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Preparation of Light Fuel Fractions from Heavy Vacuum Gas Oil by Thermal Cracking Reaction

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Abstract

This work deals with thermal cracking of heavy vacuum gas oil which produced from the top of vacuum distillation unit at Al- DURA refinery, by continuous process. An experimental laboratory plant scale was constructed in laboratories of chemical engineering department, Al-Nahrain University and Baghdad University. The thermal cracking process was carried out at temperature ranges between 460-560°C and atmospheric pressure with liquid hourly space velocity (LHSV) equal to 15hr⁻¹. The liquid product from thermal cracking unit was distilled by atmospheric distillation device according to ASTM D-86 in order to achieve two fractions, below 220°C as a gasoline fraction and above 220°C as light cycle oil (LCO). The first fraction which was below 220°C was fractionated to light fractions (gasoline, kerosene and gas oil) by atmospheric distillation device. The fractions (gasoline, kerosene and gas oil) by atmospheric distillation device in order to obtained distillation curve for these fractions. Physical properties were recorded for these cuts to compare it with standard property test, in order to studying the possibilities of industrial uses. The maximum conversion of heavy vacuum gas oil was obtained by this process equal to 82 wt. % of feed at 540°C.

Keywords: light fuel, thermal cracking, heavy vacuum, gas oil.

1. Introduction

Vacuum gas oil is a part of petroleum hydrocarbon heavy distillate family. Vacuum distillation recovers gas oil from the residual oil; in a vacuum tower so that the boiling point temperature is reduced, this allows distillation at temperatures that are not possible in atmospheric distillation.

The thermal cracking unit is consisting of the scission of the hydrocarbon C–C bonds present in the feedstock. It is occurring when the temperature is raised (400-900) $^{\circ}$ C to a point at which the bonds that hold a molecule together are broken. Cracking reaction start to occur at a temperatures of about (315-370) $^{\circ}$ C, depending on the hydrocarbon nature of the material being cracked, feed stock type and product requirement.

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. [1]

The rate of a reaction grows with elevation of the feed stock boiling point. Feed stock containing mainly alkanes is preferable for thermal cracking plants because they decompose more readily with the formation of target products such as gas, gasoline, and middle distillate, as the same time a little coke forms.

The degree of conversion in the thermal cracking is characterized by the gasoline yield

relative to the feed stock. The degree of conversion is limited by the formation of coke and gas. The coke yield grows with increasing temperature and residence time of the stock in the reaction zone. [2].

Elevation of the cracking temperature at a constant pressure and constant degree of conversion leads to an increase in the constant of light components and to a reduction in the yield of heavy fractions and coke. [3]

The feed stock consists of a large number of individual componentsso, it is impossible to predict or follow the fate of each of these components under the action of high temperatures.

The aim of this work study the thermal cracking reaction of heavy vacuum gas oil at a temperature ranges (460-560) ° C and tested some major physical and chemical properties of light product fractions to compare it with standard property test, in order to studying the possibilities of industrial uses.

2. Experimental Work Materials

Heavy vacuum gas oil which produced from top of vacuum distillation unit in Al -Dura refinery was used as feedstock in this study. The properties of heavy vacuum gas oil were determined by laboratory of AL-Dura refinery, as shown in Table 1.

Table 1,

Physical and chemical properties of vacuum gas oil sample.

| r | |
|--------------------------------|-----------------------------|
| Characteristics | Value |
| Viscosity $(40^{0}C)$ | 48 C.st |
| Flash point (open cup) | 110 [°] C |
| PH | 7 |
| Color | brown |
| Melting point / freezing point | >15 °C |
| Initial boiling point and | 306-532 ⁰ C |
| boiling range | |
| Vapor pressure | 0.01 kpa. 20 ⁰ C |
| Relative density | 0.9 |
| Auto-ignition temperature | >220 °C |
| Specific gravity | 0.91 |
| | |

3. The Experimental Work Units

The desired quantity of HVGO(6300 ml/hr.) pumped by dosing pump at the desired flow to the evaporator. In the evaporator the feed heated to 330°C, and then enters the reactor, its volume was (420 ml).

The reactor temperature was measured by thermocouples. The product discharged to the condenser section, where the condensates are collected, for all runs in various operating temperature. The uncondensed gases are collected in gas collector. The duration time for each experiment was 30 minute.

Fig. (1) Shows the fixed bed reactor unit where experiments which took place at temperature range $460-560^{\circ}$ C and liquid hour space velocity 15hr⁻¹.

Fig. (2) Shows the distillation unit of cracking liquid products which were achieved in atmospheric distillation unit which consist of heater and condenser according to (ASTM D-86) for light cuts.



Fig. 1. Photograph picture of the fixed bed reactor unit.



Fig. 2. ASTM D-86 distillation unit.



Fig. 3. Schematic flow diagram of laboratory continuous cracking unit. 1-Feed reservoir: 2- Dosing pump; 3-Preheater; 4- One way valve; 5- Reactor system; 6- Temperature controller; 7- Condenser; 8- Flow meter; 9- Control valves; 10- Separator; 11- Cooling machine.

4. Results and Discussion

4.1. Effect of Temperature on Thermal Cracking Reaction

The effect of temperature ranges (460-560)°C on the heavy vacuum gas oil conversion

and the yield of gases, gasoline, light cycle oil and coke that were studied at constant liquid hour space velocity (LHSV)15hr¹were shown in Table 2.

| Table 2, |
|---|
| Effect of temperature on liquid products from thermal cracking of heavy vacuum gas oil. |

| Temperature ° C | 460 | 500 | 540 | 560 | |
|---|------|------|-----|-----|--|
| Liquid hour space velocity hr ⁻¹ | 15 | 15 | 15 | 15 | |
| Conversion wt.% | 75.6 | 77.5 | 81 | 82 | |
| Gasoline wt.% | 49 | 51 | 52 | 52 | |
| Light cycle oil (LCO)wt.% | 24.4 | 22.5 | 19 | 18 | |
| Total liquid product wt.% | 73.4 | 73.5 | 71 | 70 | |
| Coke wt.% | 2 | 2.6 | 3 | 3.4 | |
| Gases wt.% | 15 | 18 | 22 | 24 | |
| Residue wt.% | 5.4 | 5.9 | 2 | 1.6 | |
| Losses | 4.2 | 3.5 | 2 | 1 | |

Figure 4 shows the effect of temperature ranges (460-560) ° C on the heavy vacuum gas oil conversion by thermal cracking. As shown from this figure the heavy vacuum gas oil conversion increases with increasing temperature. This may be attributed to; the increase of temperature which accelerates intermolecular motions assists the transformations of the reactants into new compounds and thus enhances the rate of chemical reaction, as mentioned also by Decroopcq [4].



Fig. 4. Effect of temperature on conversion of thermal cracking of heavy vacuum gas oil.

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Fig. (5) and fig. (6) Shows the yield of gases and gasoline respectively. The gasoline yield is chiefly affected by gas formation.

The increasing in the temperature reaction firstly increases the gasoline yield, then higher temperature gives lower gasoline yield and higher gases yield, this due to cracking gasoline itself to lighter fractions so the best temperature of thermal cracking of HVGO is 540 °C for this reason.



Fig. 5. Effect of temperature on gases yield by thermal cracking of HVGO.



Fig. 6 .Effect of temperature on gasoline yield by thermal cracking of HVGO.

Fig.(7) and fig. (8) Shows that the yield of light cycle oil (LCO) decreases by temperature increasing and slightly increases in coke yield respectively.



Fig. 7. Effect of temperature on light cycle oil yield by thermal cracking of HVGO.



Fig. 8. Effect of temperature on coke yield by thermal cracking of HVGO.

Fig. (9) Shows the thermal cracking products distribution at different temperatures ranges (460 - 560) °C and constant LHSV.



Fig. 9. Effect of temperature on thermal cracking products yield from HVGO.

The increasing in the reaction temperature firstly increases the gasoline yield then higher 560 °C temperature gives lower gasoline yield and higher gases yield, (figures 6 and figure 5). Since the conversion increases with temperature increasing, the light cycle oil decreases by temperature increasing at constant LHSV as shown from figure 7. And slightly decreases in coke yield (figure 8).

Clear pictures for thermal cracking products distribution at different temperatures ranges 480 - 540 °C and constant LHSV were presented at figure 9.

The above results agreed with those obtained by Reagan [5].

4.2. The atmospheric distillation results **4.2.1.** Heavy Vacuum Gas Oil

The results of atmospheric distillation for heavy vacuum gas oil and true boiling point distillation (TBP)were tabulated in table 3 which used to calculate some physical properties after calculate the mean average boiling point.

 Table 3

 Results of ASTMD-86 and TBP distillation for heavy vacuum gas oil.

| Volume% | ASTM D-86 (° C) | ASTM D-86 (° R) | T.B.P (^o R) | T.B.P ([°] C) |
|---------|------------------|-------------------|--|--------------------------------|
| 0 | 90 | 654 | 606 | 63 |
| 5 | 250 | 942 | 948 | 253 |
| 10 | 270 | 978 | 959 | 259 |
| 15 | 276 | 989 | 978 | 270 |
| 20 | 280 | 996 | 996 | 280 |
| 25 | 300 | 1032 | 1040 | 296 |
| 30 | 306 | 1043 | 1040 | 304 |
| 35 | 310 | 1050 | 1051 | 310 |
| 40 | 316 | 1061 | 1065 | 318 |
| 45 | 320 | 1068 | 1073 | 322 |
| 50 | 322 | 1072 | 1080 | 327 |
| 55 | 326 | 1079 | 1090 | 332 |
| 60 | 330 | 1086 | 1103 | 339 |
| 65 | 332 | 1090 | 1107 | 342 |
| 70 | 336 | 1097 | 1118 | 348 |
| 75 | 336 | 1097 | 1127 | 352 |
| 80 | 338 | 1100 | 1137 | 358 |
| 85 | 344 | 1111 | 1145 | 362 |
| 90 | 350 | 1122 | 1150 | 365 |
| 95 | 365 | 1149 | 1181 | 383 |
| 100 | 370 | 1158 | 1194 | 390 |

4.2.2. Light Fractions

The results of atmospheric distillation for light fractions (gasoline, kerosene and gas oil)

according to ASTM–D86were tabulated in table 4which used to calculate some physical properties after calculate the mean average boiling point for any fraction.

 Table 4,

 Results of ASTM D-86 distillation for (gasoline, kerosene and gas oil)

| Volume % | ASTM D-86 (° C) gasoline | ASTM D-86 (° C) kerosen | ASTM D-8 (° C) gas oil | | |
|-----------------------|---------------------------|--------------------------|-------------------------|--|--|
| Initial boiling point | 44 | 135 | 195 | | |
| 5 | 57 | 170 | 215 | | |
| 10 | 63 | 178 | 230 | | |
| 20 | 73 | 176 | 247 | | |
| 30 | 82 | 190 | 259 | | |
| 40 | 92 | 197 | 262 | | |
| 50 | 103 | 205 | 279 | | |
| 60 | 116 | 210 | 289 | | |
| 70 | 130 | 216 | 299 | | |
| 80 | 150 | 228 | 309 | | |
| 90 | 180 | 241 | 329 | | |
| 95 | 195 | 258 | | | |

5. The Physical and Chemical Properties of Fractions

Table 5 shows the properties for light fractionswhich were produced from distillation

of liquid thermal cracking for heavy vacuum gas oil, to compared it with standard property for the same fraction, in order to possibility commercial uses these fractions.

Table 5,

The results of physical properties for (gasoline, kerosene and gas oil).

| Property | | Type of fraction which were produced from liquid thermal cracking of VGO | | | standard property for fraction | | |
|----------------------------|--------------|---|----------|---------|--------------------------------|-----------|-----------|
| | | gasoline | kerosene | Gas oil | gasoline | kerosene | gasoil |
| Specific gravity. | | 0.77 | 0.81 | 0.85 | 0.72-0.77 | 0.77-0.82 | 0.82-0.86 |
| API gravity. | | 85 | 48 | 44 | 50-60 | 40-50 | 35-45 |
| T_b (°R) | | 640 | 870 | 975 | | | |
| K-index | | 12 | 12.2 | 12.3 | 11-13 | 11-13 | 11-13 |
| Molecular weight. | | 93 | 167 | 214 | 115 | 170 | 225 |
| Flash point(°k) | | 300 | 310 | 325 | Min.327 | Min.315 | Min.305 |
| Diesel Index. | | 90 | 61 | 73 | | | |
| Aniline point (°C) | | 67 | 70 | 72 | 60 | 65 | 70 |
| Viscosity at 100 °F (Cst.) | | 0.5139 | 1.3238 | 2.511 | 0.6 | 1.6 | Max.5.6 |
| refractive | Experimental | 1.4104 | 1.435 | 1.4456 | | | |
| index | Empirical | 1.4395 | 1.456 | 1.4877 | | | |
| Pour point (°k) | | 165 | 246 | 218 | Max.264 | Min.220 | Min.160 |
| Smoke point (mm) | | | 23 | | | Min.21 | |

6. Conclusion

- 1- It was concluded that the possibility produced of light fractions (gasoline, kerosene, gas oil) from heavy vacuum gas oil by thermal cracking process at different temperatures and constant space velocity at atmospheric pressure.
- 2- It was concluded that the heavy vacuum gas oil conversion increases with increasing the temperatures of thermal cracking.
- 3- Possibilty uses these light fractions for internal combustion engine or for domestic uses and diesel fuel.

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تحضير مقاطع وقود خفيفة من زيت الغاز الفراغي الثقيل بواسطة تفاعل التكسير الحراري

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الخلاصة

يتناول هذا البحث التكسير الحراري لزيت الغاز الفراغي الثقل الذي ينتج من الجزء العلوي من وحدة التقطير الفراغي في مصفاة الدورة، عن طريق عملية تكسير حراري مستمرة.- تم تصميم وتنفيذ منظومة مختبريه تجريبية في مختبرات قسم الهندسة الكيميائية في جامعة النهرين وجامعة بغداد. وقد أجريت عملية التكسير الحراري في معدل درجة حرارة تتراوح بين ٤٦٠-٥٦٠ والضغط الجوي الاعتيادي مع سرعة الفصائية (LHSV) تساوي ^{10 - س}ا. - تم تقطير السائل المنتج من وحدة التكسير الحراري بوساطة جهاز التقطير الجوي المواصفة ASTM من أجل تحقيق مقطعين، تحت ٢٢٠ م بوصفه مقطعا للبنزين وفوق ٢٢٠ م بوصفه زيتا خفيفا مدور (LCO).- تم تقطير الجزء الأول الذي كان تحت

٢٢٠ م إلى المقاطع الخفيفة (البنزين والكيروسين وزيت الغاز) عن طريق جهاز التقطير الجوي. - كذلك تم تقطير المقطر لمقاطع (البنزين والكيروسين وزيت الغاز) من خلال جهاز التقطير الجوي من أجل رسم منحنى التقطير الذي تم الحصول عليه لهذه المقاطع وذلك لحساب معدل درجة الغليان لهذه المقاطع. حساب بعض الخصائص والمو إصفات الفيزيائية والكيميائية المهمة مثل (متوسط درجة الغليان لهذه المقاطع وذلك لحساب معدل درجة الغليان لهذه المقاطع. حساب بعض الخصائص والمو إصفات الفيزيائية والكيميائية المهمة مثل (متوسط درجة الغليان لهذه المقاطع وذلك لحساب معدل درجة الغليان لهذه المقاطع. حساب بعض الخصائص والمو إصفات الفيزيائية والكيميائية المهمة مثل (متوسط درجة الغليان الهزي الذي عن المقاطع. حساب بعض الخصائص والمو إصفات الفيزيائية والكيميائية المهمة مثل (متوسط درجة الغليان، الوزن الذوعي، نقطة الوميض، نقطة الأنيلين، نقطة الدخان، الوزن الجزيئي) وذلك لمقاربتها مع المو إصفات القياسية التجارية من أجل دراسة إمكانيات الاستخدامات الصول على المقطة الدخان، الوزن الجزيئي والمات المواصفات الفيزيائية والكيميائية المهمة مثل متوسط درجة الغليان، الوزن الخريئي والمين الذي المواصفات الفيزيائية والكيميائية المهمة مثل متوسط درجة الغليان، الوزن الموزن النوعي، نقطة الوسان الفيزيائية والكيميائية المهمة مثل متوسط درجة الغليان، الوزن الموزن المواصفات الفيزيائية والكيميائية المهمة مثل متوسط درجة الغليان، الوزن الجزيئي وذلك لمقاربتها مع المواصفات القياسية التجارية من أجل دراسة إمكانيات الاستخدامات الصناعية. تم الحصول على الموان الغربي الموانية الغليان الموانية الموانية الموانية الموانية الموانية الموانية الكرونية الموانية المواني الموانية الموا

أقصبي قدر من تحويل زيت الغاز الثقيل الفراغي من هذه العملية يصل إلى ٨٢ بالوزن. ٪ عند ٥٤. م