   Hydrotreating of Coker  Gas Oil via Double Catalytic Layer

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(Handwerk and Gary 2001)

In this work, double catalytic layer (Co-Mo/γ-Al2O3, Ni-Mo/γ-Al2O3 and Co-Mo/γ-Al2O3, Pt-Pd/γ-Al2O3) were used in catalyst hydrotreating process (HDT) in order to improved characteristics of Coker gas oil such as sulfur and aromatic content. The catalysts were prepared by impregnation. This study was carried out by using fixed**-**bed rector at a temperature of 400°C, pressure of 100 atm with a volume hourly space velocity of coking gas oil (VHSV) of 1.0 h-1 and a volume ratio hydrogen/gas oil of 900Ncm3/cm3. Results showed that the sulfur and aromatics content were reduced. Also the Coker gas oil characteristics were more improved when the HDT process was carried out by (Co-Mo/γ-Al2O3, Pt-Pd/γ-Al2O3).

Keywords: catalyst, hydrotreating process (HDT), coker gas oil (CGO).

# Introduction

In recent years, use of the light fuel oil in various fields has been increasing, while its source from light oil has been decreasing. Therefore, the alternative sources were by using undesirable feedstocks such as Coker gas oil [. However, these feedstocks contain higher amount of sulfur and nitrogen. For example, Athabasca bitumen derived heavy gas oil contains 4 wt% Sulfur, 0.35 wt% Nitrogen and poisonous metals like arsenic and vanadium [, . Using the diesel fuel with this amount of compounds has a direct impact on the environment, due to the production of undesirable products such as nitrogen oxides, sulfur oxides and soot particles. In addition, the presence of these contaminants may cause problems in refining processes. For instance, the presence of nitrogen causes deactivation of catalysts[.  The European Union in April 2009, was adopted some directives whose aim is to reduce greenhouse (GHG) emissions from transportation fuels, by using feul with maximum of 10 PPM sulphur in both gasoline and diesel [ . Hydrotreating catalyst that removes heteroatoms from these feedstocks is playing an important role for upgrading the undesirable feedstooks to valuable products [7 Gary]. The hydrotreating process has been used for a long time in the petroleum-refining industry to obtain fuels with improved quality and low polluting compounds content (sulfur, nitrogen, aromatics, etc.). The traditional hydrotreating catalysts consist of some active metals such as Co and Mo are generally supported by alumina or silica alumina that are usually used in Hydrotreating process. Alumina is the famous name for aluminum oxide (Al2O3) has several thermodynamically stable transitional phases as gamma alumina, delta alumina, delta alumina, kappa alumina, theta alumina and alpha alumina. Gamma-alumina (γ-Al2O3) has been widely used in oil refineries for the hydrotreating of petroleum derivatives to improve the quality of oil products as a catalyst support [, . γ-Al2O3 has important features such as their good mechanical and textural properties and their ability to provide high dispersion of the active metals [, . A deep hydrogenation is sometimes required to increase the cetane index by aromatic hydrogenation. Nickel-based catalysts are selective for nitrogen removal in the hydrodenitrogenation reaction, while cobalt-based catalysts are selective for sulfur removal [, . There are several methods to prepare catalyst such as direct incorporation into the synthesis gel, impregnation and ion exchange[. The objective of this work to elucidate the effect of double catalytic layer on hydrotreating activity of the Coker gas oil. Hydrotreating of gas oil curried out by using  two double catalytic  layer Co-Mo/ γ-Al2O3,Ni-Mo/ γ-Al2O3 and Co-Mo/ γ-Al2O3,Pt-Pd/ γ-Al2O3 in this process.

# Experimental part

## 1-     Materials and experimental setup

The feed used for all experiments was heavy delayed coking gas oil, whose properties are presented in table 1. The precursor salts for each of the loaded metals were cobalt (II) nitrate hexahydrate, nickel (II) nitrate hexahydrate (sigma-Aldrich), heptamolbdate tetrahydrate (sigma-Aldrich), chloroplatinic acid hexahydrate and palladium (II) chloride. Gamma-alumina as a support for catalysts was used for all catalysts. The experimental program was carried out in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. Reaction conditions were at a temperature of 400°C, pressure of 100 atm with a volume hourly space velocity of coking gas oil (VHSV) of 1.0 h-1 and a volume ratio hydrogen/gas oil of 900Ncm3/cm3.

## 2-     Catalysts Synthesis

The synthesis of catalysts were prepared by successive impregnation method using the pore filling method. The composition for the loaded metals were (4% Co, 10% Mo) for Co-Mo/γ-Al2O3, (1% Pd, 0.25% Pt) for Pt-Pd/γ-Al2O3 and (6% Ni, 3% Mo) for Ni-Mo/γ-Al2O3. Conditioning of the catalyst between impregnation was achieved by drying at 160°C for 4 h and the final conditioning was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and reduction by treatment with sodium borohydride in aqueous solution at a temperature of 80°C, followed by activation in a stream of hydrogen at 450°C for 6 h.

## 3-     Catalyst characterization

The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments “Thermal Analyst 2000/2100” coupled with a module “951 Thermogravimetric Analizer”.

The surface area and pore volume was calculated from adsorption–desorption isotherms using the multi-point Brunauer–Emmett–Teller (BET) method based on the data in the partial pressure P/P0 range from 0.01 to 0.95.

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| Characteristics | value |
| Density, g/cm³ | 0.9442 |
| Total aromatics, %vol | 64 |
| Polyaromatics, % vol | 34.1 |
| Sulfur, %gr | 0.1621 |
| Aniline point,  ̊ʗ | 2 |
| Freezing point, ̊ʗ | -37 |
| Flash point, ̊ʗ | 97 |
| Average molar mass, kg/kmol | 210 |

# References

Handwerk, Glenn, and James Gary. 2001. *Petroleum Refining*. CRC Press. doi:10.1201/9780824745172.