

## RESEARCH ARTICLE

## CATALYTIC CRACKING OF HEAVY OIL OF ALIF FIELD – MARIB - YEMEN

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## Abstract

The study presents the results of the catalytic cracking process of heavy oil of the Alif – Marib field in Yemen. The best conditions of the process, pressure, temperature, and using zeolite HZSM-5 as catalyst were selected. Based on the characteristics of the heavy oil, the analyses were done using a gas chromatography technique and catalytic cracking unit designed in the laboratory of Chemical Engineering and Petrochemical faculty at Al-Baath University- Syria., refining process was done in Refining Company- Homs. The results of simple distillation of the cracking products at different range of temperature were (Gasoline= 19.5%; Kerosene=15%; Light gas oil= 36%; Distillate residue= 29.5%) and gases (CH<sub>4</sub>= 67.55 %; C<sub>2</sub>H<sub>4</sub>= 14.66 %; C<sub>2</sub>H<sub>6</sub>= 7.48 %; H<sub>3</sub>H<sub>8</sub>= 9.24%; C<sub>4</sub>H<sub>10</sub>=1.06 %).

Extraction by sulfuric acid was done. An 84.044% oil-free aromatic has been gotten. In order to remove total paraffins from the oily cut that has a high pour point, different solvents were used. The properties of the oily cut from which the paraffin wax was removed gave encouraging results.

**Keywords:** Catalytic cracking, HZSM-5 zeolite, Extraction, Heavy oil, Gases.

## 1. Introduction

The first oil production block in the Republic of Yemen is Block (18), located in (Marib-Shabwa) Basin, with area of (8.497) km<sup>2</sup> (Figure 1). It is operated by Safer Exploration and Production Operation Company. It is one of the biggest oil blocks. The main reservoirs in the block are (Alif Sand) and (Seen Sand). In general, it contains 14 fields with an average production of (35,000) barrel oil per day [1, 2] The produced oil is light with density between (35-48 API), in addition to a big amount of gas as a reserve, which is neither invested nor exploited so far.

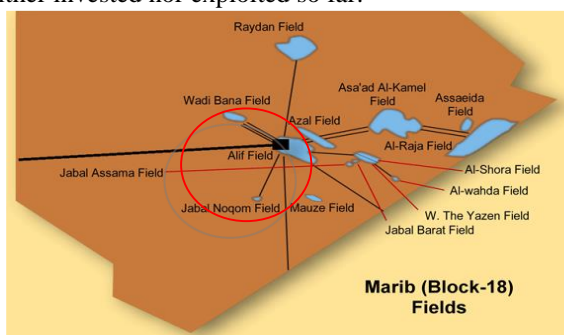


Fig. 1: Mareb (Block- 18) Fields (showing Alif field location)

Liquid fuels are likely to remain in demand by society for transport applications due to the high energy density and ease distribution for such fuels. One approach to expand the contribution of renewable carbon- source for use as transport fuel is to employ indirect liquefaction technology followed by fuel refining. The steps involved in the transformation of the renewable carbon-source to liquid transport fuels are synthesis gas production, liquefaction and refining [3]. The liquefaction process determines the nature of the material that must be refined and there are two industrially practiced indirect liquefaction process, namely, methanol synthesis [5] and Fischer – Tropsch synthesis [6].

Zeolite type can be easily obtained over a wide range of compositions directly by synthesis and/or after various post treatments. Moreover, various compounds can be introduced or even synthesized within the zeolite pores. This explains why zeolite can be used as acid, base, acid-base, redox and bifunctional catalysts, most of the applications being however in acid and in bifunctional catalysis [4, 15]

At present, the oil refining industry is faced with important challenges, such as the processing of heavier and more

contaminated crudes, the increasing demand for higher quality transportation fuels with reduced emissions of contaminants, and the need for more petrochemical feedstock (e.g. olefins, aromatics). In this context, there is no doubt that zeolite (and related molecular sieves) can help refiners to achieve the new goals. Recent advances in zeolite synthesis and post-synthesis modifications are expected to contribute to the development of improved catalysts and processes. [7].

The Fluid Catalytic Cracking (FCC) process remains the primary molecular weight reduction method practiced in modern petroleum refineries. While originally designed for cracking the Overhead stream from vacuum distillation units, known as vacuum gas oil, most FCC units currently operate with some higher boiling vacuum distillation bottoms (residue) in the feed.

Designing catalysts to tolerate the high level of metal contaminants in the residue, while still maintaining high conversion and selectivity, is a key issue of FCC catalyst design.

The impact of more stringent clean air requirements continues beyond the refinery gates, as lower gasoline sulfur levels are being mandated to reduce automobile emissions. Gasoline produced by the FCC process is the primary source of sulfur in the refinery gasoline pool [8].

Fortunately, FCC catalyst technology is again providing an answer in the form of low sulfur gasoline FCC catalysts and catalyst additives.

The operational constraints of a Fluid Catalytic Cracking Unit (FCCU) to produce certain products does not depend on its technology or operating conditions, but also on the characteristics and quality of the feedstock that determine its potential to produce the desired product.

The previous studies approve that Marib crude oil was the best one in Yemen [9, 10].

The aim of study is to carry out catalytic cracking of heavy oil or diesel of Alif field- Marib – Yemen using suitable technology over zeolite type HZSM- 5.

## 2. Materials and Methods

The catalytic cracking was carried out by using a semi-industrial laboratory unit located in the laboratory of Chemical and Petrochemical Engineering faculty – Al-Baath University in Homs – Syria as shown in Figure (2), it consists of : (1) cracking reactor, (2) cooler, (3) condenser, (4) strupper..

The catalyst used is zeolite HZSM- 5 (Zeolite Socony Mobile-5 synthetically prepared since HZSM-5 is highly active in catalytic cracking.

The catalytic cracking carried out for a heavy oil or diesel oil derivative range at (330-370 °C) that resulting from the studied of crude oil (Table 1).

**Table 1:** General characterization of diesel oil of Alif field-Marib at (330 – 370 °C)

| Character and measurement unit | Results | Method of test        |
|--------------------------------|---------|-----------------------|
| Distilled percent vol. %       | 6.62    | ASTM D-2892           |
| Specific gravity at 15.6 °C    | 0.8595  | ASTM D-1298           |
| Specific gravity API           | 33.13   | ASTM, D 5002) method. |
| Viscosity at 37.8 °C Cst       | 7.6288  | ASTM D-445            |
| Viscosity at 98.9 °C Cst       | 0.8938  | ASTM D-445            |
| Pour point °C                  | 9.0     | ASTM D-97             |
| Carbon Conradson CCR w%        | 0.0052  | ASTM D-189            |
| Flash point °C                 | 160.0   | ASTM D-93-77          |
| Refraction degree $n_D$ 20     | 1.4810  | ASTM D-1218           |
| Sulfur percent w%              | 0.12    | ASTM D-1266-70        |

### A. A conditions applied during the experiment were:

Temperature 500 °C; pressure 1.3 bar; volumetric velocity 9.832 h<sup>-1</sup> ; residence time 0.102h ; The amount of HZSM- 5 zeolite used in the experiment is 32.74 g ; The volume of zeolite used is 47.50 cm<sup>3</sup>. The volume of inlet heavy gas oil in one hour is 467 cm<sup>3</sup>; The height of catalyst in the first region of the reactor is calculated as follows:

$$V = (d^2/4) * L$$

$$L = 4V/d^2$$

$$L = (47.5*4) / (2.8)^2 = 7.71 \text{ cm}$$

where:

V = Volume of catalyst (in cm<sup>3</sup>)

L = The height of catalyst in the reactor (in cm)

d = The diameter of the reactor (in cm)

The specifications of the raw material (the heavy oil) entering into the cracking unit are mentioned in Table (1).

After completing the experiment which was during one hour:

- The volume of liquid accumulated was 400 cm<sup>3</sup>,
- The gas meter reading the output gas was 1000 cm<sup>3</sup>/81 sec.
- The volume of gas released during the experiment was 44.4 L/hr. = 0.044m<sup>3</sup>/hr.

### B. Cracking products distillation:

The liquid resulting from cracking was distilled by simple distillation method in order to know the yield of gasoline, we divided the parts of liquid from the cracking as follows:

The first cut off 52- 150 °C; second cut off 150-250 °C; the third cut off 250- 330 °C ; The fourth cut off > 330 °C

### C. Cracking gas analysis

We took a sample of the gases resulting from cracking unit and performing a gas chromatographic analysis for it.

Gas chromatography was performed using a model DC-200

The applicable conditions are:

A = 4; P = 70 psi ; Gas pressure = 5Kg / cm<sup>2</sup>; sheet speed 10 ml / min ; Temperature = (0-60) °C

Several experiments were conducted on the oily cut (370 - 490) °C resulted from the studied crude oil, for removed the tar (paraffins components), these experiments were as follows:

- Purification with concentrated sulfuric acid
- Extraction of paraffin wax from this cut with selective solvents

**D. Extraction by sulfuric acid**

The oily cut was treated with sulfuric acid, and the result of the experiment was 84.044% oil free of aromatic compounds.

**E. Extraction of paraffin wax from the oily cuttings by solvents**

This experiment aims to remove total paraffins from the oily cut that has high pour point by solvents. The following solvents: benzene and toluene and acetone were used as a precipitant. The weight ratio of benzene: toluene: acetone was = 35:10:55 respectively.

We took the same ratio of the solvent to the different samples, the results of the experiments shows in (Table 5), Several experiments were conducted on the oily cut from which the paraffin wax was extracted, the sample solvent ratio was 3: 1, and the results were summarized in (Table 6).

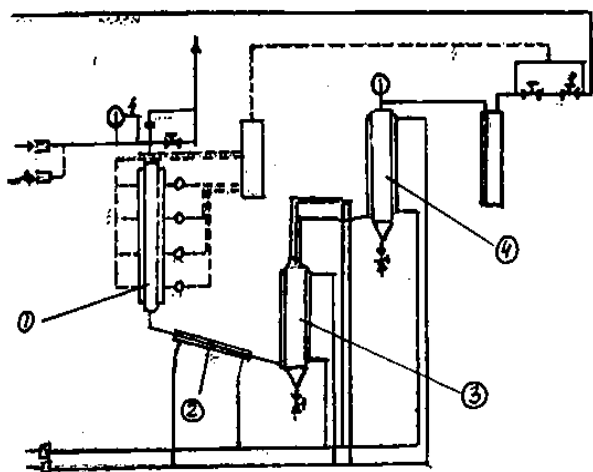


Fig. 2: Catalytic cracking unit

**3. Results and Discussion**

The results of the simple distillation of the cracking products can be summarized in Table 2 below.

Table 2: The results of the simple distillation of the cracking products

| Components ratio % vol. | Components names                       | Numbers |
|-------------------------|--|---------|
| 67.55                   | Methane-air CH <sub>4</sub>            | 1       |
| 14.66                   | Ethylene C <sub>2</sub> H <sub>4</sub> | 2       |
| 7.48                    | Ethane C <sub>2</sub> H <sub>6</sub>   | 3       |
| 9.24                    | Propane C <sub>3</sub> H <sub>8</sub>  | 4       |
| 1.06                    | Butane C <sub>4</sub> H <sub>10</sub>  | 5       |

Table 3 shows the result of the gas chromatographic analysis of the released cracking gases. In addition, Figure 3 shows the scheme analyses of the same gases.

Table 3: Gas chromatographic analysis of cracking gases

| Volumetric distillate % | Range cut off °C | Cut off            |
|-------------------------|------------------|--------------------|
| 19.5%                   | 52-150           | Gasoline           |
| 15%                     | 150-250          | Kerosene           |
| 36%                     | 350-250          | Light gas oil      |
| 29.5%                   | >330             | Distillate residue |

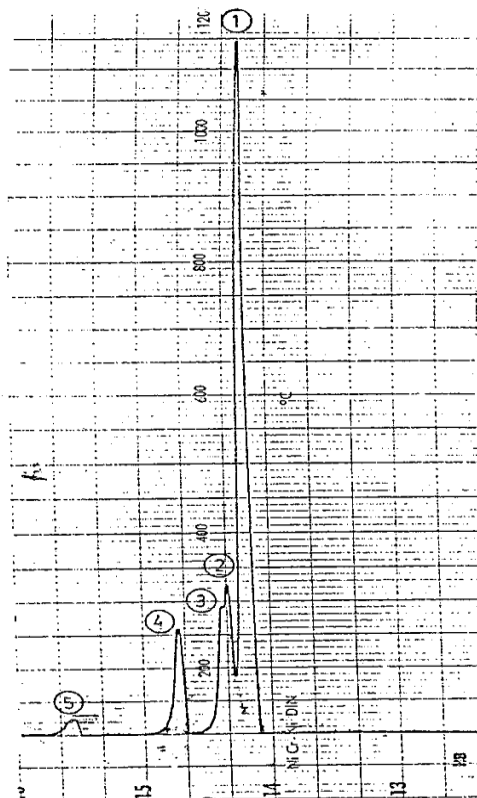


Fig. 3: Chromatography analysis of gases producing by catalytic cracking of heavy oil (diesel).

The Characteristics of the fractions produced from cracking yields distillation are showed in Table 4.

**Table 4:** Characteristics of the fractions cracking distillation

| ViscosityCst             | Sulfur %wt. | Specific gravity 60/60 °F | Range of cut-off °C       |
|--------------------------|-------------|---------------------------|---------------------------|
|                          | 0.0326      | 0.7315                    | Gasoline (52-150) °C      |
|                          | 0.1959      | 0.7970                    | Kerosen (150-250) °C      |
| <b>5.6279 at 100 °F</b>  | 0.1992      | 0.8605                    | Light diesel (250-330) °C |
| <b>16.7172 at 100 °F</b> | 0.3530      | 0.8926                    | Residue> 330 °C           |

As shown in Table 4 each straight run cut is sent to a refining process that was developed specifically for the conversion of that boiling fraction, which is direct application of the principle of molecular management. The reason for this approach is threefold. First, transport fuels have defined boiling ranges. Second, different transport fuels have different fuel specifications. Third, the molecular composition in each cut is different and depending on the composition there can be significant changes in the reaction chemistry.

The fuel specifications impose molecular requirements on each boiling fraction. Think of refining as a collection of conversion processes that can manipulate the molecular composition of each boiling fraction so that it meets the requirements imposed by the fuel specifications to produce a marketable product. An overview of fuel specifications and how it influences refining can be founding general texts on petroleum refining [11].

The wax existing in crude oil mostly contains paraffin hydrocarbon (C18-C36) recognized as paraffin wax and naphthenic hydrocarbon (C30-C60). The hydrocarbon element of wax is able to present in several phases, i.e., gas, liquid, and particles (solids).

**Table 5:** The material balance of extraction of paraffin wax

| % loss      | % wax paraffins | %separated oil | Solvent: sample ratio |
|-------------|-----------------|----------------|-----------------------|
| <b>3.52</b> | 14.21           | 82.27          | 1 : 1                 |
| <b>4.14</b> | 17.1            | 78.76          | 1 : 2                 |
| <b>5.2</b>  | 26.85           | 67.95          | 1 : 3                 |

**Table 6:** Properties of the oily cut from which the paraffin wax was removed

|               |                           |
|---------------|---------------------------|
| <b>5.9770</b> | Viscosityat °F 210 Cst    |
| <b>0.2323</b> | Sulfur% wt.               |
| <b>0.8959</b> | Specific gravity 60/60 °F |

Nevertheless, over the years several studies reported on the fluid catalytic cracking of wax over

FAU, MFI and BEA catalysts [12, 13, 14]. It is commonly noted that high wax conversion is possible eading to high C3-C4 gas yields, low coke yield and low aromatic content.

This is consistent with what one would expect from the cracking of a high hydrogen-to-carbon ratio material. As with petroleum, fluid catalytic cracking of wax employing MFI leads to more propene than over the other zeolite catalysts.

## 4. Conclusion

Amount and kind of producing products of catalytic cracking depends on the nature of catalyst used in the process, in addition on the characteristics of the crude as well as on the system of the process.

The producing products of catalytic cracking are gas, gasoline, light diesel as main products, the properties of products of catalytic cracking such as gas obtained a high percentage of isobutene and less percentage of fractions C<sub>1</sub>, C<sub>2</sub>. Gasoline obtain high percentage of olefin hydrocarbons, and the percentage of naphthenehydrocarbons will be more than in gasoline produced by thermal cracking. Thus, such chemical composition of gasoline will give good properties for preventing knocking.

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## التكسير الحفزي للوقود الثقيل لحقل ألف - مارب - اليمن

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## المُلخَص

هذه الدراسة تبين نتائج التكسير الحفزي للمازوت الثقيل لحقل ألف في مارب - اليمن. تم اختيار أفضل الشروط من ضغط ودرجة حرارة وباستخدام الزيوليت HZSM-5 كعامل حفاز. استنادا لخصائص الزيت الثقيل الذي تمت دراسته في معمل كلية الهندسة الكيميائية والبتروولية في مدينة حمص - سوريا ومصفاة حمص باستخدام جهاز الكروموتوجرافي حيث تم تصميم وحدة التكسير في مختبر الكلية. أوضحت مختلف القطفات المأخوذة كعينات للدراسة النتائج التالية (جازولين = 19.5%، الكيروسين = 15%، مازوت خفيف 36%، بواقي التقطير 29.5%) أما نتائج تحليل الغازات فكانت (CH<sub>4</sub> = 67.55%، C<sub>2</sub>H<sub>4</sub> = 14.66%، C<sub>2</sub>H<sub>6</sub> = 7.48%، C<sub>3</sub>H<sub>8</sub> = 9.24%، C<sub>4</sub>H<sub>10</sub> = 1.06%). تمت عملية بواسطة حمض الكبريتيك، حيث تكون مانسبته 84.044% من الزيت الخالي من المركبات العطرية. ومن أجل إزاحة البرافينات للقطفة الزيتية ذات درجة الانصباب المرتفعة، تم استخلاص الشمع البرافيني بواسطة مذيبات مختلفة، وبينت التجربة نتائج مشجعة. كما أجريت عدة تجارب على القطفة الزيتية المستخلص منها الشمع البرافيني وذلك عند نسبة عينة مذيب = 1:3 وكانت النتائج (اللزوجة عند 210 °F = 5.976، نسبة الكبريت = 0.2323%، الكثافة النوعية = 0.8959).

الكلمات المفتاحية: التكسير الحفزي، زيوليت HZSM-5، استخلاص، مازوت ثقيل، غازات.

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