



A Comparative study on hydrocracking and hydrovisbreaking combination for heavy vacuum residue conversion



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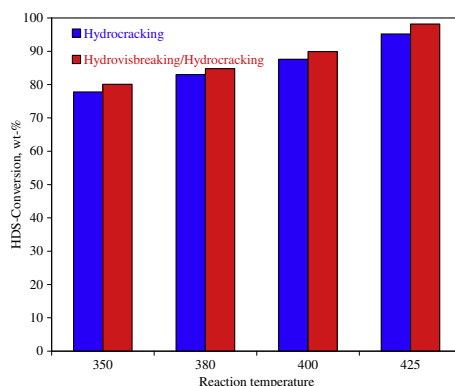
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HIGHLIGHTS

- A process scheme; hydrocracking and a combination with hydrovisbreaking were done.
- Hydrocracking under reaction temperatures was conducted using hydrocracking catalyst.
- The heavy residue was converted to produce high quantity and quality fuel fractions.
- A combination of hydrovisbreaking–hydrocracking inhibited fast catalyst deactivation.
- Best conversions and light fuel productions were resulted from contaminants reduction.

GRAPHICAL ABSTRACT

The results of the two successive running hydrovisbreaking–hydrocracking processes (i.e. combination) had relaxed reaction conditions, high HVR conversion and higher HDS reaction compared to hydrocracking process. The combination process characterized with liquid distillates of low sulfur contents, high middle distillates yield, and long catalyst regeneration period. In addition, the remaining heaviest residue fraction, i.e. 350⁺, represents either boiler fuel feedstock or a heavier product used as feedstock for other conversion processes (catalytic cracking or delayed coking) due to its acceptable quality. Comparison of hydrodesulfurization (HDS) under hydrocracking and successive hydrovisbreaking/hydrocracking-combination processes at variable reaction temperatures.



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ABSTRACT

Upgrading of heavy vacuum residue (302.3 ppm Ni + V, 4.36 wt% S, and 13 wt% asphaltenes) into valuable lighter fuels has been studied in a batch autoclave reactor by hydroconversions over bifunctional sulfided catalyst W–Ni–P/SiO₂–Al₂O₃, at different reaction temperatures, 350–425 °C and 12 MPa hydrogen pressure. The activity of the sulfided catalyst towards hydrocracking reactions scheme alone has been compared with a combination scheme (hydrovisbreaking followed by hydrocracking) in order to produce light fractions suitable for automotive fuels. The catalyst gave, at higher temperature 425 °C, about 80% feedstock conversion, 5% coke make, 98% hydrodesulfurization (HDS) and 73% asphaltenes reduction, when applying the combination scheme, compared with hydrocracking alone. The presence of hydrogen in the hydrovisbreaking reaction medium was necessary to limit coke production. These results indicated that hydrovisbreaking was a suitable alternate treatment option for heavy vacuum residue before hydrocracking process.

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1. Introduction

Upgrading of heavy petroleum residues into valuable light fractions has attracted more attention due to growing worldwide demand for transportation petroleum fuels from declining reserves of light crude oils. Hydrocracking processes are commercially available to process a wide range of different characteristics feedstock to produce a broad range of products [1,2] and deeply to remove heteroatoms. Most of hydrocracking catalysts are dual functional catalysts. They have hydrogenation–dehydrogenation function as well as acidic function. The cracking activity was controlled mainly by the support, which is acidic in nature, whereas the hydrogenation–dehydrogenation activity is due to the metals loaded on the support [3,4]. Even though, the Egyptian refineries need to maximize the amount of premium products from each barrel of crude or heavy residues as environment-friendly products. Consequently, understanding the variable options for residue processing and their impact on refinery yields and economics allows the refiner to select the optimum residue-processing route consistent with both the quantity and quality of the available residue and the required products distribution. This can overcome by selecting some upgrading methods, either by addition of hydrogen, or rejecting carbon, or using a combination of both methods [5–9].

Attempts to increase conversion of heavy oils during visbreaking will bring on sediments deposition. However, this can change by the use of hydrovisbreaking [10]. Among the thermal process of hydroconversion, the hydrovisbreaking differs from visbreaking in the addition of excess hydrogen in the thermal treatment. One attractive option to achieve the maximum benefits is by combining various technologies. That is, using more than one process to upgrade heavy petroleum, in such a way the advantages of each approach are put together in an integrated process scheme and this synergy may yield higher benefits than using a single process. Some of these have been already reported and tested at commercial scale while others are still being proposed and under evaluation. The Institute Francais du Petrole (IFP) has proposed variants of processes that call for the use of hydrogenating atmospheres, i.e. hydrovisbreaking [10]. Through comparison of the chemical analogies of visbreaking, hydrovisbreaking and hydrocracking [11], found that the driving force of the conversion reaction is essentially thermal activation in the applied temperature ranges.

Hydrogen in the usual hydrovisbreaking reactions of petroleum residues or heavy oils has an inhibitor effects on condensation reactions that leads to coke formation. In this study, hydrovisbreaking is a possible alternate option prior to hydrocracking process, named as a combination scheme. A comparative study of hydrocracking and a combination of hydrovisbreaking followed by hydrocracking of heavy vacuum residue was studied, in order to produce light or middle distillates within the environmental specifications.

2. Experiments

2.1. Raw materials

Strait-run heavy vacuum residue, SR-HVR obtained from an Egyptian refinery, Suez Oil Processing Company (SOPC) was used as a feedstock for hydrocracking and hydrovisbreaking–hydrocracking combination experiments. The characteristics of the feedstock are shown in Table 1.

2.2. Hydrocracking reactivity experiments

Hydrocracking of petroleum, heavy vacuum residue HVR (350 g) was performed in a batch bench-scale autoclave reactor (500 mL, Parr-model 7575, USA). The total amount of the available

Table 1

Properties of heavy vacuum residue (>565° + C) feedstock.

Characteristic	
Specific gravity at 70 °C	0.993
API-gravity	18.6
Total sulfur, wt%	4.36
Conradson Carbon Residue (CCR), wt%	18.7
Nickel content, wppm	138.0
Vanadium content, wppm	164.3
Asphaltenes (n-C ₇ insoluble), wt%	13.0
C/H, wt%	84.8/10.2
SARA, wt%:	
Saturates	24.2
Aromatics	35.7
Resins	17.7
Asphaltic resins	9.4

commercially pre-sulfiding catalyst was 35 g. The catalyst was composed of 15 wt% W, 4 wt% Ni, as metal oxides, and 1.2 wt% phosphor as promoter, loaded on silica–alumina support. Its characteristics are; surface area of 220 m² g⁻¹, pore volume of 0.48 cm³ g⁻¹ and pore size of 4.5 nm and 9.6 nm, which characterized as mesoporous materials [12,13]. This catalyst showed WO/NiO and silica/alumina ratios of 3.6 and 3.8 respectively, and its sulfur content after sulfidation was 5 wt%. The experiment runs were carried out at different reaction temperatures of 350–425 °C under a total hydrogen pressure of 12 MPa, and catalyst-to-feed ratio of 1:10 (wt/wt) and run period of 3 h. The products (gases and liquids) were collected and quantified for further analysis.

Hydrovisbreaking of the petroleum vacuum residue (350 g) was performed in the same batch-autoclave reactor, without catalyst addition. The experiment runs were carried out under the same operating conditions of hydrocracking runs. After each hydrovisbreaking run, the autoclave was allowed to cool down to room temperature and the reaction pressure was recorded, purged out the produced gases to quantify, then the autoclave was opened, and reloaded with the required sulfide catalyst (35 g). The combination experiment runs were carried out under the previous hydrocracking operating conditions.

2.3. Analysis of products

The liquid products of hydrocracking and combination runs were separated by distillation into four fractions (gasoline, kerosene, gas oil and residue) in order to obtain fractions suitable as transportation fuels. Physicochemical properties of all analyzed fractions were determined using the standard test procedures designated for petroleum products. Solid spent of the investigated catalyst after purging the liquid products was collected and washed with toluene under reflux to remove adsorbed residual oil whereas solids obtained (spent catalyst and coke) were dried at 100 °C. Dried spent catalyst was regenerated by oxidation under air atmosphere at 500 °C during period time of 4 h, and the amount of coke was determined as the weight difference among solid after and before calcinations.

3. Results and discussion

3.1. Hydrocracking reactivity experiments

Fig. 1 represents the conversion of the HVR as a function of temperature variables through production of total liquid yields, hydrocarbon gases, and coke formation. The highest yields of gases and coke were produced after the run of hydrocracking at temperature of 425 °C. On the other hand, the liquid yield was decreased at this temperature.

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