INTRODUCTION

The interest in heavy crude oils has been increasing with growing worldwide energy demand. The heavy crude oils have a high content of the bottom of residual, and their fractionation renders low amounts of distillates with large investment in distillation plants; so, converting the large molecules (mainly residual) into low molecular weight fractions is an important process. The hydrocracking (HCK) is a process that converts the large molecules (such as VGO) into middle distillates such as gasoline. Improving selectivity of the hydrocracking catalysts to produce middle distillates for high-quality diesel is a long-lasting challenge. The main problems involved in the heavy crude oil hydrocracking are pore diffusion limitations preventing the access of large molecules to the active sites and the rapid deactivation of the catalyst by coke and metal deposition. These problems require bifunctional catalysts having a support with (1) sufficient pore diameter to improve the metal deposition and pore diffusion; (2) sufficient acidity to crack large molecules, while limiting over cracking and coke formation; and (3) optimum dispersion of active metals. The alumina and silica oxides could have a positive impact on the hydrocracking process and make them attractive as supports for the heavy oil hydrocracking catalysts.
were characterized using several techniques such as \( \text{NH}_3 \)-TPD, BET, XRF, and XRD. The catalyst performance was investigated in the VGO hydrocracking and discrete lumping kinetic equations of this process were investigated. The kinetic model represents the temperature at which the reaction is best performed. On the other hand, it is possible to use kinetics to obtain suitable reaction conditions to produce a specific oil cut. Many studies have examined the hydrocracking process modeling. Some of them are as follows. In 2005, Sergio Sanchez et al. proposed a 5-lump kinetic model for hydrocracking of heavy oils which is in good agreement with experimental values. In 2009, Ignacio Elizalde et al. investigated continuous kinetic lumping modeling to moderate hydrocracking of heavy oil. In 2010, Ignacio Elizalde et al. modeled the effect of pressure and temperature on the heavy crude oil hydrocracking by the continuous kinetic lumping approach. In 2012, Ignacio Elizalde and Jorge Ancheyta investigated the continuous kinetic lumping in hydrodesulfurization and hydrocracking of heavy residue oil. In 2016, Alexander Quitian and Jorge Ancheyta developed experimental methods for developing kinetic models for hydrocracking reactions. In this investigation, slurry phase catalyst using batch reactors is investigated. In 2019, Guillermo Félix and Jorge Ancheyta used separate kinetic models to predict liquid, gas, and coke yields in heavy oil hydrocracking. In 2020, Vicente Sámano et al. discussed a methodology for estimating kinetic parameters based on sensitivity analysis. In the present study, the performance of the Ni-Mo-F_{3.6}/ASA-Al_{2}O_{3} catalyst has been investigated in the VGO hydrocracking process and the production of 4 oil cuts of gas, naphtha, kerosene, and diesel in this process has been formulated.

2 | EXPERIMENTAL

2.1 | Materials

The commercial alumina, ammonium heptamolybdate, and nickel nitrate were provided from Tehran Oil Refinery (Iran). The \( \text{N}- \text{hexadecane (n-C16)} \) was purchased from Merck, Darmstadt, Germany.

2.2 | Preparation of support

ASA-Al_{2}O_{3} support was prepared according to the following method. The support contains 70% of \( \text{Al}_{2}O_{3}-\text{SiO}_{2} \) and 30% of \( \gamma-\text{Al}_{2}O_{3} \). \( \text{Al}_{2}O_{3}-\text{SiO}_{2} \) is containing \( \gamma-\text{Al}_{2}O_{3} \) and 90 wt.% SiO₂. The mixture of powders was loaded into the mixer with \( Z \)-folded blades. Then, the mixture was pepticized by nitric acid under stirring for 30 min (acid modulus: 0.03-0.05). The obtained paste was extruded using the plunger extruder VINCI with a Teflon spinneret and a trilobular hole at a pressure of 3.5-4.0 MPa and a velocity of plunger moving of 1.2 mm s^{-1}. Extrudes were dried for 4 hours at 120°C in airflow and calcined at 415°C for 4 hours. Then, 30% of \( \gamma-\text{Al}_{2}O_{3} \) was added to the above mixture. Extrudes were dried and calcined as above. The obtained support was divided into 2 parts. The preparation of this support is in accordance with the reference.\(^9\)

2.3 | Catalyst preparation

The nickel–molybdenum–fluoride catalyst was prepared using the incipient wetness co-impregnation method (\( \text{pH} \approx 5.4 \)) using an aqueous solution with one part of the obtained support donated as ASA-Al_{2}O_{3}. Aqueous solutions with the appropriate amounts of nickel nitrate, ammonium heptamolybdate, and ammonium fluoride to obtain 15.0 wt.% MoO_{3}, and 4.0 wt.% NiO, and 3.6 wt.%F. The impregnated catalysts were dried in air at 120°C for 2 hours and calcined at 415°C for 4 hours. The supported catalyst is denoted as Ni-Mo-F_{3.6}/ASA-Al_{2}O_{3}. The preparation of the Ni-Mo-F_{3.6}/ASA-Al_{2}O_{3} catalyst is like that of the Ni-Mo-F_{3.6}/ASA-Al_{2}O_{3} catalyst, but no fluoride was used in the preparation of the Ni-Mo-F_{0}/ASA-Al_{2}O_{3} catalyst.

2.4 | Catalyst characterization

The BET surface area (\( S_{\text{BET}} \)), pore size (PS), and pore volume (PV) of the catalysts were measured using conducting nitrogen adsorption/desorption analysis using Micromeritics ASAP 2010 at 77 K. Before analysis, the sample was degassed at 350°C for 2 hours.

The XRD patterns of the produced catalysts were recorded using a Bruker Advance diffractometer with DA Vinci geometry using Ni-filtered CuK-\( \alpha \) radiation (40 kV, 30 mA) instrument. The catalysts (0.2 g) were ground in a mortar to a particle size of 38 \( \mu \)m. The occurrence of the respective oxidized species of the metal–incorporated wide-angle analyses were performed for all catalysts. In this case, 20° range was scanned between 10° and 80°.

\( \text{NH}_3 \) temperature-programmed desorption (\( \text{NH}_3 \)-TPD) to determine the relative acidity of the samples was performed
at ICB-CSIC in a Micromeritics Pulse Chemisorb 2700. Two-hundred milligrams of the sample to disobey water and impurities from the sample was outgassed in airflow. To do this, the sample at a rate of 10°C min⁻¹ from room temperature to 600°C was heated and held at this temperature for 60 min. Then, the sample was cooled down to 50°C and ammonia was introduced into the system afterward the physically adsorbed ammonia was purged. The system at a rate of 10°C min⁻¹ was heated to 600°C and the chemisorbed ammonia was determined with a thermo-conductivity detector (TCD). The TCD read the NH₃ concentration, which was converted into µmol g⁻¹ min⁻¹ unit and then plotted against the temperature. The number of acid sites was determined by integrating the area under the curve for each type of acidity (weak, medium, and strong) and expressed in molecules of NH₃ adsorbed per temperature interval. In this investigation, TCD detector calibration based on ASTM D1552 and according to existing standards was calibrated for online analysis of light hydrocarbons up to 5-carbon hydrocarbons. C₅ and hydrocarbons were analyzed offline by GC contains FID detector.

Element contents of the Ni-Mo-F₀/ASA-Al₂O₃ and Ni-Mo-F₃.₆/ASA-Al₂O₃ catalysts were determined by X-ray fluorescence spectroscopy (XRF) using a Philips PW 2404. Fine powders of the dry catalysts were analyzed (for F content) or after they were fused with a suitable flux at 1000 ºC and cast into the shape of a glass bead (for Ni, Mo, Si, Al, and F contents).

### 2.5 N-hexadecane (N-C₁₆) hydrocracking

N-hexadecane hydrocracking was carried out on a steel tubular fixed-bed upflow reactor. About 1.00 g catalysts were filled in the reactor and reduced by H₂ gas at pressure 30 bar and a space velocity of 200 h⁻¹ with constant heating rate from ambient to 453 K and maintained at this temperature for 1 hours. The reaction conditions are as follows: injection rate of 30 cm³ h⁻¹ and H₂/oil = 175 nL/L, 30 bar, WHSV = 3 kg (L⁻¹ h⁻¹), and LHSV = 4.2 h⁻¹. The reaction temperature was 573 K. After catalyst testing, the reactor was depressurized under hydrogen flow at 573 K for 3 hours. Then, the flow was switched to nitrogen and the temperature decreased to room temperature. Finally, liquid products were analyzed.

### 2.6 VGO Hydrocracking

The VGO hydrocracking in the presence of the Ni-Mo-F₃.₆/ASA-Al₂O₃ catalyst was done at three 380, 395, and 410°C temperatures, and pressure of 10 MPa. The rest of the conditions are similar to the section 1.4.1. The experimental setup schematic is illustrated in Figure 1.

### 2.7 Analytical procedures of liquid products

Liquid products were recovered after each reaction and were analyzed by the gas chromatography (GC). An Agilent Technologies 7890A Chromatographer fitted with a Mass Selective Detector (5975C VL MSD with Triple-Axis Detector) was used to measure the amount of each fraction distribution of the liquid product. The GC was equipped with a capillary column (Rtx 5 MS, HT-30 m long, 25 µm film thickness) and was operated in split mode (split ratio 1:25) with helium as a carrier gas. A calibration using data processed by Agilent MSD Chemistation (Rev E.02.02.1413) was performed to evaluate the percentage of the material.

### 3 KINETIC MODELING

#### 3.1 Discrete lumping kinetic equation

The various discrete lumping models were proposed to understand the reaction kinetic of VGO hydrocracking. At the different temperatures, all the second and third conversions, that is, diesel, kerosene, and naphtha conversions, into lighter cuts generally take place. Because in the 380–410°C temperature range, the second and third conversions are low, it can be assumed that 4 oil cuts of kerosene, diesel, naphtha, and gas are produced in 4 parallel reactions from the VGO hydrocracking. So, in this study a simple network of 4 reactions in parallel considered the whole hydrocracking process as a system. The VGO hydrocracking reactions are shown in

![FIGURE 1 Schematic of the experimental setup](image-url)
The kinetic equations of VGO hydrocracking using Ni-Mo-F₃/ASA-Al₂O₃ catalyst are given as follows:

The differential kinetic equation of the VGO is as follows:

\[-r_F = (k_1 + k_2 + k_3 + k_4) F \rightarrow \frac{dF}{dt} = -(k_1 + k_2 + k_3 + k_4) F\]  

The differential kinetic equation of the produced diesel in the VGO hydrocracking follows from Equation 2:

\[\frac{dD}{dt} = k_1 F = k_1 e^{-(k_1 + k_2 + k_3 + k_4) t}\]  

The differential kinetic equation of the produced kerosene is given as follows:

\[\frac{dK}{dt} = k_2 F = k_2 e^{-(k_1 + k_2 + k_3 + k_4) t}\]  

The differential kinetic equation of the produced naphtha is given as follows:

\[\frac{dN}{dt} = k_3 F = k_3 e^{-(k_1 + k_2 + k_3 + k_4) t}\]  

The differential kinetic equation of the produced LPG is given as follows:

\[\frac{dG}{dt} = k_4 F = k_4 e^{-(k_1 + k_2 + k_3 + k_4) t}\]  

The solved equations are as follows by assuming the zero amounts of diesel, kerosene, naphtha, and LPG at first:

\[D = \frac{-k_1}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4) t} + \frac{k_1}{(k_1 + k_2 + k_3 + k_4)}\]  

\[K = \frac{-k_2}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4) t} + \frac{k_2}{(k_1 + k_2 + k_3 + k_4)}\]  

\[N = \frac{-k_3}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4) t} + \frac{k_3}{(k_1 + k_2 + k_3 + k_4)}\]  

\[G = \frac{-k_4}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4) t} + \frac{k_4}{(k_1 + k_2 + k_3 + k_4)}\]  

In Equations 1-9:

- \(F\) is the amount of the initial feed (VGO) in terms of mass ratio
- \(D\) is the amount of the produced diesel in terms of mass ratio
- \(K\) is the amount of the produced kerosene in terms of mass ratio
- \(N\) is the amount of the produced naphtha in terms of mass ratio
- \(G\) is the amount of the produced gas in terms of mass ratio
- \(k_1, k_2, k_3,\) and \(k_4\) are in terms of \(\frac{1}{\text{lit. sec}}\)

The kinetic constants \((k_1, k_2, k_3,\) and \(k_4)\) were calculated by fitting the experimental data in the VGO hydrocracking and the Equations 6, 7, 8, and 9, using the Levenberg-Marquardt algorithm.

| T A B L E 1 List of symbols |
|-----------------------------|
| **Symbols**                  | **Description**                  |
| DMDS                        | Dimethyl disulfide               |
| ASA                         | Amorphous silica–alumina cracking |
| VGO                         | Vacuum gas oil                   |
| LPG                         | Liquefied petroleum gas          |
| \(F\)                       | Feed                             |
| \(r_F\)                     | Consumption rate of feed         |
| \(t\)                       | Time                             |
| \(\frac{dF}{dt}\)           | Change feed-to-time ratio        |
| \(\frac{dt}{dt}\)           | Time change                      |
| \(D\)                       | Diesel                           |
| \(\frac{dD}{dt}\)           | Change diesel-to-time ratio      |
| \(N\)                       | Naphtha                          |
| \(\frac{dN}{dt}\)           | Change naphtha-to-time ratio     |
| \(G\)                       | Gas                              |
| \(\frac{dG}{dt}\)           | Change gas-to-time ratio         |
| \(k_1, k_2, k_3\)           | Kinetic constants                |

**FIGURE 2** Schematic of the VGO hydrocracking reaction
## RESULTS AND DISCUSSION

### 4.1 Catalyst characterization

The calcined catalysts were prepared by the impregnation method, and it was tried to achieve the same amount of the metal loadings (as presented in Table 2). In all catalysts, the amount of nickel is about 3.8-4.0 wt.%, but this amount is in the range of 14.7-15.2 wt.% for molybdenum.

The textural properties derived from adsorption–desorption isotherms of nitrogen on the NiMoF_0/ASA-Al_2O_3 and NiMoF_3.6/ASA-Al_2O_3 calcined catalysts are shown in Table 2 and Figure 3. The prepared catalysts exhibit a high BET surface area and are classified as mesoporous. According to Table 2, with increasing F\(^{-}\), the pore diameter is slightly increased, the pore volume is kept the same, and the specific surface area is decreased. This could be due to the F\(^{-}\) damage to the thin wall between holes, which would decrease the specific surface area.\(^{11}\) Besides, the generated bulk AlF_3 in the NiMoF_3.6/ASA-Al_2O_3 catalysts has a much smaller specific surface area than ASA-Al_2O_3 in absence of the fluoride ion.\(^{12}\)

The shape of N\(_2\) adsorption–desorption isotherm for the Ni-Mo-F\(_0\)/ASA-Al\(_2\)O\(_3\) and Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalysts is type IV, and this displays mesoporous materials. The hysteresis loop for this catalyst can be categorized by H\(_2\) type.\(^{13}\) On the other hand, the hysteresis loop for the catalyst prepared in the presence of F\(^{-}\) exhibits a mixture of cylinder type (H1) of pores.\(^{13}\) As shown, textural properties are affected by the incorporation of HF. The addition of HF leads to a decrease in low diameter mesoporous.

The XRD patterns of the Ni-Mo-F\(_0\)/ASA-Al\(_2\)O\(_3\) and Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalysts are shown in Figure 4. The \(\gamma\)-alumina, SiO\(_2\), NiO, and MoO\(_3\) phases are observed in the XRD patterns of all catalysts and NiF\(_2\), and AlF\(_3\) phases are observed in the XRD patterns of the Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalyst (Figure 4). The 2 diffraction peaks appeared at 2\(\theta\) = 45.9° and 66.7° were assigned to the \(\gamma\)-Al\(_2\)O\(_3\) crystalline phase.\(^{14,15}\) However, the observed peaks for the Ni-Mo-F\(_0\)/ASA-Al\(_2\)O\(_3\) catalyst were broader than that of the Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalyst. Several main diffraction peaks of MoO\(_3\) were detected at 2\(\theta\) = 23.5°, 25.7°, and 27.4°.\(^{15}\) The observed peaks revealed the MoO\(_3\) particles were well dispersed on the catalyst’s surface. A main diffraction peak located at 2\(\theta\) = 37.3° could be attributed to the NiO crystalline phase.\(^{16}\) The presence of F\(^{-}\) in the Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalyst structure caused to slightly shift the wavelengths of \(\gamma\)-Al\(_2\)O\(_3\), MoO\(_3\), and NiO to the higher values. Several main diffraction peaks of NiF\(_2\) were detected at 2\(\theta\) = 26.7 and 60.8°. Three diffraction peaks appeared at 2\(\theta\) = 37.2, 58.0, and 63.5° were assigned to the AlF\(_3\) crystalline phase.

The TCD signal with respect to the temperature for the NiMoF\(_0\)/ASA-Al\(_2\)O\(_3\) and NiMoF\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) catalysts are presented in Figure 5.

The surface acidity properties of all Ni-Mo oxide catalysts were investigated by means of NH\(_3\)-TPD, and results are presented in Table 3.

According to Table 3, the density of the strong acid sites (I) is increased and that of the strong acid sites (II) is decreased with increasing the amount of F\(^{-}\) and this is in accordance with the reference.\(^{17}\) The loadings of the fluoride ion to the Ni-Mo/ASA-Al\(_2\)O\(_3\) catalyst significantly change the structure of the surface acid sites. Figure 5 and Table 3 show a low-temperature peak at about 260°C (site I) and a high-temperature peak at about 410°C (site II). The low-temperature site is probably due to the ammonia coordinated to the aluminum species, while the high-temperature site is related to the protonic acidity. In this study, the reaction was conducted at temperature 300°C, so the acid site (I) should be considered in the analysis of acidic properties of the used catalyst in the n-C\(_{16}\) hydrocracking.

Generally, the hydrocracking reactions in other word the hydrogenation and cracking are performed on the catalyst. First, hydrogen gas and feed vapor are placed on the catalyst. Then, the catalytic cracking process is performed and finally the hydrogenation process. The higher the acidity of the catalyst, the greater the amount of gas feed placed on it, resulting in a higher reactivity. This could justify an increase in the hydrocracking process along with an increase in the acidity of the catalyst. The addition of the fluoride ions to the catalyst increases the deterioration and the acidity of the catalyst, and can justify the increase in hydrocracking. This could approve the fact that higher acidity means more activity and more coking that is why the catalyst deteriorates.\(^{18-21}\)

### Table 2: Chemical compositions and textural properties of Ni-Mo catalysts

| Catalyst             | F (wt.%) | Si (wt.%) | Ni (wt.%) | Mo (wt.%) | \(S_{\text{BET}}\) (m\(^2\)/g) | \(V_t\) (cm\(^3\)/g) | \(d_{\text{av}}\) (Å) |
|----------------------|----------|-----------|-----------|-----------|---------------------------------|------------------------|----------------------|
| Ni-Mo-F\(_0\)/ASA-Al\(_2\)O\(_3\) |          | 2.9       | 3.8       | 15.2      | 158.2                           | 0.3925                 | 99.24                |
| Ni-Mo-F\(_{3.6}\)/ASA-Al\(_2\)O\(_3\) | 3.7      | 3.4       | 3.9       | 14.8      | 140.9                           | 0.3766                 | 108.9                |

\(^{a}\)Specific surface area

\(^{b}\)Pore volume

\(^{c}\)Average pore size
4.2 Effect of the fluoride ion in the hydrocracking

Following the paper, the highest selectivity and yield to produce the diesel oil cut were obtained when the Ni-Mo/ASA-\(\text{Al}_2\text{O}_3\) catalyst is used in the VGO hydrocracking; so, the Ni-Mo/ASA-\(\text{Al}_2\text{O}_3\) was used as the catalyst in the n-C\(\text{16}\) hydrocracking. The 2 Ni-Mo-F\(_0\)/ASA-\(\text{Al}_2\text{O}_3\) and Ni-Mo-F\(_{3.6}\)/ASA-\(\text{Al}_2\text{O}_3\) catalysts were synthesized with identical porosity and active phase to investigate the effect of the catalyst formulation on the n-C\(\text{16}\) hydrocracking. The catalyst activity in the n-C\(\text{16}\) hydrocracking was investigated in 573 K with a content H\(_2\)/hydrocarbon molar ratio of 175 at a total pressure of 3 MPa. The total percentages of the product in the n-C\(\text{16}\) hydrocracking in the presence of the catalysts are given in Table 4.

Cracking activity is significantly influenced by the strength of the site type rather than the total concentration. So, this could be the reason that the amount of product in the presence of both catalysts is almost close to each other. The amount of the liquid products decreases but that of gas products increases with increasing the fluoride functional group to the Ni-Mo/ASA-\(\text{Al}_2\text{O}_3\) catalyst. This enhancement could be due to increasing the catalyst acidity and activity and this is in accordance with the reference. The mass distribution of the products in the n-C\(\text{16}\) hydrocracking in the presence of the catalysts is shown in Figure 6.

Most products in the presence of the Ni-Mo-F\(_0\)/ASA-\(\text{Al}_2\text{O}_3\) catalyst is the 10-carbon compounds, while, that is the

| Catalyst                  | Acid amount [mmol g\(^{-1}\)-cat] |
|---------------------------|----------------------------------|
|                           | Acid site I                      | Acid site II                     |
|                           | Strength (°C)                    | Density (mmol g\(^{-1}\))        | Strength (°C) | Density (mmol g\(^{-1}\)) |
| NiMoF\(_0\)/ASA-\(\text{Al}_2\text{O}_3\) | 263                              | 0.8863                           | 420           | 0.6574                    |
| NiMoF\(_{3.6}\)/ASA-\(\text{Al}_2\text{O}_3\) | 262                              | 0.9856                           | 438           | 0.1386                    |
8 and 9-carbon compounds in the presence of the F-promoted catalyst, in other words, the production of smaller compounds is more in the presence of the F-promoted catalysts. This could be due to the increase in the catalyst acidity and activity. The conversion and selectivity of the HCK catalyst can be impacted by several factors such as the zeolite porosity, the hydrogenation over the catalyst metal sites, acidity sites numbers, and the proximity between the 2 catalytic functions. Due to the electron-killing power of the fluorine electronegative element, it could be said the acidity concentration of Lewis sites of the F-containing catalyst is increased. On the other hand, the hydrocracking process takes place in the Brønsted acidity sites of the catalysts. Due to increasing the yield of the hydrocracking process when the F-promoted catalysts are used compared to the nonpromoted catalyst, it could be concluded that the presence of fluoride increases both the Lewis and Brønsted acidity sites of hydrocracking catalyst. This could approve the mechanism of the HCK process that, first, hydrogen gas and feed vapor are placed on the catalyst, resulting in a higher reactivity. This could justify an increase in the hydrocracking process with the catalyst acidity.

In a bifunctional catalyst, the balance between the 2 catalytic functions, cracking and hydrogenation, highly impacts the catalytic properties. Improve the strength of the hydrogenation function could be resulted in a significant increase in the conversion and selectivity toward desired products by increasing the rate of the carbocation desorption, reducing limiting the extent of secondary cracking.

### Kinetic equations of the VGO hydrocracking process

In the other part of this investigation, the performance of the promoted catalyst was studied in the VGO hydrocracking and discrete lumping kinetic equations of this process were investigated. The kinetic model represents the temperature at which the reaction is best performed. On the other hand, it is possible to use kinetics to obtain suitable reaction conditions to produce a specific oil cut. One of the most important factors influencing the hydrocracking process is temperature;

**TABLE 4** Total percentage of the products in presence of the 2 catalysts

| Catalyst                      | Conversion (%) | Gaseous products (%) | Liquid products (%) |
|-------------------------------|----------------|----------------------|---------------------|
| NiMoF₀/ASA-AL₂O₃              | 88.44          | 4.64                 | 95.36               |
| NiMoF₃.₆/ASA-AL₂O₃            | 98.83          | 8.14                 | 91.86               |

**FIGURE 6** Mass distribution of the products in the n-hexadecane conversion
| Temperature (°C) | Time (h) | Diesel (wt.%) | Kerosene (wt.%) | Naphtha (wt.%) | LPG (wt.%) |
|-----------------|----------|--------------|----------------|---------------|------------|
| 380             | 0.00     | 0.00         | 0.00           | 0.00          | 0.00       |
|                 | 0.30     | 0.86         | 0.25           | 0.12          | 0.02       |
|                 | 0.40     | 1.04         | 0.34           | 0.15          | 0.02       |
|                 | 0.50     | 1.25         | 0.40           | 0.19          | 0.03       |
|                 | 0.60     | 1.72         | 0.50           | 0.25          | 0.04       |
|                 | 1.00     | 2.55         | 0.78           | 0.38          | 0.06       |
|                 | 2.00     | 5.00         | 1.50           | 0.80          | 0.12       |
|                 | 4.00     | 9.60         | 2.80           | 1.65          | 0.30       |
|                 | 6.00     | 13.80        | 4.00           | 2.30          | 0.40       |
| 395             | 0.00     | 0.00         | 0.00           | 0.00          | 0.00       |
|                 | 0.30     | 1.078        | 0.50           | 0.25          | 0.04       |
|                 | 0.40     | 1.26         | 0.58           | 0.33          | 0.05       |
|                 | 0.50     | 1.53         | 0.70           | 0.41          | 0.07       |
|                 | 0.60     | 2.06         | 1.00           | 0.52          | 0.09       |
|                 | 1.00     | 3.06         | 1.40           | 0.78          | 0.13       |
|                 | 2.00     | 6.02         | 2.80           | 1.47          | 0.27       |
|                 | 4.00     | 11.40        | 5.20           | 2.90          | 0.60       |
|                 | 6.00     | 16.00        | 7.20           | 4.10          | 0.80       |
| 410             | 0.00     | 0.00         | 0.00           | 0.00          | 0.00       |
|                 | 0.30     | 1.63         | 1.44           | 0.99          | 0.10       |
|                 | 0.40     | 1.90         | 1.77           | 1.15          | 0.13       |
|                 | 0.50     | 2.47         | 2.18           | 1.46          | 0.16       |
|                 | 0.60     | 3.17         | 2.85           | 1.90          | 0.26       |
|                 | 1.00     | 4.73         | 4.27           | 2.82          | 0.37       |

(Continues)
so, this parameter has been discussed in the present paper. The time in the paper is related to the time it takes for the products to be extracted from the reactor and shows the trend of changes in manufactured products during the reaction. The VGO hydrocracking in the presence of the Ni-Mo-F3.6/ASA-Al2O3 catalyst was done at three 380, 395, and 410°C.
temperatures, and pressure of 10 MPa. The rest of the conditions are similar to section 2.6. Experimental data obtained from the VGO hydrocracking in the presence of the catalyst and the 380-410°C temperature range are listed in Table 5.

The time in Table 5 corresponds to the measurement the time at a spatial temperature and velocity of VGO. First, the product has been left the reactor column; then, analyses of them show the percentage of the VGO conversion per extraction. By fitting the experimental data and equations (1-9) in the Levenberg-Marquardt algorithm, the procedures of the product changes in the VGO hydrocracking are calculated and the results are shown in Figure 7.

Figure 7 shows that in the temperature range of 380-410°C, with increasing the residence time, the reaction products increase. This is in accordance with scientific articles. The kinetic equations are fitted to the experimental data at the temperatures, 380-410°C. The deviation was low between the experimental data of the diesel, kerosene, naphtha, and LPG obtained in VGO hydrocracking and the discrete lumping kinetic equations. The average absolute deviation was also lower than the experimental data (about 5%) on the studied condition.

Generally, the oil cuts could be converted to each other at temperatures above 380°C but, since, the production rate of the oil cuts in the VGO hydrocracking is more than the conversion rate of them into the smaller ones in the 380-410°C temperature range, changes in the oil cuts, diesel, kerosene, naphtha, and gas, in the 380-410°C temperature range, are related in its production from VGO hydrocracking and converting them into smaller cuts could be considered zero.

The VGO conversion in the hydrocracking process is increased with rising temperature, and this could approve the fact that the VGO hydrocracking is thermally controlled. The amount of deviation between experimental data and equations is increased with rising temperatures, and this could be due to converting the produced heavy cuts, such as diesel, into lighter ones. In other words, discrete lumping model in higher temperatures, above 410°C, should be more complex and the heavier cuts, such as diesel, kerosene, and naphtha, are converted into the lighter ones.

In Figure 7, the graphs for diesel, kerosene, naphtha, and gas produced from the VGO hydrocracking become closer as the temperature rises and this could be a confirmation of the conversion of the heavier oil cuts such as diesel, kerosene, and naphtha into the lighter cuts at higher temperatures.

The kinetic constants, $k_1$, $k_2$, $k_3$, and, $k_4$, were calculated by fitting the experimental data and kinetic equations using the Levenberg-Marquardt algorithm. Based on the Arrhenius equation (Equation 10), the Arrhenius constants ($k_0$) and activation energy ($E_a/R$) of VGO hydrocracking were calculated.

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} (10)

The kinetic constants at different temperature are listed in Table 6.

The $k$ constant is related to the reaction rate, and it has a negative value, because the reaction rate decreases over time. Results of the activation energy and the kinetic constants in Equation 10 and the model are listed in Table 7.

According to Table 7 and Figure 2, the kinetic constants of the reaction to produce diesel from the VGO hydrocracking is less than 3 other reactions, the production of gas, naphtha, and kerosene. In other words, the rate of the Reactions 2, 3, and 4 in Figure 2 is more than that of the Reaction 1. That means the gas, naphtha, and kerosene production is controlled thermodynamically, but the diesel production is controlled kinetically, but the diesel production is controlled thermodynamically and this could justify the diesel production.

The low activation energy of a reaction indicates that the production rate of the product during the reaction is high. But whether this reaction occurs during the process is high or low can be explained by thermodynamic equations.

### 5 | CONCLUSIONS

The influence of the fluoride addition to the Ni-Mo/ASA-Al$_2$O$_3$ catalyst was investigated. First, 2 catalysts, Ni-Mo-F$_3$/ASA-Al$_2$O$_3$ and Ni-Mo-F$_3$/ASA-Al$_2$O$_3$, were prepared by the impregnation method and tested in the n-hexadecane hydrocracking as a model component, and compared with each other. The results of this study are as follows:

1. The cracked product yields increased with increasing the acidic site strong.
2. The fluoride modifies the morphology of support (surface area, pore volume, pore size distribution, and crystalite phase) and forms a new functional group on the γ-alumina surface.
3. Appropriate balance between textural and acidic properties of catalysts can impact selectivity of the crude oil hydrocracking.

The performance of the Ni-Mo-F$_3$/ASA-Al$_2$O$_3$ catalyst was investigated in the VGO hydrocracking and the obtained results of this process are formulated by discrete lumping.

| $E_a/R$ | $E_a/R$ | $E_a/R$ | $E_a/R$ | $ln(k_{01})$ | $ln(k_{02})$ | $ln(k_{03})$ | $ln(k_{04})$ |
|---------|---------|---------|---------|-------------|-------------|-------------|-------------|
| 9750.9  | 26817   | 29005   | 26581   | 11.227      | 36.074      | 38.836      | 33.451      |

**TABLE 7** Activation energy and kinetic constants of the model
model and kinetic constants of these equations for the catalyst were calculated by fitting experiment data and the equations in the Levenberg-Marquardt algorithm. The results of this section are as follows:

1. The amount of producing diesel, kerosene, naphtha, and gases is increased with increasing the temperature.
2. The hydrocracking process is thermally controlled.
3. Larger produced oil cuts convert into smaller oil cuts at all temperatures, but this conversion is more as the temperature is raised.
4. At all temperatures above 380°C, all oil cuts can be converted to each other, but this conversion rate is temperature-dependent and increases with increasing reaction temperature.

**REFERENCES**

1. Li W, Zhu J, Qi J. Application of nano-nickel catalyst in the viscosity reduction of Liaohe extra-heavy oil by aqua-thermalysis. *J Fuel Chem Technol.* 2007;35(2):176-180. https://doi.org/10.1016/S1872-5813(07)60016-4
2. Leyva C, Ancheyta J, Travert A, et al. Activity and surface properties of NiMo/SiO₂–Al₂O₃ catalysts for hydroprocessing of heavy oils. *Appl Catal A Gen.* 2012;425-426:1-12. https://doi.org/10.1016/j.apcata.2012.02.033
3. Vermeiren W, Gilson J-P. Impact of zeolites on the petroleum and petrochemical industry. *Top Catal.* 2009;52(9):1131-1161. https://doi.org/10.1007/s11244-009-9271-8
4. Thakur DS, Thomas MG. Catalyst deactivation in heavy petroleum and synthetic crude processing: a review. *Appl Catal A.* 1985:15(2):197-225. https://doi.org/10.1016/S0166-9834(00)81837-0
5. Vogelaar BM, Eijsbouts S, Bergwerff JA, Heizswoolf JJ. Hydroprocessing catalyst deactivation in commercial practice. *Catal Today.* 2010;154(3):256-263. https://doi.org/10.1016/j.catod.2010.03.039
6. Ho TC. Modeling of reaction kinetics for petroleum fractions BT. In: Hsu CS, Robinson PR, eds. *Practical Advances in Petroleum Processing.* New York, NY: Springer, New York; 2006:653-694.
7. Astariita G, Ocone R. Lumping nonlinear kinetics. *AIChE J.* 1988;34(8):1299-1309. https://doi.org/10.1002/aic.690340808
8. Astariita G. Lumping nonlinear kinetics: Apparent overall order of reaction. *AIChE J.* 1989;35(4):529-532. https://doi.org/10.1002/aic.690350402
9. Dik PP, Klimov OV, Koryakina GI, et al. Composition of stacked bed for VGO hydrocracking with maximum diesel yield. *Catal Today.* 2014;220-222:214-132. https://doi.org/10.1016/j.catod.2013.07.004
10. Barkhordari A, Fatemi S, Daneshpayeh M, Zamani H. Development of a kinetic model for modeling the industrial VGO hydrocracker accompanied by deactivation. *Int J. Chem React Eng.* 2010;8:10.2202/1542-6580.1982.
11. Olorunyolemi T, Kydd RA. The effect of fluoride addition on the catalytic activity of galium-aluminium mixed oxides and Ni-Mo supported on them. *Catal Lett.* 1999;63:173-178.
12. Benítez A, Ramírez J, Fierro JLG, López Agudo A. Effect of fluoride on the structure and activity of NiW/Al₂O₃ catalysts for HDS of thiophene and HDN of pyridine. *Appl Catal A Gen.* 1996;144(1):343-364. https://doi.org/10.1016/0926-860X(96)00121-4
13. Looi PY, Mohamed AR, Tye CT. Hydrocracking of residual oil using molybdenum supported over mesoporous alumina as a catalyst. *Chem Eng J.* 2012;181-182:717-724. https://doi.org/10.1016/j.cej.2011.12.080
14. Looi PY, Mohamed AR, Tye CT. Hydrocracking of residual oil using molybdenum supported over mesoporous alumina as a catalyst. *Chem Eng J.* 2012;181:717-724. https://doi.org/10.1016/j.cej.2011.12.080
15. Causzi D, Deltratti M, Predieri G, et al. Synthesis of MMoO₄/SiO₂ catalysts (M=Ni or Co) by a sol-gel route via silicon alkoxides – Stabilization of beta-NiMoO₄ at room temperature. *Catal Lett.* 1999;182:125-135.
16. Zhao D, Bao S, Zhou W, Li H. Preparation of hexagonal nanoporous nickel hydroxide film and its application for electrochemical capacitor. *Electrochem Commun.* 2007;9:869-874.10.1016/j.elecom.2006.11.030
17. Guo X, Song M, Zhao X, Zhao L. Effect of fluoride promoter on the catalytic activity of NiWF₆–Al₂O₃ for hydrodenitrogenation and hydrodesulfurization of coal tar. *J Fuel Chem Technol.* 2016;44(11):1326-1333. https://doi.org/10.1016/S1872-5813(16)30056-1
18. Olorunyolemi T, Kydd RA. The effect of fluoride addition on the catalytic activity of gallium–aluminum mixed oxides and Ni–Mo supported on them. *Catal Lett.* 1999;63(3):173-178. https://doi.org/10.1023/A:1019054013022
19. Ali MA, Tatsumi T, Masuda T. Development of heavy oil hydrocracking catalysts using amorphous silica-alumina and zeolites as catalyst supports. *Appl Catal A Gen.* 2002;233(1):77-90. https://doi.org/10.1016/S0926-860X(02)00121-7
20. Tailleur RG. Hydrocracking catalyst to produce high quality Diesel fraction. In Gaingneaux E, De Vos DE, Grange P, Jacobs PA, Martens JA, Ruiz P, Poncelet G, eds. *Scientific Bases for the Preparation of Heterogeneous Catalysts*. Oklahoma: Elsevier; 2000:321-329.
21. Saab R, Polychronopoulou K, Zheng L, Kumar S, Schiffer A. Synthesis and performance evaluation of hydrocracking catalysts: A review. *J Ind Eng Chem.* 2020;89:83-103. https://doi.org/10.1016/j.jiec.2020.06.022
22. Francis J, Guillen E, Bats N, Pichon C, Corma A, Simon LJ. Design of improved hydrocracking catalysts by increasing the proximity between acid and metallic sites. *Appl Catal A Gen.* 2011;409-410:140-147. https://doi.org/10.1016/j.apcata.2011.09.040
23. Bautista FM, Campelo JM, Garcia A, et al. Fluoride and sulfate treatment of AlPO₄–Al₂O₃ catalysts. I. Structure, texture, surface acidity and catalytic performance in cyclohexene conversion and cumene cracking. *J Catal.* 1994;145(1):107-125. https://doi.org/10.1006/jcat.1994.1013
24. Koltunov KY, Sobolev VI. Efficient cleavage of cumene hydroperoxide over HUSY zeolites: The role of Bronsted acidity. *Appl Catal A Gen.* 2008;336(1):29-34. https://doi.org/10.1016/j.apcata.2007.08.019
25. Weitkamp J, Ernst S. Factors influencing the selectivity of hydrocracking in zeolites BT. In: Barthomeuf D, Derouane EG, Hölдерich W, eds. *Guidelines for Mastering the Properties of Molecular
Sieves: Relationship Between the Physicochemical Properties of Zeolitic Systems and Their Low Dimensionality. Boston, MA: Springer, US; 1990:343-354.

26. Juárez EM, García FJO, Hernández PS. Hydrocracking of vacuum residue by homogeneous catalysis. *Fuel*. 2014;135:51-54.10.1016/j.fuel.2014.05.070

27. Hew KL, Tamidi AM, Yusup S, Lee KT, Ahmad MM. Catalytic cracking of bio-oil to organic liquid product (OLP). *Bioresour Technol*. 2010;101(22):8855-8858. https://doi.org/10.1016/j.biortech.2010.05.036

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