

RECOVERING AMMONIUM MOLYBDATE CATALYST IN THE HOMOGENOUS PHASE TO UPGRADE HEAVY CRUDE OIL

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Abstract

Producing more valuable products from heavy oil fraction is significant due to decreasing light and sweet crude oil sources, and increasing the demand for transportation fuels such as gasoline and naphtha. Molybdenum is a precious metal which is an active catalyst for upgrading purposes; therefore, the recovery and re-usage of that from the residue produced during the hydroprocessing processes is a mandatory step from economic viewpoints. In this work, a novel method for recovering ammonium molybdate catalyst used in hydroprocessing of extra heavy oil is presented. Results confirm that the recovered catalyst can upgrade the heavy feed stock the same as the fresh commercial catalyst

Keywords: Regeneration; Hydroconversion; Ammonium molybdate; Heavy oil; Upgrading; sodium molybdate.

1. Introduction

Higher fuel prices and environmental constraints have focused attention on upgrading residue to improve profitability of the refinery. Hydroconverting of heavy oil in order to produce more valuable products are becoming important due to the economic factors [1]. The residual fuel oil demand continues to decline, while, at the same time, there is an increasing demand for motor fuels [2].

Nowadays, catalyst contains of molybdenum (Mo) has attracted great potential in petroleum refining industry due to its applications in many desulfurization and hydrogenation processes [3]. Due to on-going environmental concerns and regulations, the recycling and re-utilization of spent hydrotreating catalyst are important for the protection of environment and recovery of valuable metals [4].

However, the resources of high grade ore are depleted due to careless exploitation day by day. The quantity of spent non-reusable hydro-desulfurization spent catalysts produced per year is around 120,000 tons (dry basis) [5]. Due to strict legislation, the land disposal of these residues, which was practiced in the past, is no longer advisable [6].

Typically, molybdenum is produced from molybdenite ore/concentrate by pyrometallurgical calcinations, or from high grade molybdenite ore concentrates by alkali/acid leaching. In order to achieve the best method to recover molybdenum from spent catalysts, various processes have been proposed such as: electro-oxidation, acid leaching and alkali leaching, chlorination, lime-roasting, salt-roasting, bioleaching and roasting with soda salts [7].

In this work, the recovery and re-usage of ammonium molybdate catalyst used for hydroprocessing of extra heavy crude oil in a bench scale batch reactor is described. This novel process recently has been developed by Research Institute of Petroleum Industry (RIPI) to produce light fractions from heavy cuts using ammonium molybdate as a catalyst in a homogenous phase [8]. This advanced process can be alternatively used for pre-processing of

extra heavy crude oil for refineries, and regeneration of the catalyst can make it so attractive from economical viewpoints.

2. Process description

2.1. Fresh catalyst preparation

In this research, the ammonium molybdate tetrahydrate (CAS No. 12054-85-2) was used as the residue upgrading catalyst. This powder was dissolved in the de-ionized water, and then was used as the fresh catalyst for upgrading heavy residue oil.

2.2. Recovering process for the spent catalyst

Recovering of ammonium molybdate catalyst from residue of the hydroconversion process is shown in Figure 2. As seen, at first a roasting process at the temperature of 400-700°C is used to calcine the residue which provides an appropriate feedstock for the next step i.e., leaching. The conditions of the calcinations step is meticulously monitored and controlled. Then, the calcinated residue was cooled, and by adding ammonia solution and ammonium carbonate, it was leached at 60-80°C for 1-5 h. Finally, the product was filtered to find $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ as the recovered homogenous hydroconversion catalyst.

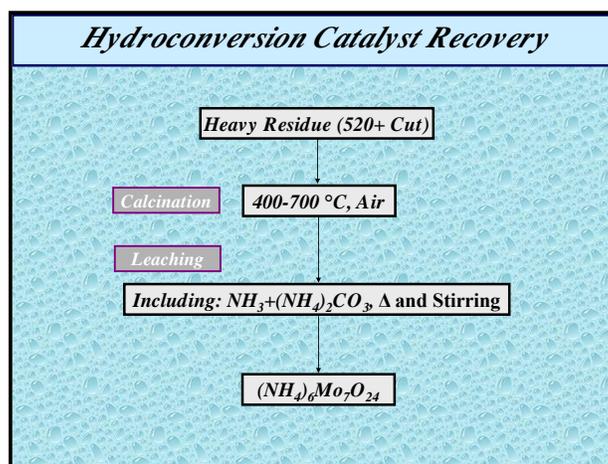


Fig. 2. Recovering process for spent hydroconversion catalyst

2.3. Hydroconversion process

To study the activity of fresh and recovered catalysts, experiments were conducted in a batch reactor. The simplified process flow diagram of hydroconverting process is presented in Fig. 1. To perform the study, 500 g of heavy crude oil (see Table 1) is mixed with 1 g of catalyst in the reactor, and the hydroprocessing reactions are performed under the hydrogen pressure of 70 bar, temperature of 440°C, hydrogen to hydrocarbon ration of 1200 (vol/vol), and the residence time of 20 min. This process is protected by a US Patent (7585406 B2)^[9].

Table 1 Specifications of heavy crude oil used for hydroconversion process

| Indices and units | Feed 350+Cut) | Indices and units | Feed (350+Cut) |
|------------------------------------|---------------|-------------------------------|----------------|
| Specific Gravity 15.6/15.6°C (API) | 1.02 (6.6) | Asphaltenes % mass | 16 |
| Kinematic viscosity (cSt.) | | Elemental Composition, % mass | |
| at 60°C | 8406 | C | 85.2 |
| at 100°C | 448.2 | H | 6.8 |
| Sulphur Content, % mass | 3.95 | N | 0.8 |
| Conradson Carbon Residue %mass | 16.3 | O | 0.3 |
| Wax Content, % mass | 7.5 | S | 5.7 |
| Flash Point, °C | 266 | Pour point, °C | 28 |

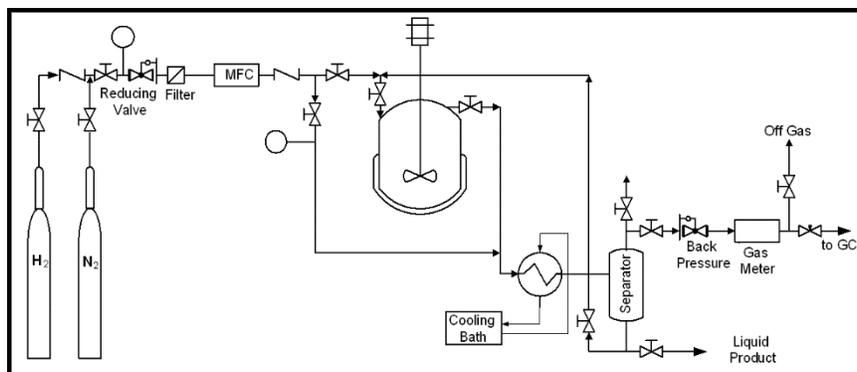


Figure 1. Flow diagram of pilot scale hydroconversion process

3. Results and discussions

By using the X-ray analysis, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ phase was detected for the both fresh and spent catalysts. It is concluded that both catalysts contain Mo in the form of ammonium salt. Therefore, the proposed recovering process can successfully extract the active metal i.e., Mo from the residue oil of hydroconversion process.

After carrying out hydroprocessing according to the process described in the section 2.3, the comparison between the feed and corresponding products to the fresh and recovered catalysts are presented in Table 2.

Table 2 Specifications of feed and products of hydroconverting process

| Specification | Feed | Product | |
|-------------------|-------|----------------|--------------------|
| | | Fresh catalyst | Recovered catalyst |
| Gravity (API) | 6.6 | 22.33 | 22.84 |
| Asphaltene (wt.%) | 16 | 6.2 | 6.19 |
| TBP curve (vol.%) | °C | °C | °C |
| IBP | 386.9 | 76.5 | 16.2 |
| %5 | 432.8 | 147.4 | 79.2 |
| %10 | 545.9 | 191.6 | 124.9 |
| %30 | 648.5 | 302.9 | 246.9 |
| %50 | 705.4 | 358.1 | 355.1 |
| %70 | 782.3 | 517.7 | 469.1 |
| %90 | 860.3 | 727.1 | 705.1 |
| %95 | 877.8 | 811.1 | 784.1 |
| FBP | 894.2 | 888.5 | 887.6 |

Table 2 shows that both fresh and recovered catalysts can convert about 90 % of heavy residue oil to the lighter cuts. But, the desired product should have the boiling range less than 350°C, i.e., naphtha, kerosene and diesel. So, it is obvious that the efficiency of hydroconversion process is about 50% for both catalysts. Moreover, the significant amount of conversion is related to the medium and heavy aromatic compounds, included in the cuts with the boiling temperature ranges from 350°C to 780°C (IBP to TBP 70%) in the feed. However, both catalysts cannot upgrade the ultra heavy aromatics present in the 780+°C cuts. This phenomenon is completely evident from the violent increment in boiling temperature of product from TBP 70% to 90% (from 517.7°C to 727.1°C, and from 469.1 °C to 705.1°C cut temperature points for the products of fresh and recovered catalysts, respectively).

Figure 3 demonstrates the distillation curve of feed and products of fresh and recovered catalysts, respectively. From this figure it can be concluded that the upgrading activity of recovered catalyst is close to the fresh one which confirms the efficient recovering process of spent catalyst presented in this research.

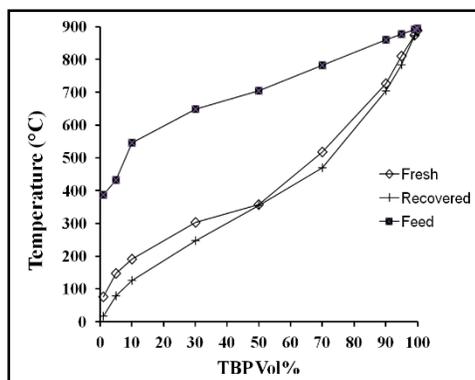


Figure 3. Hydroconversion product using fresh and recovering catalyst vs. heavy feed

4. Summary

The recent strength and stability of crude oil prices and advances in refining technology have raised the prospect of a major expansion in upgrading non-conventional extra-heavy crude oil resources. It is obvious to make that more attractive from the economic aspects, recovering of molybdenum as a precious material is so momentous. In this work, attempts were made to recover the homogenous ammonium molybdate catalyst used for upgrading a heavy feedstock i.e., 350+°C cut of an Iranian extra-heavy crude oil. To do such a task, performance tests were carried out in an autoclave with the volume of one liter under the pressure of 70 bar, temperature of 440°C, H₂/HC molar ratio of 1200, and the residence time of 20 min. Results showed that after recovering the catalyst in the homogenous phase using a proposed method, the conversion of upgrading was approximately the same as the commercial catalyst i.e., the ammonium molybdate tetrahydrate without any pre-processing.

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