

# Catalytic Valorization of Heavy Crude Oil Via Aquathermolysis with $\text{Mo}_2\text{C/S-ZrO}_2$ System

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## ABSTRACT

Catalytic aquathermolysis emerges as a new approach to valorize heavy crude oil into lighter compositions with industrial compatibilities. Although several catalytic systems have been tested, certain critical issues remained unresolved. Therefore, the potential of  $\text{Mo}_2\text{C/S-ZrO}_2$  as a candidate for upgrading a heavy crude oil with API gravity value of  $12.0^\circ$  was evaluated at the laboratory scale. Successful designed of the  $\text{Mo}_2\text{C/S-ZrO}_2$  catalyst was established via FT-IR and XRD studies. Both techniques revealed features that were consistent with disappearance of  $\text{MoO}_3$  in  $\text{MoO}_3/\text{S-ZrO}_2$  precursor and consequent formation of  $\beta$ -type  $\text{Mo}_2\text{C}$ . Interestingly, the tetragonal form of  $\text{ZrO}_2$  was also unaltered by the carburization treatment (i.e.  $\text{CH}_4/\text{H}_2$ ,  $750^\circ\text{C}$ , 1.5 h). Additionally, the associated physicochemical properties were strongly responsible for viscosity reduction from 250.25 mPas to 78.30 mPas. Similarly, resins and asphaltenes were successfully ruptured into lighter saturates and aromatics during the process. Thus, the  $\text{Mo}_2\text{C/S-ZrO}_2$  system has good potential for this application.

**Keywords:**  $\text{Mo}_2\text{C/S-ZrO}_2$ ; Design and Characterization; Aquathermolysis; Catalytic performance.

## 1.0 INTRODUCTION

The supply of adequate energy resources is a critical factor for economic growth, sustenance and the stability of a nation (Galadima and Muraza, 2019; Galadima et al., 2024). Primarily, crude oil, natural gas and other fossil fuels have been contributing to the global supply for many decades. Although several arguments existed that the renewables (including biofuels) will form good replacements to the fossil fuels, the actual situation is directly parallel to these theories (Mutezo and Mulopo, 2021; Holechek et al., 2024). Specifically, the biofuels and other renewables can only complement a share of < 25% of the global energy requirements. Therefore, the fossil fuels will continue to provide the world with sources of energy and petrochemicals. According to the recent statistics, the fossil fuels provided a total of 464 quadrillion btu of the fuel required by different sectors (i.e. power supply, industry, transport, buildings and household-based consumption). The data further revealed that the energy requirement for these sectors will increase by 16 to 54% between 2021 and 2050 (Hannah et al., 2024). Among the fossil fuels, crude oil will continue to be responsible for the largest energy supply across the global regions. In fact, an average demand of 40-60% would be experienced by many developing countries. Another key important statistic postulated by OPEC documented that in December, 2023, the crude oil reserves are mainly located in OPEC countries (i.e. 1241.33 bbls, 79.1%). Similarly, countries around the Middle East are responsible for 67.3% of

these crude oil deposits (OPEC, 2024). However, a key challenge highlighted is the decline in the light crude oil reserves in the next decades.

To establish a balance between the growing crude oil demand and the possible extinction of the light reserves, several stake holders emphasized on the development of technologies that will facilitate feasible extraction of the heavy crude oil reserves. Catalytic aquathermolysis is one of these technologies strongly considered by researchers, policy makers and industry. It specifically involved the application of water/steam, heat and catalysts such as metals, acids or bases (homogeneous/heterogeneous) to reduce the viscosity of the heavy crude oil and transform it into light counterpart with compatibility for extraction based on the available technologies. During the process, bond ruptures are triggered especially for resins and asphaltenes for conversion into saturates and light aromatics. Typically, the degradation of C-C, C-O, C-N and C-S bonds proceeds with production of liquid hydrocarbon products (i.e. typical of light compositions) and emission of gaseous substances like  $\text{H}_2\text{S}$ ,  $\text{NO}_x$  and C1-C4 hydrocarbons. Both laboratory and field studies conducted to date utilized catalysts such as zeolites, oxides, metals and ionic liquids (Vakhin et al., 2021). However, the required process efficiency is still limited by cost-inconsistencies, catalyst decay, low viscosity reduction and other challenges thereby necessitating the need for the designing more promising catalyst systems.

The current research therefore focused on the synthesis and characterization of  $\text{Mo}_2\text{C/S-ZrO}_2$  catalyst as a potential candidate for upgrading a Nigerian-based heavy crude oil into lighter compositions.

## 2.0 EXPERIMENTAL STUDIES

### 2.1 Sampling of Heavy Crude Oil

The heavy crude oil was obtained from a field in Niger Delta, Nigeria (OML 53, Omerelu Field; 4.8472°N, 6.9746°E). The sample was transported in cleaned and dried plastic containers and kept under laboratory conditions prior to further analysis.

### 2.2 Preparation and Characterization

#### 2.2.1 Catalyst Preparation

The precursor (i.e.  $\text{MoO}_3/\text{S-ZrO}_2$ ) was developed through wetness impregnation technique by combining 25% (w/w) of  $\text{MoO}_3$  particles with balance of  $\text{SO}_4^{2-}/\text{ZrO}_2$  material. Water and temperature conditions were 100  $\text{cm}^3$  and 120°C, respectively. The resulted  $\text{MoO}_3/\text{S-ZrO}_2$  material was later converted into  $\text{Mo}_2\text{C/S-ZrO}_2$  (i.e. the carbided form) by treatment with 25%  $\text{CH}_4$  in  $\text{H}_2$  at 750°C for 1.5 h carburization period.

#### 2.2.2 Heavy Oil Characterization

Standard procedures approved by ASTM were carefully adopted for all the characterization studies. Initially, the virgin heavy crude oil was examined for its API gravity value in line with the method recommended in D 287. Similar technique was later employed to assess the change in API gravity value for the treated heavy oil. Other parameters such as viscosity (mPas) and SARA compositions (%) were derived with strict compliance to the principles captured in D 445 and D 4124, respectively.

#### 2.2.3 Catalyst Characterization

Surface and other physicochemical properties of the catalyst were established by adsorption with  $\text{N}_2$  at the liquid state temperature using a BELCAT approved porosimeter. FT-IR spectra were obtained for the region 1000-4000  $\text{cm}^{-1}$  after 100 scans to monitor the transformation of  $\text{MoO}_3$  into the  $\text{Mo}_2\text{C}$  phase. These studies were complemented with the aid of Bruker D8 XRD equipment for diffraction studies. The machine was operated using  $\text{CuK}\alpha$  as the radiation source.

#### 2.2.4 Catalyst Evaluation

Aquathermolysis with the designed catalyst system was conducted under improved lab-scale conditions. The glass reactor was charged with heavy oil : water (ratio of 70 : 30, % volume), leading to a total reactants volume of 150  $\text{cm}^3$ , 2.0g of catalyst and maintained at 120°C for a period of 1.5 h under constant stirring. Exit gases from

the process were adequately evacuated to mitigate unwanted pressure development and radical-assisted heavy compounds reversal.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Heavy Oil

The virgin heavy crude oil was analyzed to establish its fundamental properties and the results obtained are shown in Table 1. Specifically, the API gravity value of 12.0° indicated the crude oil to be heavy in its chemical compositions. This result exhibited good agreement with the viscosity data (i.e. 250.25 mPas), which is consistent with the range of viscosities for normal grade heavy crude oils. Results of the SARA compositions further agreed with these details. The lighter hydrocarbons (i.e. saturates and aromatics) constituted only 25.90% of the crude oil sample whereas the heavier components (i.e. resins and asphaltenes) accounted for 74.10% of the sample. Depending on the grade, formation properties and allied parameters, heavy crude oils can exhibit 50 to 80% of total resins and asphaltenes composition.

**Table 1. Characterization results for the virgin heavy oil before aquathermolysis.**

| PARAMETER        | VALUE/RESULT |
|------------------|--------------|
| API (°)          | 12.0         |
| Viscosity (mPas) | 250.25       |
| Saturates (%)    | 12.50        |
| Aromatics (%)    | 13.40        |
| Resins (%)       | 40.10        |
| Asphaltenes (%)  | 34.00        |

### 3.2 Precursor and Catalyst

The results derived from  $\text{N}_2$  adsorption of the precursor and the carbide catalyst (i.e.  $\text{MoO}_3/\text{S-ZrO}_2$  and  $\text{Mo}_2\text{C/S-ZrO}_2$ ) are provided in Table 2. Pronounced reduction in the BET surface area was established. This specific effect could be assigned to the consequences of the carburization conditions (i.e.  $\text{CH}_4/\text{H}_2$ , 750°C) that triggered partial agglomeration of particles. Thus, the interaction caused a reasonable decreased in active BET surface area from 122  $\text{m}^2\text{g}^{-1}$  for  $\text{MoO}_3/\text{S-ZrO}_2$  to 95  $\text{m}^2\text{g}^{-1}$  for the  $\text{Mo}_2\text{C/S-ZrO}_2$  catalyst system. However, the BJH pore volume exhibited an opposite trend yielding 0.0143 and 0.1726  $\text{cm}^3\text{g}^{-1}$  for the respective materials. Generally, the various results revealed adequate active surfaces and pore characteristics required to catalyse a reaction of interest by the  $\text{Mo}_2\text{C/S-ZrO}_2$  material. A major noticeable feature was the increased in the concentration of active and accessible Mo species responsible for the catalytic performance.

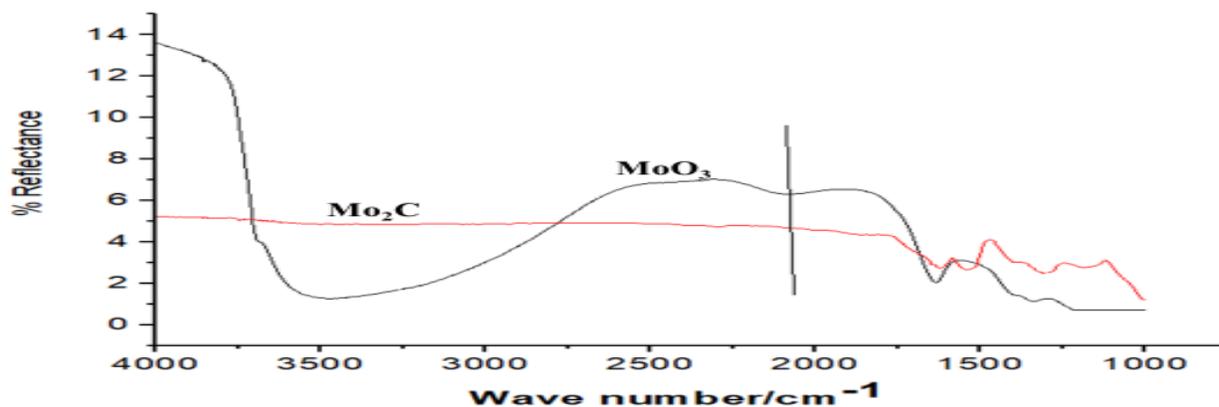
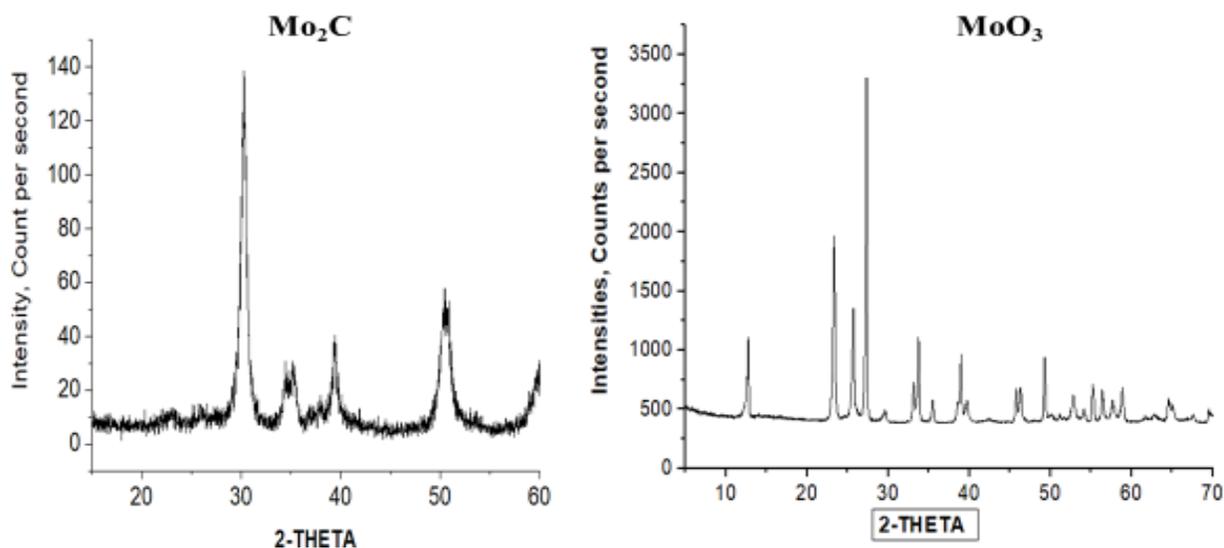
**Table 2. Data obtained via N<sub>2</sub>-adsorption with porosimeter.**

| PARAMETER   | MoO <sub>3</sub> /S-ZrO <sub>2</sub> | Mo <sub>2</sub> C/S-ZrO <sub>2</sub> |
|---|--------------------------------------|--------------------------------------|
| BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )        | 122                                  | 95                                   |
| BJH Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )        | 0.0143                               | 0.1726                               |
| Density of Mo species at surface (atoms/nm <sup>2</sup> ) | 8.20                                 | 11.50                                |

As depicted in the FT-IR spectra (i.e. Figure 1), disappearances of key vibrational features were prominent. Broad and overtone peaks that were respectively associated with surface-adsorbed water molecules and Mo=O characteristics of MoO<sub>3</sub> disappeared following the carburization treatment of MoO<sub>3</sub>/S-ZrO<sub>2</sub> precursor (Yang et al., 2023; Lv et al., 2024). This specific trend supported the formation of the desired Mo<sub>2</sub>C/S-ZrO<sub>2</sub>. Other noticeable peaks that were

observed (i.e. 1700-1000 cm<sup>-1</sup>) with both materials are clear characteristics of the various stretching and vibrations of the S-ZrO<sub>2</sub> (i.e. S=O, Zr-O and Zr-O<sub>2</sub>-Zr).

The x-ray diffraction (XRD) patterns further confirmed the transformation of MoO<sub>3</sub> into the Mo<sub>2</sub>C phase. Specifically, features that are characteristics of the β-form of Mo<sub>2</sub>C were apparent and resulted from the disappearance of thus peaks attributed to the parent MoO<sub>3</sub> system (Xu et al., 2023; Ravuri et al., 2024; Redda et al., 2024). The retention of other peaks associated with the S-ZrO<sub>2</sub> support revealed that the CH<sub>4</sub>/H<sub>2</sub> atmosphere had a negligible effect on the structural integrity of the tetragonal ZrO<sub>2</sub> material (i.e. no phase transition or degradation was observed).

Figure 1. Typical FT-IR spectra depicting the change in features of MoO<sub>3</sub> to Mo<sub>2</sub>C.Figure 1. Typical XRD spectral patterns depicting the change in features of MoO<sub>3</sub> to Mo<sub>2</sub>C

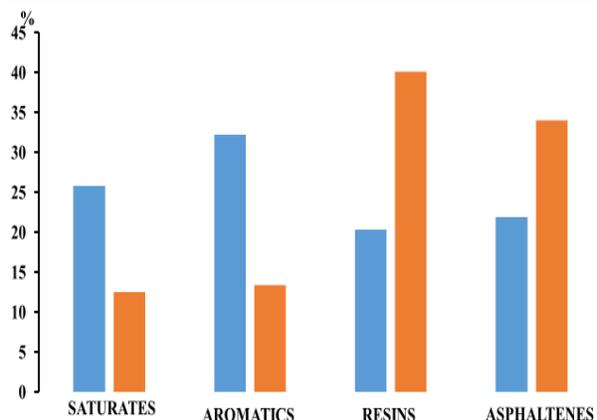
### 3.3 Mo<sub>2</sub>C/S-ZrO<sub>2</sub> Testing

The results derived from the lab-scale catalyst-mediated aquathermolysis of the heavy crude oil sample are provided in Table 3. Specifically, when compared with the data for the virgin heavy crude oil (i.e. Table 1), the API gravity value changed from 12.0 to 38.0°. A similar trend could be observed for the viscosity which reduced from 250.25 mPas to 78.30 mPas. Hence, the testing conditions employed were apparently positive in transforming the virgin crude oil into lighter counterpart.

**Table 3. Characterization results for the heavy oil after aquathermolysis.**

| PARAMETER        | VALUE/RESULT |
|------------------|--------------|
| API (°)          | 38.0         |
| Viscosity (mPas) | 78.30        |
| Saturates (%)    | 25.80        |
| Aromatics (%)    | 32.20        |
| Resins (%)       | 20.30        |
| Asphaltenes (%)  | 21.90        |

During the aquathermolysis process, a catalyst commonly behaves by triggering ruptures of different types of bonds that include C-C, C-O, C-S, C-N and degradation of long chain molecules into lighter counterparts with emissions of both liquid and gaseous products (Muraza and Galadima, 2015; Tirado et al., 2023; Mukhamatdinov et al., 2024). Therefore, as illustrated in Figure 3, the associated cleavages of such bonds in resins and asphaltenes accounted for their reduction in concentrations with a pronounced improvement in the amounts of saturates and aromatics when the aquathermolysis process was successfully carried out. The Mo<sub>2</sub>C/S-ZrO<sub>2</sub> therefore exhibited the necessary active sites required to facilitate the overall reaction. Acidic and/or basic sites in catalysts are always the primarily desirable features that must be present for the catalytic aquathermolysis to occur unhindered (Galadima and Muraza, 2020; Felix et al., 2024; Thangaraj and Lee, 2024). From the details depicted by Figure 3, the chances of reverse reactions possibly due to radical formation and recombination could be ruled out.



**Figure 3. Effect of Mo<sub>2</sub>C/S-ZrO<sub>2</sub> treatment on the SARA compositions of heavy crude oil under the aquathermolysis conditions. Orange Colours (Before Testing) and Blue Colours (After Testing)**

### 4.0 CONCLUSION

A new catalyst Mo<sub>2</sub>C/S-ZrO<sub>2</sub> was successfully developed via impregnation of MoO<sub>3</sub> with S-ZrO<sub>2</sub> to formulate the precursor MoO<sub>3</sub>/S-ZrO<sub>2</sub> and subsequent carburization under CH<sub>4</sub>/H<sub>2</sub> atmosphere at 750°C. The transformation process was congenially confirmed by the results of both FT-IR and XRD studies. Furthermore, data from N<sub>2</sub>-adsorption showed the resulted catalyst to exhibit good BET surface area (95 m<sup>2</sup>g<sup>-1</sup>), pore volume (0.1726 cm<sup>3</sup>g<sup>-1</sup>) and surface density of active Mo species of 11.50 atoms/nm<sup>2</sup>. These favourable physicochemical properties accounted for the positive role of the overall catalyst (Mo<sub>2</sub>C/S-ZrO<sub>2</sub>) during aquathermolysis of a heavy crude oil (API = 12.0°). Overall, the test results revealed successful conversion of heavy compounds (i.e. resins and asphaltenes) into lighter products (i.e. saturates and aromatics) with properties similar to those of light-grade crude oil. These details were further confirmed by the experienced viscosity reduction of initial feed from 250.25 mPas to 78.30 mPas. The catalyst Mo<sub>2</sub>C/S-ZrO<sub>2</sub> can be considered a promising candidate for aquathermolysis of heavy oil.

### 5.0 ACKNOWLEDGEMENT

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