Study the Effect of Catalyst -to- Oil Ratio Parameter (COR) on Catalytic Cracking of Heavy Vacuum Gas Oil

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ABSTRACT

This work deals with the production of light fuel cuts of (gasoline, kerosene and gas oil) by catalytic cracking treatment of secondary product mater (heavy vacuum gas oil) which was produced from the vacuum distillation unit in any petroleum refinery. The objective of this research was to study the effect of the catalyst -to- oil ratio parameter on catalytic cracking process of heavy vacuum gas oil feed at constant temperature (450 °C). The first step of this treatment was, catalytic cracking of this material by constructed batch reactor occupied with auxiliary control devices, at selective range of the catalyst -to- oil ratio parameter (  2, 2.5, 3 and 3.5) respectively. The conversion of heavy vacuum gas oil which was obtained, reaches to (50, 70, 75 and 80) % for (2, 2.5, 3 and 3.5 catalysts -to- oil ratio parameter respectively. The second step for this study was distillation of this cracking heavy vacuum gas oil liquid by atmospheric distillation device for these several catalyst -to- oil ratio parameter, according to obtained light fuel cuts (gasoline, kerosene and gas oil). The percentage volume of light fractions at various COR are (7, 25 and 18) for COR 2, (10, 20 and 40) for COR 2.5, (10, 30 and 35) for COR 3 and (15, 30 and 35) for COR 3.5 which separates according to its boiling point. The light cuts were distilled by atmospheric distillation device in order to obtained distillation curve. The third step was study the major physical and chemical properties for feed (heavy vacuum gas oil) and catalytic cracking liquid of HVGO at various COR with its light fuel fractions, the results refers to acceptable properties compared with other commercial properties.

Key word. Catalytic Cracking Reaction, Heavy vacuum gas oil, Catalyst to oil ratio parameter
INTRODUCTION
The purpose of catalytic cracking reaction is to convert high boiling petroleum feedstocks to lower boiling products by cracking the hydrocarbon in the feed. During cracking, the condensed type molecules, such as naphthalene or anthracene, are converted into lower molecular weight hydrocarbons. The main kinds of feedstock for catalytic cracking are fractions generally boiling within the range of 200 – 500 °C. The refiners employed amorphous or synthetic silica – alumina catalysts. After cracking of heavy vacuum gas oil, fractional distillation separates light fuels and unconverted oil. Crude oils are mainly constituted of hydrocarbons mixed with variable amounts of sulfur, nitrogen, and oxygen compounds. (Speight, J.G. 1999). Crude oils are not used directly as fuels or as feedstock for the production of chemicals, this is due to the complex nature of the crude oil mixture and the presence of some impurities that are corrosive or poisonous to processing catalysts (Speight, J.G. 1999). Crude oils are refined to separate the mixture into simpler fractions that can be used as fuels, lubricants, or intermediate feedstock to the petrochemical industries. (Speight, J.G. 1999). Heavy vacuum gas oil (HVGO) is complex mixtures of high molecular weight compounds. They consist of aromatic, aliphatic and naphthenic hydrocarbons, typically having carbon numbers from C_{20} to C_{50}, together with asphaltenes and smaller amounts of heterocyclic compounds containing sulphur, nitrogen and oxygen. (Alkilani, A. Haitham, et al., 2007) Vacuum gas oils are high boiling point petroleum cuts (350-550°C). HVGO consists primarily of the residue from distillation or cracking units in there refinery. (Pillion L. Z, 2005). The increasing demand for transportation fuels such as gasoline, kerosene and diesel has led to an increased value for the atmospheric residue as a feedstock for vacuum distillation and for cracking processes. (Gary, J. H., and Handwerk, G. H 2001) Treatment in any thermal process results in the formation of gases, gasoline, middle distillate fractions (kerosene and gas oil), heavy residual fractions, and coke. The yield, relation between the reaction product’s and the properties of these products depend on many factors, but the main role is played by the composition of the feed stock, the temperature, pressure and duration of the reaction. (Alan G. Lucas 2001). Mohammed et al. 2013 study the catalytic cracking of vacuum gas oil at reaction temperature range 440 – 500 °C and weight hour space velocity range 10 – 25 h⁻¹ the conversion at 500 °C and WHSV 10 h⁻¹ was 50.2 % and gasoline yield was 24.8 %. Reagan 1968 studied the catalytic cracking wax at the reaction temperature range 470 – 500 and catalyst to oil ration 0.2 – 0.8 by zeolite catalyst and the conversion reaches to more than 85%. Lappas et.al 1986 study the catalytic cracking for wax at reaction temperature 460, 500, 538 and 565°C and catalyst to oil ratio 2 – 12 to produce light fuels and the conversions ranges from 70 to 90 wt.%. Mori et al. study the thermal cracking of heavy oil at the reaction temperature 400 – 630 °C to produce the light oil and cracking gas to form by product carbon. The objective of this research was to study the effect of different catalyst -to- oil ratio on catalytic cracking process of heavy vacuum gas oil feed at constant temperature (450 °C).
2. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Heavy vacuum gas oil (HVGO)
The raw material for this study was heavy vacuum gas oil matter, which was obtained from the unit of vacuum distillation of AL-Dura refinery, which was used as a feedstock in this work and its major physical and chemical properties were listed in table 2.

2.1.2 Catalyst
The catalyst that will be used for cracking heavy vacuum gas oil and other matters like (slack wax, vacuum residue, furfural extract oil,…etc.) was prepared by previous work, have some major properties were listed in table 1.

| Table 1. Properties of catalyst.                                      |
|---------------------------------------------------------------------|
| Characteristics          | Value   |
| Average pore diameter A₀ | 9       |
| Surface area, m²/gm.     | 230     |
| Granular size, mm        | 3-8     |

2.2. Procedure of the work:-
The process of catalytic cracking of heavy vacuum gas oil feed were carried out in designed batch reactor unit Fig.1, and Fig.2, made of carbon steel and its volume about 300 ml., which contain two valves, upper for inlet raw material and down for discharge product, occupied with many auxiliary parts, like (electrical heater, thermocouple, timer, temperature controller, hood).
The desired quantity (110 ml) of the (HVGO) fed in the reactor, which contains amount of prepared zeolite catalyst, used as catalytic cracking reaction with ratio of feed, and by several runs with various amount of catalyst -to- oil ratios (2, 2.5, 3 and 3.5) that will be used as variable parameter for catalytic cracking process. The cracking will be occurred with constant temperature at 450 °C inside the reactor which controlled by temperature controller and pressure about (80 – 90) atmosphere. The results of cracked HVGO liquid were listed in Table 2.
The second step is, distillation process that will be done by ASTM- D86 device; (which consist of heater, condenser, Flask) on the heavy vacuum gas oil feed and cracked liquid fuel and its light products to final distillation temperature is 350 °C and the results were listed in table 2. And finely calculate the major physical and chemical properties of the heavy vacuum gas oil feed and cracked HVGO liquid also its light fuel fractions (gasoline, kerosene and gas oil) in order to compare it with commercial types and possibilities of use it in various usages.
Figure 1. Laboratory batch reactor device.

Figure 2. Flow diagram of experimental batch reactor unit with controls system.

3. RESULTS AND DISCUSSION

3.1. Atmospheric distillation (ASTM D-86 method)
The analysis of the heavy vacuum gas oil and different cracked HVGO liquid, for all these ranges of catalyst -to- oil ratio results are shown in table 2.

Table 2. Atmospheric distillation for HVGO feed and cracked HVGO liquid feed at different catalysts -to- oil ratio.

| Volume % | HVGO feed °C | The cracked HVGO liquid feed at different catalyst -to- oil ratio |
|----------|--------------|---------------------------------------------------------------|
| Conversion % | 2 | 2.5 | 3 | 3.5 |
| 0        | 198 | 80  | 65  | 68  | 60  |
| 5        | 262 | 166 | 100 | 110 | 90  |
| 10       | 266 | 190 | 165 | 184 | 164 |
| 15       | 280 | 210 | 256 | 200 | 178 |
Table 2. represents the atmospheric distillation results for HVGO feed and cracked HVGO liquid feed in different amount of catalyst -to- oil ratio of catalytic cracking feed in reactor.

Can noticed from the above results, the cracking will be occurs in all selected catalyst -to- oil ratio, but at different conversion according to amount of COR. So the conversion of HVGO reaches to 50% at COR equal to 2, also the conversion of HVGO reaches to 70 % at COR equal to 2.5 and the conversion of HVGO reaches to 75 % at COR equal to 3, but the best conversion is reaches to 80% at COR equal to 3.5, due to their high conversion and high amount of gasoline product as shown in figure 7.

Based on the maximum of the gasoline yield and middle distillate yield, it could be said that the best catalyst -to- oil ratio of catalytic cracking reaction is 3.5.

3.2 Physical and chemical properties for HVGO feed and catalytic cracking products.

The physical and chemical properties of HVGO at 450 °C for different catalyst to oil ratio (2, 2.5, 3 and 3.5) are shown in tables 3, 4, 5 and 6.

The properties of the catalytic cracking process for HVGO feed at 450 °C and at the catalyst -to- oil ratio of 2 are shown in Table 3.

Table 3. Physical and chemical properties for HVGO feed and its fractions.

| Property                  | ASTM D method | HVGO feed | The cracking liquid product | Gasoline product | Kerosene product | Gas oil product |
|---------------------------|---------------|-----------|------------------------------|------------------|------------------|----------------|
| Specific gravity          | ASTM D1298    | 0.973     | 0.9446                       | 0.898            | 0.9554           | 0.973          |
| API gravity               | ASTM D1298    | 13.962    | 18.3                         | 26.1             | 16.6             | 13.92          |
| Mean average boiling point,° C | ASTM D86     | 320       | 245                          | 156              | 244              | 330            |
| Molecular weight          | equation      | 228       | 169.4                        | 118              | 166              | 238            |
| Refractive index          | ASTM D1218    | 1.5015    | 1.497                        | 1.478            | 1.497            | 1.510          |
| Viscosity 40 °C cSt       | ASTM D445     | 50        | 6.5                          | 4.5              | 4.5              | 5.6            |
| Viscosity 100°CcSt        | ASTM D445     | 5.2       | 1.9                          | 1.5              | 1.6              | 1.5            |
| Aniline point °C          | ASTM D611     | 36        | 20                           | 5                | 16               | 39             |
| Flash point °C            | ASTM D93      | 162       | 110                          | 46               | 108              | 168            |
| Hydrogen %                | equation      | 13.36     | 12.3                         | 12.6             | 11.8             | 11.6           |
Heavy vacuum gas oil feed rich with undesirable components such as aromatics, oxygen, nitrogen, and sulfur. So, the physical and chemical properties of HVGO feed such as API gravity or specific gravity, density, viscosity and others properties are considerably influenced by high boiling point temperature for constituents, like these undesirable components that concentrated in HVGO feed, so it is important to characterize the heaviest fractions of HVGO feed in order to determine their properties as shown in tables 3, 4, 5 and 6. HVGO feed has high molecular weight so, has high ability to crack to produce light fractions like, gasoline, kerosene and gas oil. The cracking liquid product with lower mean average boiling point gives more gasoline yield until distillation temperature 350 °C, at a catalyst -to- oil ratio equal 3.5 and this correct for others COR, but in different volume % content of gasoline, kerosene and gas oil, which separates according to its boiling point (IBP, 180 °C) for gasoline cut,(180, 250 °C) for kerosene cut and (250, 350 °C) for gas oil cut, as shown in Table 2.

On the other hand the properties of the catalytic cracking for HVGO feed at 450 °C and at the catalyst -to- oil ratio of 2.5 are shown in Table 4.

Table 4. Physical and chemical properties for HVGO feed and it fractions.

| Property               | HVGO feed  | The cracking liquid product | Gasoline product | Kerosene product | Gas oil product |
|------------------------|------------|-----------------------------|------------------|------------------|----------------|
| Specific gravity       | 0.973      | 0.948                       | 0.9294           | 0.95             | 0.965          |
| API gravity            | 13.962     | 17.76                       | 20.75            | 17.45            | 15.13          |
| Mean average boiling point °C | 320       | 260                         | 165              | 250              | 360            |
| Molecular weight       | 228        | 181                         | 118              | 172              | 273            |
| Refractive index       | 1.5015     | 1.491                       | 1.480            | 1.483            | 1.496          |
| Viscosity (40 °C) cSt  | 50         | 5.6                         | 4.5              | 9                | 11             |
| Viscosity (100 °C) cSt | 5.5        | 1.75                        | 1.5              | 2.3              | 2.5            |
| Aniline point °F       | 36         | 24                          | -3               | 20               | 52             |
| Flash point °C         | 162        | 120                         | 52               | 112              | 190            |
| Hydrogen %             | 13.36      | 11.9                        | 12.1             | 11.8             | 11.7           |
| Sulfur %               | 2.754      | 2.88                        | 2.44             | 2.61             | 3.08           |
| Carbon %               | 83.886     | 85.22                       | 85.46            | 85.59            | 85.218         |
| C/H                    | 6.278      | 7.16                        | 7.06             | 7.25             | 7.28           |
| Aromatic %             | 24.18      | 47                          | 43.93            | 48.63            | 50.2           |

Also the properties of the catalytic cracking for HVGO feed at 450 °C and at the catalyst -to- oil ratio of 3 are shown in Table 5.
Table 5. Physical and chemical properties for HVGO feed and it fractions.

| Property                        | HVGO feed | The cracking liquid product | Gasoline product | Kerosene product | Gas oil product |
|---------------------------------|-----------|-----------------------------|------------------|------------------|-----------------|
| Specific gravity                | 0.973     | 0.93                        | 0.8826           | 0.935            | 0.964           |
| API gravity                     | 13.962    | 20.65                       | 28.82            | 19.83            | 15.285          |
| Mean average boiling point       | 320       | 270                         | 170              | 244              | 350             |
| C                               | 228       | 194                         | 128              | 171              | 248             |
| Molecular weight                | 1.5015    | 1.488                       | 1.477            | 1.4865           | 1.508           |
| Viscosity (40 °C) cSt           | 50        | 6                           | 4.5              | 5                | 5.8             |
| Viscosity (100 °C) cSt          | 5.5       | 1.9                         | 1.6              | 1.7              | 1.8             |
| Aniline point °F                | 36        | 34                          | 15               | 22               | 48              |
| Flash point °C                  | 162       | 126                         | 56               | 108              | 183             |
| Hydrogen %                      | 13.36     | 12.1                        | 12.8             | 12               | 11.6            |
| Sulfur %                        | 2.754     | 2.678                       | 1.7              | 2.745            | 3.5             |
| Carbon %                        | 83.886    | 85.22                       | 85.5             | 85.255           | 84.9            |
| C/H                             | 6.278     | 7.04                        | 6.68             | 7.1              | 7.32            |
| Aromatic %                      | 24.18     | 43.93                       | 32.96            | 45.5             | 51.76           |

Also the properties of catalytic cracking for HVGO feed at 450 °C and at the catalyst –to- oil ratio of 3.5 are shown in Table 6.

Table 6. Physical and chemical properties for HVGO feed and it fractions.

| Property                        | HVGO feed | The cracking liquid product | Gasoline product | Kerosene product | Gas oil product |
|---------------------------------|-----------|-----------------------------|------------------|------------------|-----------------|
| Specific gravity                | 0.973     | 0.93                        | 0.869            | 0.959            | 0.962           |
| API gravity                     | 13.962    | 20.65                       | 31.33            | 16.1             | 15.59           |
| Mean average boiling point       | 320       | 286                         | 165              | 240              | 360             |
| C                               | 228       | 208                         | 128              | 162              | 275             |
| Molecular weight                | 1.5015    | 1.500                       | 1.476            | 1.490            | 1.508           |
| Viscosity (40 °C) cSt           | 50        | 6                           | 5.5              | 5.8              | 6.4             |
| Viscosity (100 °C) cSt          | 5.5       | 1.85                        | 1.75             | 1.85             | 1.9             |
| Aniline point °F                | 36        | 39                          | 19               | 14               | 52              |
| Flash point °C                  | 162       | 138                         | 52               | 105              | 190             |
| Hydrogen %                      | 13.36     | 12.1                        | 12               | 11.7             | 11.6            |
| Sulfur %                        | 2.754     | 3.078                       | 1.194            | 2.9              | 3.437           |
| Carbon %                        | 83.886    | 84.822                      | 86.8             | 85.4             | 84.96           |
| C/H                             | 6.278     | 7.01                        | 7.23             | 7.3              | 7.32            |
| Aromatic %                      | 24.18     | 43.93                       | 45.5             | 50.2             | 51.76           |

As shown from Tables (3, 4, 5 and 6) the physical and chemical properties for fuel fractions (gasoline, kerosene, and gas oil) which are product from treatment heavy vacuum gas oil at various catalyst -to- oil ratio and constant temperature 450 °C, acceptable for commercial uses due to their similar property with commercial one. So can said, success will be occur to convert secondary product mater HVGO to another light fuel fractions (gasoline, kerosene and gas oil) which are
produced from crude oil, and which is useful to use as automobile for gasoline cut and domestic uses for kerosene cut and diesel fuel for gas oil cut.

Table 7. Some properties of commercial light fractions.

| Light fraction | Specific gravity | Flash point °C | Viscosity 40 °C sCt | Final boiling point (°C) | Cetane number |
|----------------|------------------|----------------|----------------------|--------------------------|---------------|
| Gasoline       | 0.775            | 2              | 0.9                  | 190                      | ---           |
| Kerosene       | 0.81             | 38             | 1.5                  | 258                      | ---           |
| Gas oil        | 0.85             | 54             | 5.6                  | 350                      | 53            |

3.3 Effect of temperature on volume heavy vacuum gas oil distillation
In order to study the effect of the temperature on the process with the accumulated volume percentage HVGO was studied with increasing of temperature of the process.

![Figure 3. Atmospheric distillation for HVGO feed.](image)

**Figure 3.** Atmospheric distillation for HVGO feed.

**Fig. 3** shows the relationship between the temperature and volume distillation curve for HVGO feed. By this distillation curve, can calculate the mean average boiling point for HVGO feed its equal 320 °C and by this temperature with specific gravity, can calculate another property for example molecular weight by empirical equation and other properties which listed in Tables 3, 4, 5 and 6, and then to compare it with commercial product to know the benefit of this work.

3.4 Distillation curve for heavy vacuum gas oil feed and HVGO cracked at various catalysts –to- oil ratio

**Fig.s 4, 5, 6 and 7** shows the relationship between the temperature and volume % distillation curve for HVGO feed and HVGO feed cracked in 2, 2.5, 3 and 3.5 catalyst -to- oil ratio respectively. The mean average boiling point temperature for HVGO feed cracked in (2, 2.5, 3 and 3.5) catalyst -to- oil ratio equal to (245, 260, 270 and 286°C) respectively as shown in **Fig.s 4, 5, 6 and 7**, that’s
mean, when this temperature is low it means, this cracked feed have high content in light fractions (gasoline, kerosene and gas oil) than another COR ratio cracking. The percentage volume of light fractions in various COR ratio are (7, 25 and 18) for COR ratio 2, (10, 20 and 40) for COR ratio 2.5, (10, 30 and 35) for COR ratio 3 and (15, 30 and 35) for COR ratio 3.5 which separates according to its boiling point (IBP, 180 °C) for gasoline cut, (180, 250 °C) for kerosene cut and (250, 350 C) for gas oil cut, as shown in Table 2.

![Figure 4](image1)

**Figure 4.** Atmospheric distillation for HVGO feed cracked at the catalyst -to- oil ratio of 2.

![Figure 5](image2)

**Figure 5.** Atmospheric distillation for HVGO feed cracked at the catalyst -to- oil ratio of 2.5.
As shown from Table 2, by various catalyst to oil ratio (2, 2.5, 3 and 3.5) ability to convert HVGO as a feed to another light benefit fuel fractions in high conversion, which reaches to more than 80% and in different amount of the light fraction products according to their boiling point (IBP, 180 °C) for gasoline cut, (180, 250 °C) for kerosene cut and (250, 350 °C) for gas oil cut, but the more economic one is 3.5 of catalyst -to-oil ratio due to their high conversion 80% and high amount of light cut production (15, 30 and 35).
4. CONCLUSIONS

1- The ability of catalytic cracking for secondary product matter, heavy vacuum gas oil (HVGO) at different catalyst-to-oil ratio and constant temperature 450 °C and pressure about 90 atmosphere and period reaction time about to 30 minute but the best one was at COR ratio equal 3.5 for economic consideration (conversion and amount of light fractions).

2- Possibilities to obtained light fuel fractions (gasoline, kerosene, and gas oil) from catalytic cracking of secondary product matter (HVGO) with acceptable properties products according to standard properties.

3- Possibilities to use these light products to automobile for gasoline cut and domestic uses for kerosene cut and diesel fuel for gas oil cut.

5. ABBREVIATION

| Abbreviation | Description                        |
|--------------|------------------------------------|
| HVGO         | Heavy Vacuum Gas Oil               |
| COR          | Catalyst-to-Oil Ratio             |
| ASTM         | American Society for Testing and Material |
| WHSV h⁻¹     | Weight Hour Space Velocity         |
| IBP (°C)     | Initial Boiling point             |

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