Zn/HY-Zeolite as a Catalyst for Upgrading Iraqi Heavy Crude Oil Using Aquathermolysis Method

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Abstract. Upgrading heavy crude oil from East of Baghdad oilfield using a high pressure reactor with steam supplied and toluene as hydrogen donor has been investigated through aquathermolysis process. Synthesized Zn/HY Zeolite, which is characterized by XRD, SEM, EDX, FT-IR, BET-surface area and pore volume has been employed as a bi-functional catalyst. Statistical design of experiment (DOE) is also applying in determine the optimum operating conditions of aquathermolysis reaction under different temperatures, time and weight percentage of catalyst with the targeted response being the viscosity after upgrading. The extent of upgrading might be established through various analyses of the initial unconventional oil and final produced crude oil. These were included the measurements of oil density, API gravity, oil viscosity, flash point, pour point, sulfur content and yield of light and intermediate fractions. The results show that the optimum operating conditions are found at 0.25 wt% of catalyst, 231.25°C and 30 h reaction time. The experimental data under these conditions has confirmed that the viscosity and sulfur are decreased by 67.25% and 55.58% respectively, whilst the API has increased up to 24.5. The response surface regression model equation in coded unit for viscosity reduction percentage has been established.

1. Introduction
Recently, with the depletion of conventional oil reserves in the world, heavy oil becomes a worldwide interest to meet future demand for petroleum products [1], in which 70% of remaining oil reserves is bitumen and heavy oil [2]. But the exploitation, transportation and utilization of heavy crude oil is still limited [2, 3], because of its high density and viscosity and high contents of asphaltene and resin in addition to abundant amount of heteroatom such as O, S and N [4]. Therefore, various methods are used to the recovery of heavy oil (i.e. Cyclic Steam Stimulation (CSS), Steam Flooding, Steam-Assisted Gravity Drainage (SAGD), In Situ Combustion (ISC) etc.) [5, 6]. Aquathermolysis is one of the popular and effective technologies to retrieve the heavy oil [7], in which cracking, hydrogenation, and desulfurization can take place by using steam under a high pressure in order to improve the crude oil properties [8].
Hyne et al. in 1982 had simplified the reaction of aquathermolysis according to the following chemical equation [9]:

\[ \text{RCH}_2\text{CH}_2\text{SCH}_3 + 2\text{H}_2\text{O} = \text{RCH}_3 + \text{CO}_2 + \text{H}_2 + \text{H}_2\text{S} + \text{CH}_4 \]

During this reaction, the free radicals may be created with the polymerization reactions and composing bigger molecules. This guides to the creation of more viscous oil in place of decreasing the viscosity. Thus, various catalysts should be used to prevent free radical formation and increase the viscosity diminution [5, 8]. Catalysts development is very important which can enable the extent of oil conversion to be increased and the aquathermolysis process to become more economically attractive [9]. Catalysts can be classified according to the stage within which they are active. As a rule, catalyst might be dissolved in the oil, water, or suspended as particles [10]. The dispersed and oil soluble catalysts are mentioned to be partially more active than dissolved catalyst in water [8, 11]. This study is focusing on Zn/HY-Zeolite as a bi-functional catalyst for aquathermolysis reaction because it has a highly surface area and larger-pore structures in combination with both acidic and metallic sites. Zeolites are hydrated aluminosilicate minerals produced by using interlinked tetrahedral of silica (SiO4) and alumina (AlO4). Y zeolite has 3D network of cavities and inter channels, consequently it can be separated to molecular of various sizes and therefore it can be utilized in various industrial application [12].

2. Experiments

2.1. Materials

Ludox AS-40, Sodium Aluminate, Sodium Hydroxide (96%) and Ammonium Chloride (99.8%) all have purchased from Sigma Aldrich Germany, Zinc Chloride (99%) from Geekee Biotech China. Additionally, Toluene (99%) as a hydrogen donor is supplied from Alpha Chemika India. The heavy crude oil is used as a feed has been obtained from East of Baghdad oilfield with the properties scheduled in (Table 1).

| Table 1. The physical properties of used heavy oil. |
|-----------------------------------------------|
| **DENSITY, SP.GR** | 0.9224 G/CM³, (20°C) |
| **VISCOSITY** | 47.87 g/cm.s or cP, (50°C) |
| **API** | 21.9, (20°C) |
| **POUR POINT** | -25°C |
| **FLASH POINT** | 80°C |
| **SULFUR CONTAIN** | 4.52 wt.% |
| **YIELD OF LIGHT AND INTERMEDIATE FRACTIONS** | Temperature for fraction (°C) % Yield of fraction |
| Light Naphtha (IBP 45-75) | 1.2 |
| Heavy Naphtha (75-175) | 13.2 |
| Kerosene (175-225) | 6.4 |
| gas oil (225-340) | 20 |
| Total | 40.8 |

2.2 Synthesis and impregnation processes

2.2.1. Synthesis of Na-Y zeolite

The NaY-Zeolite is prepared by making two types of solutions depending on a chemical recipe for
the FAU [13]. The first one is called the "Seed gel" is prepared by blending: distilled water, ludox "SiO2", sodium aluminate "NaAl2O3" and sodium hydroxide "NaOH" in a plastic bottle and then mixing for at least 10 min. The product is left for aging at 25ºC for 24 h. The other called "Feedstock gel" is prepared by blending: distilled water, ludox "SiO2", sodium aluminate "NaAl2O3" and sodium hydroxide "NaOH". All these components are stirred for 10 min. A certain amount of the seed gel has been added slowly to the feedstock gel. The mixture is also stirred for 20 min then being kept for crystallization purpose in the dryer at 100°C for 18 h. The sample is taken out of the dryer and centrifuged for 10 min and washed with distilled water until the pH is decreased to about 8. Finally, the NaY-Zeolite sample is dried overnight at 110°C as shown in block diagram (Figure 1).

2.2.2. Preparation of NH4Y and HY zeolite types

Ion exchange method is used to exchange Na+ ions within NaY zeolite framework with NH4+ ions within NH4Cl solution by preparing 100 ml of NH4Cl solution (0.5M) and then adding 1gm of synthesized NaY-Zeolite to this solution. The mixture is heated at 80°C beneath reflux condition with regular mixing for 1h. After that, the NH4Y-Zeolite form is filtered off, washed several time with distilled water, is centrifuged and then dried at 100°C. The ion exchange process is repeated several times under the same conditions until the level of Na+ within Y-framework becomes less than 0.5%. Heat treatment (i.e. calcination process) is required after multi-stage ion exchange procedure in order to prepare an anhydrous crystalline HY-Zeolite (i.e. acidic form of Y-Zeolite) and decomposes the NH4+ cations into ammonia and protons according to the following equations [14]. This process is performed in a furnace for 2 h. at 450°C under dry airflow.

$$NaZ_{(s)} + NH_4^+_{(aq)} \leftrightarrow Na^+_{(aq)} \downarrow + NH_4Z_{(s)}$$  \hfill (1)

$$NH_4Z_{(s)} \xrightarrow{\Delta} NH_3(g) \uparrow + Hz_{(s)}$$ \hfill (2)

2.2.3. Preparation of Zn/HY-Zeolite

Basically, 1 gm of Y-Zeolite catalyst is placed in a 100 ml solution of zinc chloride in order to the impregnation of 1% from Zn metals on the framework structure of HY-Zeolite. Under reflux condition the mixture is heated at 80 °C with constant mixing for 4 h. After that, the impregnated Y-Zeolite is separated off, washed several times with distilled water, and centrifuged for 15 min. and then is dried at 110 °C overnight to obtain the product of bi-functional zeolite catalyst. After that, the furnace is used to reduce metal at 350°C for 2 h under gas flow rate of 10 °C/min.
2.3. Catalytic aquathermolysis reaction of the heavy crude oil

Catalytic aquathermolysis reaction is carried out in a 300 ml stainless steel autoclave (high pressure reactor) as shown in (Figure 2). Briefly, heavy oil, water and hydrogen donor (Toluene) are added to the reactor at 75%, 15%, 10 vol% ratio, respectively with certain weight percentage of Zn/HY-Zeolite. Then the reactor is closed and heated at a rate of 4°C/min until reached the reaction temperature under a high pressure (e.g. pressure range of 30 to 45 bar according to the steam temperature). When the aquathermolysis reaction is completed, the reaction mixture is cooled to room temperature and afterward transferred to a 500 mL flask, after that utilizing a condenser to get rid of residual water, catalysts and affords the heavy oil sample ready for further analysis. In this study, Central Composite design (CCD) has been chosen for the aquathermolysis process to discover the optimum conditions. CCD is used in this work with three independent variables: reaction time, temperature, and catalyst weight percent. The CCD matrices consist of 20 runs for three variables covering the full design and working up models of the second order by using regression analysis program (Design-Expert 11 Software).
3. Results and Discussion

3.1 Characterization of the catalyst

3.1.1 X-ray Diffraction (XRD) analysis

The XRD patterns for the zeolite samples are shown in Fig. 3 in which the major diffractions of the samples are occurred at a 2-theta range of 5 to 40 degrees. It can be seen that a structure of synthesized zeolite-NaY sample has approximately the same pattern in comparison with the standard zeolite Y [15]. The percentage degree of crystallinity of each zeolite Y sample is calculated from the intensities of the main peaks given from the XRD machine according to the below equation by dividing the sum of main peak intensities of the synthesized zeolite Y on the sum of main peak intensities of the reference zeolite Y [14, 15]. (Table 2) shows the degree of crystallinity of synthesized samples, which almost high crystallinity. The results show that the crystallinity of catalysts follows the trend: Y-Zeolite > Zn/Y-Zeolite.

\[
\text{Deg. of cryst. \%} = \frac{\sum \text{intensities of the peaks of zeolite sample}}{\sum \text{intensities of the peaks of reference sample}} \tag{3}
\]

Zinc metals within Zn/Y-Zeolite pattern in (Figure 3) have no diffraction peaks because the quantity of zinc loaded over zeolite is too small; and can also be attributed to interference within zeolite-Y structure. Another possible explanation is that the zinc dispersed well during metal impregnation, and therefore cannot be detected when using XRD. Moreover, the intensities of some characteristic peaks decrease within Zn/Y-Zeolite pattern due to the loaded transition metals into zeolite framework which can slightly decrease the crystallinity and that agree with Kristiani et. at. [16], and also indicates that the impregnation process does not obviously influence the zeolite Y structure.
Table 2. XRD-data of the synthesized zeolite-Y samples.

| 2θ ° | Intensity (I) | 2θ ° | Intensity (I) | Intensity (I) |
|------|--------------|------|--------------|--------------|
|      | Zeolite      |      | Zeolite      | Zn/Zeolite   |
| Standard Faujasite | | Samples | | |
| 6.233 | 100          | 6.2459 | 100          | 100          |
| 15.640 | 53           | 15.5844 | 60          | 57           |
| 20.360 | 38           | 20.2703 | 37          | 40           |
| 23.635 | 59           | 23.5348 | 92          | 81           |
| 27.042 | 39           | 26.9170 | 63          | 62           |
| 30.730 | 22           | 30.6023 | 29          | 34           |
| 31.378 | 49           | 31.2487 | 72          | 74           |
| 32.432 | 16           | 32.3059 | 26          | 30           |
| 34.053 | 15           | 33.9239 | 29          | 27           |
| Total | Σ391         | Total | Σ508        | Σ505        |
| % Degree of crystallinity using the standard | 130% | 129% |
| faujasite as a reference | |

Figure 3 XRD-pattern of synthesized Y Zeolite, Zn Zeolite

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra for the zeolite samples are given in (Figure 4) generally, every infrared spectrum of prepared zeolite seems to be comparable to the structural units for the reference commercial Y-zeolite, and is appropriate with XRD results. Absorption bands in the 453–490 cm⁻¹ region can be referred to the T-O bending mode (i.e. Si-O/Al-O). The band watched in the 715–816 cm⁻¹ region is owing to T-O-T symmetric stretching. This band is seen to be minimal intense with reference to the asymmetric stretching vibration of (Si/Al)O₄ units, which may be observed as a large peak with high intensity near on 1014–1173 cm⁻¹. An absorption band at 1400 cm⁻¹ is attributed to the NH₄. Strong IR absorption in the spectral region of 1618–1647 cm⁻¹ is ascribed to the vibrational bands of framework water molecules. Likewise, the broad band in the 3159–3583 cm⁻¹ region is almost because of the surface hydroxyl group (i.e. OH: hydrogen linked to the oxygen ions of the lattice structure). Generally all metals and its oxide, give the FT-IR peaks at lower wave number ranging from 424-459 cm⁻¹.
3.1.3 Energy dispersive X-Ray (EDX) Analysis

It is important for zeolite catalysts to have a small amount of sodium, since sodium reduces the acidity of the zeolite as it reacts with the zeolite acid sites and by these decreases the catalytic activity of catalyst. Sodium is usually reported as the Wt. % on catalyst. The synthesized zeolite is modified by multi-stage ion exchange procedure to produce the acidic form of Y-Zeolite with less than 0.5% of Na⁺. The Energy dispersive X-Ray (EDX) analysis has been employed to analyze the content of sodium within the zeolite structure before and after ion exchange. Shown in (Table 3). The extent of exchange is determined by the equation below:

$$\% \text{Exchange} = \frac{\text{Origin quantity of Na} - \text{Removal of Na}}{\text{Origin quantity of Na}} \times 100\%$$  \hspace{1cm} (4)

| Stages            | % exchange | Wt.% Na⁺ Content within the zeolite |
|-------------------|------------|------------------------------------|
| Before ion exchange | 0.0       | 11.8                               |
| First ion Exchange | 64.4       | 4.2                                |
| Second ion Exchange | 86.4    | 1.6                                |
| Third ion Exchange | 88.1       | 1.4                                |
| Fourth ion Exchange | 98.3       | 0.2                                |

The overall (Si/Al) ratio in the bulk structure of prepared zeolite can be determined by EDX analysis as shown in (Figure 5-a). Bulk (Si/Al) ratio was found to be (2.06) and this value is matching the outcomes of Matti et. al. [17] and Marcelo et. al. [18] researches.
Furthermore, EDX gives an indication about the weight percent of transition metal that impregnated within the zeolite structure (i.e. approximately 0.7 wt.%) as shown in (Figure 5-b).

**Figure 5-a.** EDX-spectrum of NaY zeolite catalyst

**Figure 5-b.** EDX-spectrum of Zn/HY zeolite catalyst

### 3.1.4 Scanning electron microscopy (SEM) Analysis

The surface morphologies of Y-zeolite samples are obtained by utilizing scanning electron microscopy. (Figure 6-a) with magnification up to 10 µm for prepared NaY zeolite appears the segregated Y-crystals with sharp edges and without clear agglomeration and that agrees with Nsai et. al. [19]. SEM also has demonstrated that no geometric change can be noticed in Zn/HY-zeolite crystals after multi-stage ion exchange and metal loading as shown in (Figure 6-b). It indicates that no crystalline transformation has occurred within Y- structure during the modifications.
3.1.5 Surface Area and Pore Volume Analysis

Surface area and pore volume are determined based on Brunauer Emmett and Teller (BET) method and are summarized in (Table 4). The surface area of HY-Zeolite presents a good agreement with Scott et al. [20]. BET surface area of Zn/HY-Zeolite appears to be less than HY-Zeolite. These results may be caused by several factors. Metal ions can fill part of the channels and/or pores within the catalyst structure and cause some of the opening pores to be blocked, thereby reducing their volume and decreasing the overall BET-surface area of zeolite-Y this agrees with the results obtained by Ramli et al. [21] and Lopes et al. [22].

| Catalysts    | Surface Area (m²/g) | Pore Volume (cm³/g) |
|--------------|---------------------|---------------------|
| HY-Zeolite   | 428.12              | 0.22                |
| Zn/HY-Zeolite| 416.46              | 0.20                |

3.2 Central composite design for aquathermolysis process by used Zn/HY-Zeolite

The proposed data from CCD model is used as a reaction conditions to carry out the experimental work inside the pressurized rig. Twenty experiments have been done under pressure ranging from 30 to 45 bar according to the steam temperature with the viscosity of products measured by means of BROOKFIELD DV-II Viscometer. Summarized in (Table 5). The results indicate that the increase in the percentage of viscosity reduction due to the increasing of: Y-catalyst amount, temperature, and time within the reaction. Yet, increasing the temperature more than 235° C leads to a slow increase of the viscosity reduction. Also, the viscosity reduction has increased by increasing the time of reaction, but when the time becomes more than 30 h, the viscosity reduction has slightly decreased because the deactivation of the catalyst along the reaction time.
Table 5. Experiments experienced by a design expert.

| #  | Catalyst (wt%) | Temperature (°C) | Time (h) | % Viscosity reduction |
|----|----------------|------------------|----------|-----------------------|
| 1  | 0.2            | 212.5            | 24       | 57.83                 |
| 2  | 0.2            | 212.5            | 12       | 33.38                 |
| 3  | 0.25           | 193.75           | 18       | 43.17                 |
| 4  | 0.2            | 212.5            | 24       | 57.16                 |
| 5  | 0.2            | 212.5            | 36       | 55.75                 |
| 6  | 0.2            | 250              | 24       | 60.71                 |
| 7  | 0.2            | 212.5            | 24       | 56.39                 |
| 8  | 0.25           | 231.25           | 30       | 70.73                 |
| 9  | 0.25           | 193.75           | 30       | 67.92                 |
| 10 | 0.15           | 193.75           | 30       | 61.35                 |
| 11 | 0.25           | 231.25           | 18       | 48.25                 |
| 12 | 0.1            | 212.5            | 24       | 54.56                 |
| 13 | 0.2            | 212.5            | 24       | 62.71                 |
| 14 | 0.2            | 175              | 24       | 43.64                 |
| 15 | 0.2            | 212.5            | 24       | 58.83                 |
| 16 | 0.15           | 231.25           | 18       | 45.71                 |
| 17 | 0.15           | 193.75           | 18       | 41.38                 |
| 18 | 0.15           | 231.25           | 30       | 64.48                 |
| 19 | 0.2            | 212.5            | 24       | 55.97                 |
| 20 | 0.3            | 212.5            | 24       | 61.47                 |
3.3 Analysis of Variance (ANOVA)

The results which are given in (Table 5) are analyzed by employing the central composite design (CCD) as displayed in Table 6, which consists of several terms. They can be defined as follows:

Model: The row model displays how much difference in the response may be explained by the model. The model is detached into specific terms and analyzed independently. Residual: The residual row demonstrates how much variation in the response remains mysterious. Lack of Fit: is the value that the model expectations miss the noticing. Pure Error: is the value of the difference between running replication. Sum of Squares: is the sum of the squared variations between the global mean and the amount of variance shown in this row source. df: Degrees of Freedom; number of parameters evaluated to calculate the source’s sum of squares. Mean Square: also called variance, the sum of squares divided by df. F Value: investigation for comparing the source’s mean square to the residual variance. P Value: also called Prob > F, which is the Probability, equals the integral under the curve of the F-distribution that lies beyond the observed F-value.

Figure 7. 3D effects of variables on the percent of viscosity reduction
The ANOVA analysis shows that the F value is 9.80. The P value is 0.0007 (i.e. lower than 0.05). This indicates that the quadratic model chosen is significant due to magnitudes being higher than 0.05 are not significant. The suitability of the models is actually regulated in with the coefficient of determination $R^2$. The models give high $R^2 = 0.8982$. Besides, a reasonable agreement with the adjusted determination coefficient is found. In this work, the Adj-$R^2$ value is 0.8066. The values of $R^2$ and Adj-$R^2$ are higher than 0.8 which is high enough to support a high connection between the predicted and observed values. This indicates that the regression model provides a great explication of the interaction between the factors and the response (Viscosity Reduction %). Equation of the surface regression response model in coded unit for the viscosity is illustrated by means of the following equation:

$$R_1 = 58.54 + 1.94A + 3.09B + 8.17C + 0.0538AB + 1.06AC - 0.4337BC + 0.1619A^2 - 1.30B^2 - 3.20C^2 \ (5)$$

Where:

- $R_1 =$ viscosity reduction (%)
- $A =$ catalyst weight percent (%)
- $B =$ temperature (°C)
- $C =$ time (h)

According to the above equation, the coefficient values of variables (i.e. catalyst amount, temperature and time) are $+1.94$, $+3.09$, and $+8.17$, respectively. The highest coefficient value is of the time and this means that the time being the most effective and significant variable then temperature and catalyst amount. The positive values of coefficients mean that the increase of all variables lead to increase the percentage of viscosity reduction. Also, these results and (Figure 7) show the interaction effect of the three variables, where the interaction coefficient values of amount of catalyst/temperature, amount of catalyst/time and temperature/time are $+0.0538$, $+1.06$, - $0.433$, respectively. This means that a good interaction effect is occurred between amount of the catalyst and time than other interaction variables and the negative charge of $(-0.433)$ means a negative relation between temperature and time. But in general, the interaction effect of catalyst amount /temperature and temperature/time are not significant in the process.

### Table 6. ANOVA regression model of process; analysis of variance.

| Source | Sum of Squares | df | Mean Square | F-value | p-value |
|--------|----------------|----|-------------|---------|---------|
| Model  | 1583.66        | 9  | 175.96      | 9.80    | 0.0007  | significant |
| A-A    | 59.95          | 1  | 59.95       | 3.34    | 0.0976  |
| B-B    | 153.08         | 1  | 153.08      | 8.53    | 0.0153  |
| C-C    | 1067.82        | 1  | 1067.82     | 59.50   | <0.0001 |
| AB     | 0.0231         | 1  | 0.0231      | 0.0013  | 0.9721  |
| AC     | 9.01           | 1  | 9.01        | 0.5020  | 0.4948  |
| BC     | 1.51           | 1  | 1.51        | 0.0839  | 0.7780  |
| A²     | 0.6593         | 1  | 0.6593      | 0.0367  | 0.8518  |
| B²     | 42.37          | 1  | 42.37       | 2.36    | 0.1554  |
| C²     | 257.55         | 1  | 257.55      | 14.35   | 0.0036  |
| Residual | 179.47      | 10 | 17.95       |         |         |
| Lack of Fit | 149.28   | 5  | 29.86       | 4.94    | 0.0521  | not significant |
| Pure Error | 30.19    | 5  | 6.04        |         |         |

The outline of analysis of variance (ANOVA) is displayed in (Figure 8) and (Table 7). The obtained results prove that the quality of the model is appropriate with the assumption of ANOVA. (Figure 8-a)
describes the plotting of normal probability of residuals from the least square fit and once plotted, the points where located almost over a horizontal line and the normality assumption seems to be convincing. (Figure 10-a) reveals the normal distribution indicating that the assumptions can be accepted and there is no visible problem with normality. In addition, the input factors have had an impact on the responses. (Figure 10-b) describes the actual and predicted values which are closed to each other. (Figure 10-C) illustrates the random scatter plot of residuals against the predicted values. The anticipated results were displayed as haphazardly dispersed about the zero line, signifying that the difference being constant and nonlinear connection can be existed.

### Table 7. Report for the result from ANOVA.

| Run Order | % Actual value of viscosity reduction in Table 5 | % Predicted value of viscosity reduction | Residual |
|-----------|-----------------------------------------------|----------------------------------------|----------|
| 1         | 57.83                                         | 58.54                                  | -0.7089  |
| 2         | 33.38                                         | 29.40                                  | 3.98     |
| 3         | 43.17                                         | 43.33                                  | -0.1565  |
| 4         | 57.16                                         | 58.54                                  | -1.38    |
| 5         | 55.75                                         | 62.08                                  | -6.33    |
| 6         | 60.71                                         | 59.53                                  | 1.18     |
| 7         | 56.39                                         | 58.54                                  | -2.15    |
| 8         | 70.73                                         | 68.08                                  | 2.65     |
| 9         | 67.92                                         | 62.66                                  | 5.26     |
| 10        | 61.35                                         | 56.77                                  | 4.58     |
| 11        | 48.25                                         | 50.49                                  | -2.24    |
| 12        | 54.56                                         | 55.32                                  | -0.7553  |
| 13        | 62.71                                         | 58.54                                  | 4.17     |
| 14        | 43.64                                         | 47.16                                  | -3.52    |
| 15        | 58.83                                         | 58.54                                  | 0.2911   |
| 16        | 45.71                                         | 48.63                                  | -2.92    |
| 17        | 41.38                                         | 41.69                                  | -0.3053  |
| 18        | 64.48                                         | 61.98                                  | 2.50     |
| 19        | 55.97                                         | 58.54                                  | -2.57    |
| 20        | 61.47                                         | 63.06                                  | -1.59    |
3.4 The evaluation of the optimum conditions

The essential objective of this study is to discover the best operating conditions (time, temperature and catalyst weight percent) which give the highest viscosity reduction by means of employing a response surface method. The desirability function has utilized to discover the optimal operating conditions as shown in (Figure 9) in which 0.25 wt% of catalyst, 231.25°C and 30 hour are the best conditions of the reaction in case of using Zn/HY-Zeolite catalyst and these values are considered economically good when compared with the other researchers.

Figure 8 (a-c). Residual plots for viscosity reduction
The analysis of the produced crude oil from the aquathermolysis reaction at these optimum conditions is shown in (Tables 8 and 9). According to Tables 1 & 8, it can be seen that the viscosity is decreased from 47.87 to about 15.68 g/cm.s and sulfur contain is decreased from 4.520 to about 2.007 wt.%, while the API is increased from 21.9 to 24.5 (i.e. by 2.6). Both flash point and pour point are decreased by 10 and 5 Celsius respectively, which indicates an increase in the volatile hydrocarbon and the ability of crude oil to flow. In addition, (Table 9) indicates an increase in the percentage of yield fractions from 40.8 to 45.6. Increasing the yield after upgrading reaction can be obviously observed in the case of kerosene and gas oil.

**Table 8.** The characterization of crude oil sample at the optimum conditions.

| Characteristic          | Value   |
|-------------------------|---------|
| Viscosity Reduction (%) | 67.25%  |
| Sulfur contain          | 55.58%  |
| Reduction (wt%)         |         |
| Density (g/cm³)         | 0.9070  |
| API                     | 24.5    |
| Flash point (°C)        | 70      |
| Pour point (°C)         | -30     |

**Table 9.** Yield of light and intermediate component of crude oil after upgrading at the optimum conditions.

| Temperature for fraction (°C) | %Yield of fraction |
|------------------------------|--------------------|
| Light Naphtha (IBP 37-75)    | 1.6                |
| Heavy Naphtha (75-175)       | 14                 |
| Kerosene (175-225)           | 7.2                |
| gas oil (225-340)            | 22.8               |
| Total                        | 45.6               |
4. Conclusions

Conclusions can be summarized as follows:

1. Zeolite-Y in various formats (i.e. NaY, NH4Y, and HY) has successfully prepared and the acidic form is loaded with Zn metal to produce a bi-functional zeolite catalyst (Zn/HY). It seems to be an efficient and useful catalyst for aquathermolysis reaction because it has a high ability to the reduction of viscosity and sulfur content of heavy oil.

2. Improvement of the physical properties of the crude oil can be achieved by aquathermolysis process under solid catalyst and low reaction temperature, which is a good way to increase both the API and the yield of the light hydrocarbons' cuts (i.e. Reduce the crude oil density).

3. Response surface methodology (RSM) has been used to enhance aquathermolysis process variables, and the results obtained are confirmed that the reaction time is the most important factor affecting aquathermolysis reaction in comparison with temperature and the amount of catalyst used.

4. According to the statistical method (i.e. Design Expert) and the experimental results, the optimum operating conditions for aquathermolysis reaction are 0.25 wt. % of catalyst, 231.25°C and 30-hour reaction time to obtain the highest reduction in the viscosity and sulfur content within the heavy oil by 67.25% and 55.58%, respectively.

5. The response of surface regression model equation in coded unit for viscosity reduction percentage is established to be: R1 = 58.54 + 1.94A + 3.09B + 8.17C + 0.0538AB + 1.06AC - 0.4337BC +0.1619A^2 - 1.30B^2 - 3.20C^2

6. The enhancement of the transportation characteristics of the crude oil can be accomplished through the catalytic aquathermolysis process, both flash and pour point can be decreased and that means an increase in the volatile hydrocarbon and the ability of crude oil to flow.

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