.24	5464.24	126.71	0.000
X2	1	76.47	76.47	1.77	<u>0.240</u>
X1*X1	1	1462.30	1462.30	33.91	0.002
X2*X2	1	105.40	105.40	2.44	<u>0.179</u>
X1*X2	1	12.25	12.25	0.28	<u>0.617</u>
API					
model	5	74.7213	14.9443	48.68	0.000
X1	1	72.5511	72.5511	236.31	0.000
X2	1	0.3865	0.3865	1.26	<u>0.313</u>
X1*X1	1	1.2887	1.2887	4.2	<u>0.096</u>
X2*X2	1	0.0967	0.0967	0.31	<u>0.599</u>
X1*X2	1	0.0625	0.0625	0.2	<u>0.671</u>

3.3 The effect of temperature and time on conversion

Figure (2) shows the effect of temperature and time on the conversion value in the temperatures range (350-450) ^{0}C and at range of time (30-60) minutes. It was found that the conversion values (50-75)% were obtained in the temperatures range (450-385) ^{0}C in a time of 60 minutes Except for the area in the temperatures range (435-419) ^{0}C and the time range (53-41) minutes , In this excluded region, the highest conversion values (greater than 75)% were obtained. The conversion decreased to (25-50) % within the temperatures range (385-376) ^{0}C in a time of 60 minutes, and the conversion continued to decrease with the decrease in temperature. From this we conclude that the conversion increases with the increase in temperature, and the highest effect of time is within the range (53-41) minutes as shown in figure (3), this was in agreement with the results of the research presented by [13].

3.4 The effect of temperature and time on API gravity

Figure (4) shows the effect of temperature and time on the ApI gravity value in the temperatures range (350-450) ^{0}C and at range of time (30-60) minutes. It was found that The highest API gravity value was approximately within the temperatures range (357-350) ^{0}C and at range of time (52-30) minutes, Then the API gravity value started decreasing as the temperature and time increased, where the lowest API gravity values were obtained at temperatures range (450-446) ^{0}C and at time of 60 minutes, where the value of the API gravity was less than 30. We conclude that the API gravity values decrease clearly when the temperature is increased, and that the increase in time also reduces the API gravity, but slightly as shown in figure (5). This was in agreement with the results of the research presented by [20].

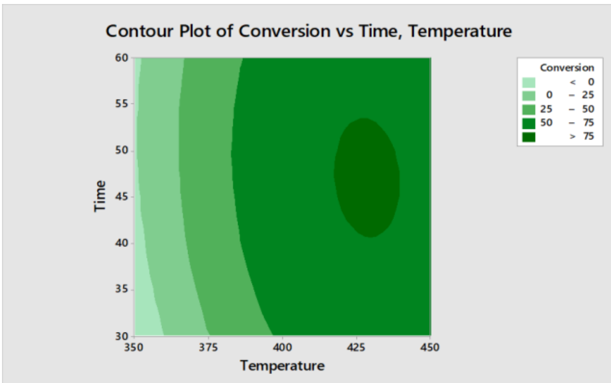

Figure 2. Counter plot temp. &time vs. conversion**.**

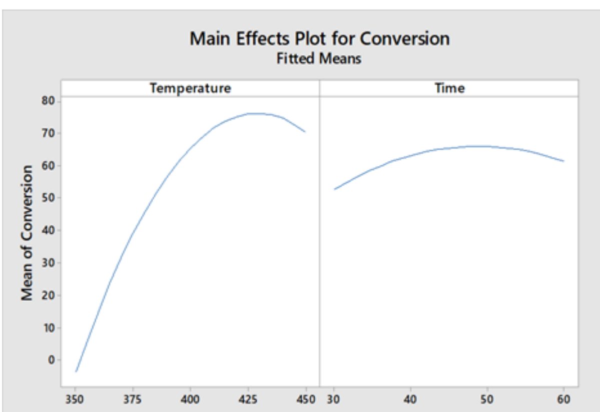

Figure 3. Effects plot for conversion.

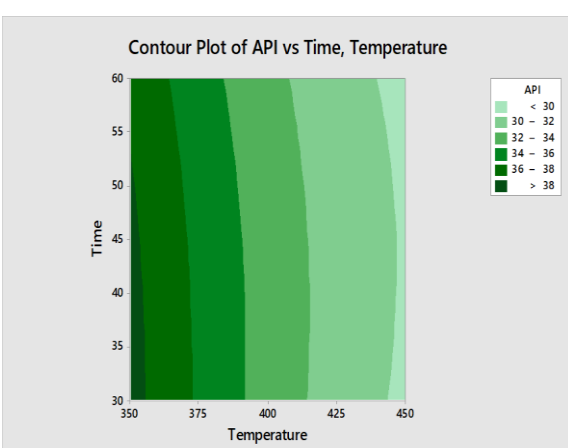

Figure 4. The contour plot API vs. Time, Temperature.

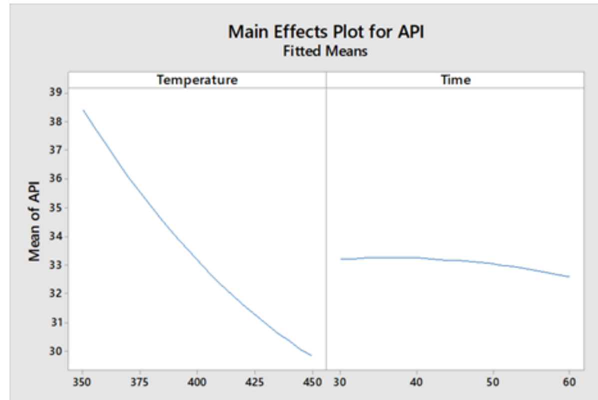

Figure 5. Effect plot for API

3.3 The confirmation and optimization test

Minitab-18 a statistical software tool was used to obtain the optimum values for operational variables as shown in table 7. The best value of the applied temperatures and reaction times were found to be 386.36 ^{0}C and 46 min, respectively. These values achieved (API gravity =34.39) and (conversion=53.39%). This means that the current design of the thermal cracker gives the best API gravity and conversion results for the producing liquid when using the optimal process conditions.

4. Conclusions

In this paper, the statistical analysis and process conditions for upgrading AR at Samawah Refinery using thermal cracking method were performed for the first time. The variables include temperature and reaction time. Response parameters are conversion ratio and API Response surface methodology (RSM) and CCD include two factors and 11 trials were used. The accuracy of the models was determined by evaluating the regression coefficient (R2) and other parameters of ANOVA, significance of the models and their conditions were evaluated at the probability level ($P < 0.05$). The results showed that the expected optimal conditions are in agreement with the experimental results. The results of the analysis showed the best conditions resulting were at a temperature of 386.36 C and at time of 46 min, and we were able to obtain a result for the thermal cracking process with specifications (API gravity =34.39) and (conversion=53.39%).

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

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