Full Length Article

Catalytic upgrading of heavy oil using NiCo/γ-Al₂O₃ catalyst: Effect of initial atmosphere and water-gas shift reaction
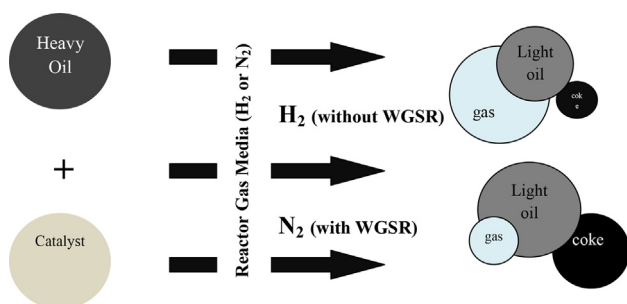
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Ni-Co/γ-alumina catalyst was prepared and tested in upgrading of heavy crude oil. The parameter studied was the type of the pressurising gas and especially its effect on the water-gas shift reaction on the upgrading. The preliminary results suggested that a combination of the cracking reaction and the original water-in-oil which triggered a low temperature water-gas shift reaction generated hydrogen in-situ for the hydrogenation reaction. To further explore this, four major experimental runs were conducted; amongst which two were without catalysts and reactor inner liner in hydrogen and nitrogen environments, two were catalytically driven with and without a liner. The experimental conditions were 380 °C, 32 bar and residence time of 2 h with a catalyst/oil ratio of 0.01. The results show that API gravity, Hydrogen/Carbon ratio and light oil yields were slightly higher for the reaction in nitrogen atmosphere without liner as compared to hydrogen with liner– 15.8°, 0.138, and 40.2 g respectively for the latter with 18.2°, 0.177, and 45 g for the former. The catalytic reaction in hydrogen environment however; produced no coke as against the 0.2 wt% coke recorded with nitrogen. Meanwhile, the reduction in sulphur content and viscosity of the nitrogen experiment were higher compared to that of hydrogen.

1. Introduction

Heavy oil is characterized with low API gravity and hydrogen to carbon ratio. It has high viscosity which hinders its free flow to the well surface during drilling, thereby leading to high transportation cost to refineries. In line with these, production of heavy oil was disfavoured [1]. Recent reports however suggested that conventional or light oil reserves are being depleted due to increased demands for petroleum products in the last decade. Therefore, heavy crude oil reservoirs and techniques of upgrading/enhancing heavy oil recovery have been

receiving attention from researchers and investors alike [1,2].

Unlike conventional light oil, exploration and production of heavy crude oil is time consuming, energy intensive and prone to environmental challenges. Accordingly, studies are directed to producing catalysts with higher hydrogenation activity and resistance to sulphur poisoning while maintaining quality [2]. Therefore, during upgrading, nitrogen instead of the highly expensive and easily explosive hydrogen would be required to pressurize the well and effect hydrocracking.

On the other hand, hydrocracking of heavy crude oil requires addition of hydrogen to enhance reactions of intermediates to more stable, low molecular weight hydrogenated products. Otherwise, unsaturated intermediate may re-polymerize into heavy high molecular weight asphaltenes. Consequently, in a bid to avoid addition of hydrogen gas, some researchers studied various parameters during crude oil upgrading in nitrogen environment [3,4]. These explored in-situ generation of hydrogen and minimized re-polymerization reactions.

In light of these, there is a need to systematically compare the catalysts performances in both hydrogen and nitrogen environments. It has earlier been investigated that after Cu and Re, Co and Ni have the highest turnover in hydrogen production among the group VIIB, VIII, and IB metals on alumina support [5]. Therefore, in this contribution, Ni-Co/γ-Al₂O₃ catalyst was used in the upgrading of heavy crude oil. The parameters monitored in the experiments include viscosity, API gravity, sulfur content and coke. Others are the saturates, aromatics, resins and asphaltenes fractions (SARA) of the resulting light oil, carbon and hydrogen contents as well as quantity of produced light oil and gases. The experiments were run in both nitrogen and hydrogen environments, with and without an inner liner in the reactor to ascertain the effect of in-situ generation of hydrogen via water-gas shift reaction on the upgrading process as shown in Eq. (1).

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1}$$

2. Materials and methods

2.1. Chemicals

The following chemicals were used: cobalt (II) nitrate hexahydrate Co(NO₃)₂·6H₂O (EMSURE), nickel (II) nitrate 6-hydrate Ni(NO₃)₂·6H₂O

Table 1
Heavy crude oil properties.

Parameter	Value
API gravity	14.560
Viscosity at 70 °C (cP)	1825
Density at 15 °C (g/cm³)	0.9682
Sulphur (wt%)	4.021
*Water in Crude (Karl Fisher ASTM D4928)	
Initial Crude	20.77 wt%
Dehydrated Crude	3.5 wt%
Elemental composition (wt%)	
C	79.24
H	13.63
N	1.10
S	4.45
Metal composition (ppm)	
Ni	9.0
V	40.0
Saturates (wt%)	17.2
Aromatics (wt%)	38.8
Resins (wt%)	27.2
Asphaltene (wt%)	12.36

* Analysis provided by a second party laboratory.

(Anala R), gamma alumina, Toluene (Sigma-Aldrich), Hexane (Fisher Scientific), DichloroMethane (DCM, Fisher Scientific), Methanol (Fisher Scientific), Cyclohexane (Fisher Scientific), Silica gel, and Potassium Carbonate (Anala R). High purity hydrogen (99.999%) and nitrogen (99.99%) were obtained from a local supplier.

Heavy crude oil was supplied from an Omani oil field. Its properties are listed in Table 1

2.2. Catalyst preparation

Ni-Co/γ-Al₂O₃ bimetallic catalysts were prepared by co-precipitation method modified from an earlier study [6]. Briefly, 370.4 mg Co(NO₃)₂·6H₂O and 371.6 mg Ni(NO₃)₂·6H₂O were dissolved in distilled water with 14.85 g γ-Alumina. Then, an aqueous solution of 0.5 Molar potassium carbonate was prepared and added to the mixed nitrate and alumina solution until pH 10 was achieved. The formed precipitate was then filtered and washed with distilled water for removing excess ions,
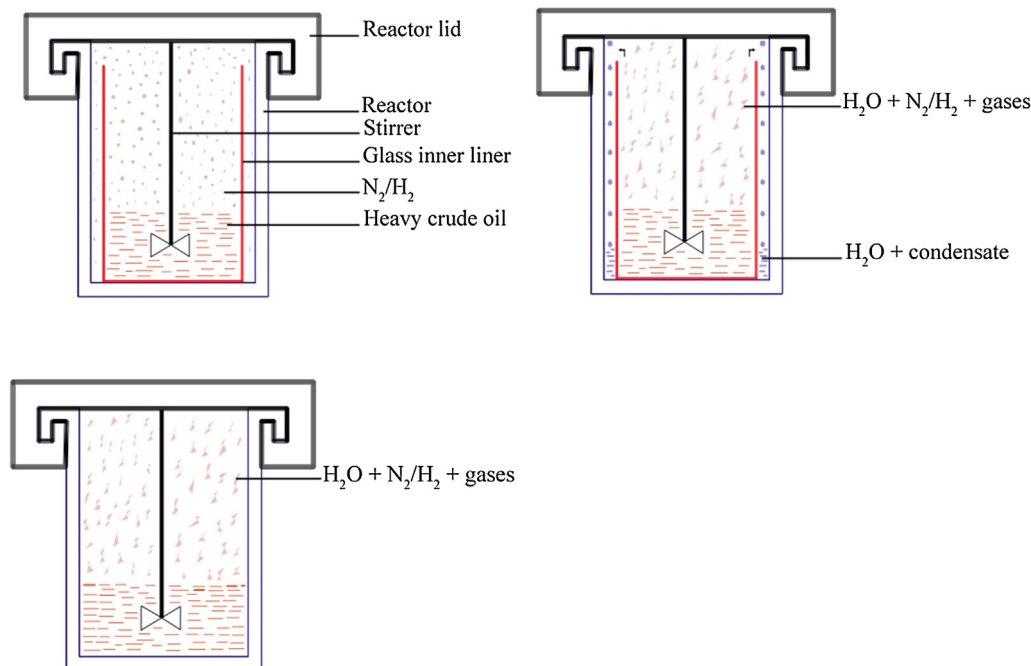

Fig. 1. Schematic of the reactor; a and b (with liner), c (without liner).