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Manganese-Based Bifunctional as an Oil–Soluble Homogenous Catalyst for in–Situ Catalytic Upgrading of High Sulfur Heavy Crude Oil

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Abstract

Manganese naphthenate ($C_{22}H_{14}MnO_4$), a black oil-soluble liquid, was used for the first time as a bifunctional homogeneous catalyst in heavy oil upgrading under steam conditions. The catalyst combines two key functions: cracking, due to the 6% manganese content, and hydrogen donation from the naphthenate component, which enhances hydrogenation reactions, increases the H/C ratio, and facilitates hydrodesulfurization. Experiments were conducted in an autoclave reactor using heavy oil with high sulfur content under three temperatures (200, 250, and 300 °C) for 24 hours, in the presence and absence of the catalyst. The study employed several analytical techniques—viscosity measurement, SARA analysis, gas chromatography (GC), and X-ray diffraction (XRD)—to evaluate catalyst performance. Gas analysis by GC showed that, without the catalyst, the total light hydrocarbon gases (ΣC_1–C_4) and H_2S reached 0.8150 wt% and 1.2960 wt%, respectively, while with the catalyst, these increased to 1.4905 wt% and 1.5400 wt%. This indicates enhanced cracking and desulfurization activity. Viscosity measurements using a Brookfield Viscometer revealed that at 300 °C, the catalyst reduced the oil viscosity from 2802 mPa·s to 1437 mPa·s, achieving a 51% reduction, compared to only 29% (to 1962 mPa·s) without the catalyst. SARA analysis showed that the light fractions (saturates + aromatics) increased from 72% in the original oil to 80.76% with the catalyst and 75.69% without it, confirming significant cracking and hydrogenation. The presence of MnS in the solid residues after reaction further supports the catalyst's participation in hydrodesulfurization. Overall, manganese naphthenate demonstrated excellent catalytic activity in upgrading heavy oil through combined cracking, hydrogenation, and desulfurization mechanisms under steam conditions, making it a promising candidate for improving the quality and flow properties of high-sulfur heavy crude oils.

Keywords: Heavy crude oil, Catalytic upgrading heavy oil, Catalytic aquathermolysis, Oil-soluble catalyst, In-situ catalytic upgrading.

استخدام محفز متجانس ثنائي الوظيفة قائم على المنغنيز قابل للذوبان في النفط كإضافة لتحسين الترقية التحفيزية في الموقع للنفط الخام الثقيل عالي الكبريت

الخلاصة:

تستُخدم نافثينات المنغنيز($C_{22}H_{14}MnO_4$) ، وهو سائل أسود قابل للذوبان في الزيت، لأول مرة كمحفز متجانس ثنائي الوظيفة في تحسين جودة الزيت الثقيل تحت ظروف البخار. يجمع هذا المحفز بين وظيفتين رئيسيتين: التكسير، بفضل محتواه من المنغنيز بنسبة 6%، و في تفاعلات الهدرجة من خلال منح الهيدروجين من النفثينات، ويزيد من نسبة الهيدروجين إلى الكربون(H/C)، ويسهل عملية إزالة الكبريت بالهيدروجين. أُجريت التجارب في مفاعل أوتوكلاف باستخدام زيت ثقيل عالي الكبريت عند ثلاث درجات حرارة (200، 250، و300 درجة مئوية) لمدة 24 ساعة، في وجود المحفز وغيابه. استخدمت الدراسة عدة تقنيات تحليلية - قياس اللزوجة، وتحليلSARA، والكروماتوغرافيا الغازية (GC)، وحيود الأشعة السينية - (XRD) لتقييم أداء المحفز.

أظهر تحليل الغازات باستخدام الكروماتوغرافيا الغازية أنه بدون المحفز، بلغ محتوى غازات الهيدروكربونات الخفيفة ΣC1-C4 وكبريتيد الهيدروجين H2S إلى 0.8150% وزناً و 1.2960% وزناً على التوالي، بينما في وجود المحفز، وصل إلى 1.4905% وزناً و 1.5400% وزناً على التوالي. يشير هذا إلى تحسن نشاط التكسير وإزالة الكبريت. وكشفت قياسات اللزوجة باستخدام مقياس لزوجة Brookfield أن المحفز، عند 300 درجة مئوية، خفض لزوجة الزيت من (2802 mPa.S) إلى (1437 mPa.S) ، وهو ما يعادل انخفاضًا بنسبة 51٪ في اللزوجة. علاوة على ذلك، في التجارب التي اجريت بغياب المحفز، كانت أدنى قيمة لزوجة عند 300 درجة مئوية هي (1962 mPa.S) وهو ما يمثل انخفاضًا بنسبة 29٪ في اللزوجة.

أظهر تحليل SARA أن الكسور الخفيفة (المشبعات + العطريات) زادت من 72% في الزيت الأصلي إلى 80.76% مع المحفز و75.69% بدونه، مما يؤكد حدوث تكسير وهدرجة كبيرين. كما يدعم وجود كبريتيد المنغنيز (MnS) في المخلفات الصلبة بعد التفاعل مشاركة المحفز في عملية إزالة الكبريت بالهيدروجين.

1. Introduction

Petroleum has become the energy source that industries can't do without in recent years, as it is the most productive and widely used compound in modern industries, from which several industries and factories around the world have been discovered and developed. It is produced in very huge volumes per day in most countries of the world because of the increasing demand for it [1]. The world's total crude oil demand is expected to rise to 123 million barrels/day by 2025, according to the Energy Information Administration (EIA). Moreover, the Organization of Petroleum Exporting Countries (OPEC) predicts that by 2025 production will be approximately 61 million barrels per day, less than half of which will be demanded. At the same time, non-OPEC countries expect oil production to rise steadily (62 million barrels a day) by 2025 [2], particularly after the end of the COVID-19 virus crisis and the start of full productivity operations of factories and plants.

The increase in demand for oil has led to the threat of conventional oil, that is why researchers recommend focusing on other alternatives to oil at a low price, among these alternatives is heavy oil, which is considered a good alternative if it is treated in an appropriate and modern way to mimic the properties of conventional oil. Here, the importance of heavy oil began with its inclusion as a stress relief solution for conventional oil and thus its participation in the global oil market[3][4]. Petroleum treatment processes become very difficult due to several factors, such as the presence of sulfur, which makes it possible to emit sulfur oxides that pose a threat to the environment. The sulfur content in heavy oil can vary widely, typically ranging from 0.5% to 5% by weight, and sometimes even higher. Sulfur compounds can cause severe corrosion in pipelines, storage tanks, and refining equipment, leading to increased maintenance costs and potential safety hazards. Additionally, sulfur compounds can poison catalysts used in various refining processes, reducing their efficiency and lifespan. Hence the importance of heavy oil and the increase in scientific studies and research into how to treat it, because a challenge due to its disadvantages, such as high viscosity, high density, low API gravity, and increased sulfur content. Also, it contains high molecular weight compounds and complex chains such as asphaltene, resins, or other elements and metals such as vanadium, and nickel, and decreased hydrogen content versus increased carbon content[5].

heavy oil that has the same disadvantages as those mentioned above and consists of four compounds (saturated, aromatic, resin, and asphalt), each of which plays an important role in the oil upgrade process, and the most important of these is the saturated compounds that play a major role in the oil upgrade process. thus, there are upgrade processes that make the oil–rich in saturated compounds through treatment with certain conditions or using of catalysts that increase the hydrogen content in exchange for the low carbon content in the oil (H/C ratio), by increasing the H/C ratio, leads reducing the viscosity since the material is rich in saturated compounds, which allows reducing the density and gravity of API to increase[6,7]. Reducing sulfur content in fuels minimizes SO_2 emissions, preventing corrosion and protecting catalysts enhances the longevity and efficiency of refining equipment, reducing operational costs and downtime. Moreover, removing sulfur improves the quality of the final products, making them more suitable for modern engines that require low-sulfur fuels to meet emission standards. This result can be obtained by using an oil–soluble catalyst, it has unrivaled advantages because of its oil solubility, which produces an extremely high degree of dispersion and reduces viscosity and organic groups. [8,9].

There are several reasons for interest regarding the oil–soluble catalyst. Among these reasons, oil–insoluble catalysts are most commonly used, which means that they do not mix with the oil and therefore have a low contribution to heavy oil upgrading. Furthermore, after steam injections, the temperature drops relatively and gradually [10], necessitating the use of a power source capable of providing sufficient heat to the process, thus aiding in the optimization of the catalytic process. As a result, it is crucial to develop a catalyst that is completely soluble in oil and can produce catalytic reactions at lower temperatures [11]. Oil–soluble catalysts are both economically and technically feasible for use in the field. The organic ligands' characteristics are critical for oil-soluble catalysts because soluble organic compounds are essentially homogenous catalysts. By introducing metal ions into the oil's internal phase, the organic ligands can act as a hydrogen donor and the metal ions as an active catalyst.[12] [10],

Several examples from the scientific literature can be used to assess the potential of oil–soluble catalysts in upgrading heavy oil aquathermolysis. Abdullah Yusuf, et al.[13] at Sultan Qaboos University synthesized NiMo-oleate as an oil–soluble viscosity – reducing catalyst. They used glycol as a hydrogen donor in this case. Results from experiments demonstrated that the viscosity decrease of heavy oils may reach 89% at 200–300 °C, 0.1% by weight catalyst, and 0.10 wt.% hydrogen donor. They proved that the thermal stability, robustness, and effectiveness of this catalyst in lowering viscosity were better than those of water-soluble catalysts [14]. Chose *Chengdong et al*.[15] oil-soluble catalysts, especially copper stearate (II) developed in labs, were utilized to accelerate heavy oil oxidation during in-situ combustion. At 25°C, the viscosity of heavy oil samples from the Republic of Tatarstan's oil field is 2071.00 mPa s, and its API gravity is 15.4. After adding copper stearate (II), Chengdong concluded that heavy oil may be catalyzed to burn with efficiency in a heterogeneous and homogeneous manner. At high temperatures, the catalyst performed a heterogeneous catalytic function in the process of fuel synthesis and combustion (coke-like residues), but at low temperatures, it performed a homogeneous catalytic role in the oxidation process. In another study, to imitate the thermal recovery conditions of an oil reservoir, Fajun Zha, et al.[16], investigated the aquathermolysis reaction of heavy oil using an oil-soluble catalyst and an autoclave. The heavy oil samples from the Liaohe oil field contained saturated compounds (24.32 wt%), resins (30.27 wt%), asphaltene (8.52 wt%), a density of 0.9680 g cm-3 (20°C), and a viscosity of 3.716 mPa.s (50°C). However, the content of resin and asphaltene dropped. The hydrogen content rose in the presence of the oil-soluble catalyst while the carbon content dropped, increasing the hydrogen/carbon (H/C) ratio [17] [18].

Many studies in upgrading heavy oil have used oil–soluble catalysts to improve heavy oil recovery processes[19,20,21,22]. These studies have proven, these catalysts play an important role in the heavy oil upgrading process, as the content of saturated compounds of low molecular weight alkanes increases and the content of resins and asphaltene decreases significantly, and they also play a role in removing impurities such as sulfur and nitrogen. By suppressing the condensation and recombination reactions that prevail in the formation of heavy compounds, the pyrolysis processes of heavy components (resin, asphaltene, polycyclic aromatics, long-chain alkanes, etc.) and hydrogenation processes are enhanced.

It is worth mentioning that the study focuses on evaluating an oil-soluble catalyst with bifunctional attributes since the oil-soluble catalyst has a homogenous composition that allows it to perform many functions simultaneously. The manganese naphthenate catalyst (C22H14MnO4) has been designed in such a way that it can effectively remove sulfur from heavy oil due to its high capacity in hydrogenation reactions due to the high naphthenate content in its chemical composition, which contributes to improving hydrodesulfurization reactions as well as desulfurization reactions as a result of metal's continuous cracking capacity for C-S bonds. Oil–soluble catalysts, such as manganese naphthenate ($C_{22}H_{14}MnO_4$) [23], are more appealing, and they were chosen for further research into their catalytic performance in the in–situ upgrading of heavy oil. It can reduce the heterogeneous atom content by cracking heavy components into light components.

2. Research Methods

2.1. Materials

2.1.1. Crude oil sample

This study used heavy oil samples from the Ashalsha oil field in Russia's Republic of Tatarstan. This has identical properties to the well-known heavy oil. Table (1) shows the composition of heavy oil, elemental analysis, and some of its physical and chemical properties.

Table (1): The properties of the initial heavy oil sample.

SARA compounds, Wt%			
Saturates	Aromatics	Resins	Asphaltene
28.051	42.173	22.967	6.820
Elemental distribution, Wt%			
C	H	S	N
83.48	11.41	0.38	4.61
Other properties			
Density, kg/m^3	Viscosity, @ 25°C, mPa.S	API gravity	
971.8	2802.4	14.1	

2.1.2. Manganese naphthenate as Oil – soluble catalyst

Manganese naphthenate ($C_{22}H_{14}MnO_4$), which was used in the present study, is an organometallic chemical compound. It is a commercial oil-soluble catalyst that is soluble in organic solvents. MACKLIN Company [24] produced the catalyst, which was a blackish solution with a molecular weight of 397.28, a density of 0.93-0.97 g/mL, and a manganese concentration between 5.5-6.5%. Furthermore, more than 90% of naphthenate, which might improve the hydrogenation processes, is represented by the remaining percentage [25]. The homogenous liquid nature of this catalyst—which effectively dissolves and homogenizes with heavy oil throughout the reaction—must be noted. Stated differently, the catalyst exhibits bi-functionality by simultaneously participating in the hydrogenation and cracking reactions. [26].

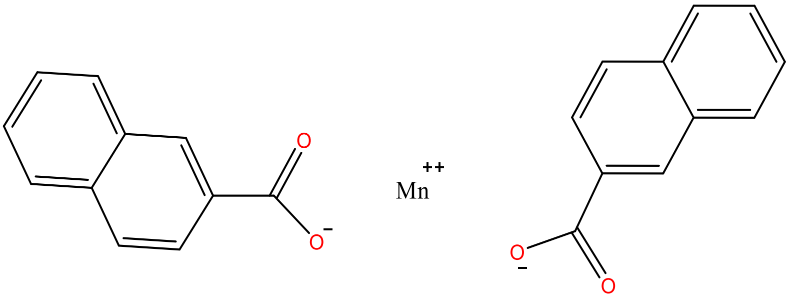

Fig. (1): Chemical structure of oil–soluble catalyst "Manganese Naphthenate"

2.2. Experimental procedures

2.2.1. Catalytic and Non-Catalytic upgrading using high pressure/temperature batch reactor with evolved gases analysis

Several catalytic and non–catalytic experiments with Ashalcha heavy oil were carried out in an autoclave reactor with a volume of 300 ml and a maximum temperature and pressure of 350 and 250 bar respectively (reactor model 4566 HP / HT, Parr Instruments Company, USA). Experiments were carried out under temperature conditions using the catalyst (crude oil with water and catalyst) at 200, 250, and 300 °C, respectively. Furthermore, experiments were conducted without the catalyst (crude oil with water) at temperatures of 200, 250, and 300 °C, respectively. Further to that, all experiments were carried out for 24 hours with oil, water, and catalyst percentages of 70%, 30%, and 2%, respectively. It should be noted that the study necessitates conducting experiments under the same conditions so that the results of the experiments can be accurately interpreted regardless of whether the catalyst is present. This method was used in the study to evaluate the activity and efficacy of the catalyst used, to identify the reaction mechanism and contrast between upgrading with and without the catalyst, and to identify the potential for water to act as a hydrogen donor in specific situations. Gas products from catalytic and non–catalytic upgrading were examined using a Gas Chromatography (GC) Chromatec-Crystal 5000 (Chromatic, Yoshkar-Ola, Russia) connected to an autoclave reactor. Physical and chemical-appropriate processing methods were used to evaluate the upgraded oil products.

2.2.2. Viscosity Measurement Procedures

The viscometer device measures fluid resistance by applying torque to the viscosity of the oil produced by a spindle immersed in the oil and rotating at uniform speeds. Furthermore, the unit of measure can be chosen from the instrument control screen, which displays all SI units of viscosity where viscosity is shown in centipoises (expressed as "cP") or milliPascals (expressed as "mPa.s"). A Brookfield Viscometer was used to investigate the viscosity of initial heavy oil and upgraded oil through the following conditions: (SP: TL6; RPM: 10,5,3,1.5,0.6,0.3; T: 20 °C).

2.2.3. SARA Analysis Procedures

The ASTM D 4124 standard defines SARA analysis as the separation of crude oil into four components (saturated, aromatic, resins, and asphaltene) both before and after the reaction for initial heavy oil samples, catalytic, and non-catalytic upgrading heavy oil. A 1:40 oil-to-heptane ratio was proposed to precipitate asphaltene in a dark medium within 24 hours. This produces a mixture of asphaltene and maltenes.

The asphaltene is separated from the maltenes using filter paper, and the maltene residue is extracted from the filter paper using an extractor. Using an open column system using solvents such as heptane, toluene, and a mixture of toluene and isopropanol (1:1), allows the maltenes to be divided into three categories: saturated, aromatic, and resins, respectively. To conclude the study, solvents are removed from hydrocarbons with an evaporator.

2.2.4. Elemental Analysis

The carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNS/O) weight percentages in various samples were investigated, and the elemental compositions of the initial heavy oil and upgraded oil were determined using a Perkin Elmer- Elemental Analyzer 2400 Series II at 1000°C in a percentage of mass.

2.2.5. X-R diffraction analysis (XRD)

D2 Phaser (Bruker Axs GmbH) was utilized to record catalyst diffraction patterns before and after upgrading. Diffractometers in Bragg-Brentano geometry used a 141.4 mm goniometer. Fixed slits were used alongside the linear (position-sensitive) LynxEye detector. For CuK radiation, X-ray sources are rated at 30 kV/10 mA. It rotated the sample along its plane. The diffraction data were processed using the software package DIFFRACSUITE. The phase analysis was performed using the ICDD PDF-2 Release 2013 diffraction database and the DIFFRAC. Eve (v-3.1) module software. [27].

2.2.6. Fourier Transform Infrared Spectra (FTIR) Analysis

FTIR spectroscopy was used in this study to examine the catalyst before and after the reaction. FTIR spectroscopy is widely regarded as one of the most effective methods for determining potential changes in the structures of heavy oil components and the structure of the catalyst used in the study before and after the upgrade [27]. For this analysis, a Vertex 70 FTIR spectrometer (Brucker, Germany) was used.

3. Results and Discussion

3.1. Evolved gases for Non-Catalytic and Catalytic heavy oil upgrading

The results in Table (2) proved the efficiency of the catalyst used in increasing the light hydrocarbon gases (C_1–C_4, etc). The total percentage of non – condensable gases (C_1–C_4) increases with increasing temperature when the catalyst is used. According to the researchers, this increase can be explained by random splitting of the side chains caused by free radical reactions that form smaller hydrocarbon radicals, resulting in the formation of light hydrocarbon gases. Furthermore, the increase in these gases is a strong indicator of the efficiency of the heavy oil upgrading reaction, which contributes to the reduction of heavy oil viscosity [28]. On the other hand, the contribution of water to the reaction can be observed through the production of CO and CO_2 gases, as one of the reasons for the production of these gases is the presence of water in the reaction that contributes to the release of oxygen during the reaction since there is no other reason for the production of oxygen because the percentage of oxygen in heavy oil they are very little. Another proposed explanation for the production of CO and CO_2 gases is the Water-shift-gas reaction, which can also be produced in the presence of carbonates during the upgrading of heavy oil with the catalyst and in the presence of water [29]. Furthermore, the percentage of hydrogen gas production increased in the presence of the catalyst as the temperature increased, indicating that hydrogen played a significant role in the promotion of unsaturated compounds and their transformation into saturated, as well as the degree of desulfurization, which corresponds to the results of H_2S gas production, which increased gradually as the temperature increased in the presence of the catalyst[30]. Moreover, the main reason for the increase in H_2S gas is due to the thermal and hydro-cracking of sulfur-containing asphaltene compounds[31], which resulted in the occurrence of desulfurization provided by the hydrogen-donating part of the catalyst (naphthenate), which plays a significant role in the hydrogenation processes that contribute to desulfurization[32].

Table (2): Evolved gases products after non–catalytic and catalytic upgrading.

Compounds	**Gases Yields, wt %**					
	Non-Catalytic upgrading			**Catalytic upgrading**		
	200 °C	**250 °C**	**300 °C**	**200 °C**	**250 °C**	**300 °C**
Σ-C_1-C_4	0.3844	0.8133	0.8150	0.5020	1.0083	1.4905
H_2	0.0029	0.0570	0.1201	0.0013	0.0735	0.0790
H_2S	0.6918	0.9380	1.2960	0.9013	1.3160	1.5400
CO	0.0082	0.0153	0.0491	0.0103	0.0674	0.0813
CO_2	3.8270	2.4011	0.6651	5.6280	3.6183	0.9750

3.2. Viscosity measurement for non-catalytic and catalytic Upgrading

The effectiveness and functionality of the oil-soluble catalyst are shown in Figure (2), which indicates the dynamic viscosity of many heavy oil samples, before and after upgrading with and without catalysts. The initial oil's viscosity at 25°C before the upgrading was 2802.4 mPa.S. Studies showed that the viscosity of the heavy oil upgrading without catalyst was 2691.7, 2332, and 2156 mPa.S. at 200, 250, and 300 °C, respectively. The heavy oil upgrading with the catalyst, achieved 1705, 1601, and 1437 mPa.S, respectively. Furthermore, the viscosity reduction rates with the catalyst were 51% at 300°C, 42 % at 250°C, and 39 % at 200°C. Because the catalyst (manganese naphthenate) has two roles in the reaction, cracking, and hydrogenation [33], and because the resin and asphaltene compounds are responsible for increasing the viscosity, the double performance of the catalyst led to a reduction in the content of resin and asphaltene. As is well known, the higher the viscosity, the more these compounds increase, because these compounds are characterized by intermolecular forces with low bonding energy, such as hydrogen bonds, coordination bonds, and van der Waals force, which increase the molecular aggregates and thus the relative molecular weight [29] [30]. As a result, it governs the role of the viscosity–reducing catalyst in releasing the small molecules encased within the heavy oil molecular aggregate. Moreover, the dissolution of the molecular aggregates and subsequent decrease in molecular weight are caused by the catalyst's ability to target the intermolecular interactions with weak bonds in the resin and asphaltene compounds. The weak energy chemical bonds (C-C, C-O, and C-S bonds) break, resulting in a decrease in molecular weight and a series of reactions that lessen molecular aggregation and improve viscosity reduction.

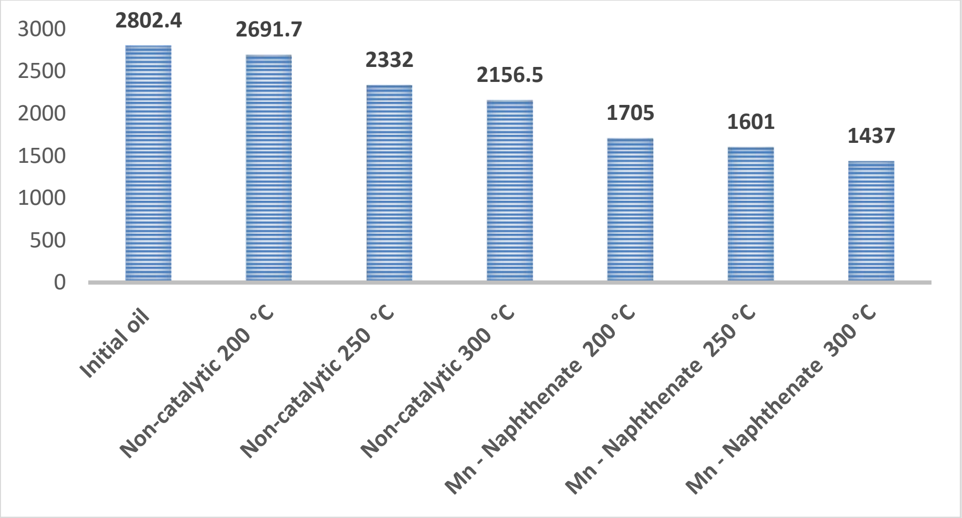

Fig. (2): Viscosity measurement at 20 °C, mPa.S before and after upgrading at 3.4 cm^{-1} Shear rate.

3.3. SARA Analysis for Non-Catalytic and Catalytic Upgrading

SARA analysis before and after upgrading in the presence and absence of a catalyst, as well as the effectiveness and efficiency of the catalyst in increasing the content of light compounds at the expense of heavy compounds, are shown in Table (3). In catalytic upgrading, we note a significant increase in saturated compounds and a decrease in aromatic, resin, and asphaltene compounds when compared to the SARA fractions for the initial heavy oil. The content of saturated compounds reached 47% at 300°C in the presence of the catalyst, while the content of heavy compounds decreased to 19% resin and asphaltene after it was 28.05% saturated compounds and 29.78% heavy compounds before upgrading. When comparing the recent results with the upgrade without catalyst, we encounter that the catalyst is effectively enhanced by increasing the content of light compounds versus the content of heavy compounds, with the content of saturated compounds reaching 31.82% as the highest value obtained during the upgrading without catalyst at a temperature of 300 °C, and the content of heavy compounds reaching 24.31% at the same temperature. We conclude that the catalyst performed effectively in increasing the light content of saturated compounds, which is the main goal of the study to increase the saturated compounds, which leads to an increase in the value of the H/C ratio, which provides a good redistribution of light and aromatic compounds. Furthermore, the lower content of unsaturated heavy compounds can be explained by the possible cracking of the C–R bonds (R = S, N, and O), as C-S bonds are thought to be among the weakest bonds in heavy oil molecules, so they break easily and thus become hydrogen donate is easier to turn into saturated compounds[36]. Because it is known that resin compounds can convert to saturated compounds in the presence of a hydrogen donor and asphaltene can convert to resins, we observe in most laboratory experiments that the percentages of decrease in heavy compounds from resin and asphaltene are slight because asphalt compensates for the decrease in resin[37]. On the other hand, we notice a significant decrease of aromatic compounds with an increase of saturated compounds, which occurs due to the presence of hydrogen donor with the liquid oil–soluble catalyst in high – efficiency in which the hydrogen donor constitutes more than 90%, so the role of the catalyst in the redistribution of SARA fractions was two-sided, the first is hydrogen donate to increase saturated compounds at the expense of unsaturated compounds. The second is the cracking of weak bonds caused by the conversion of heavy compounds to light compounds.

Table (3): SARA Fraction before and after upgrading with and without Mn-naphthenate.

SARA compounds, initial oil sample (Wt %)						
Temp. °C	**Saturate**	**Aromatics**	**Resins**	**Asphaltene**	**Light components**	**Heavy components**
	28.052	42.171	22.964	6.821	70.223	29.781
SARA compounds, non-catalytic upgrading (Wt %)						
200 °C	28.793	43.483	20.981	6.750	72.272	27.734
250 °C	29.49	45.11	19.02	6.38	74.60	25.40
300 °C	31.82	43.87	17.95	6.36	75.69	24.31
SARA compounds, catalytic upgrading with Mn-Naphthenate (Wt %)						
200 °C	37.17	38.25	18.48	6.10	75.42	24.58
250 °C	39.18	37.84	17.22	5.74	77.02	22.96
300 °C	47.04	33.72	14.01	5.21	80.76	19.23

3.4. Elemental Analysis for Non-Catalytic and Catalytic Upgrading

The results of an elemental analysis performed before and after upgrading heavy oil with and without catalyst revealed that the sulfur content in the upgraded oil was reduced during a series of experiments conducted under various thermal conditions. The desulfurization percentage was calculated in Table (4), and it increased by 3.03%, 8.45%, and 9.54% at 200°C, 250°C, and 300°C, respectively, during non-catalytic upgrading. However, during catalytic upgrading, the desulfurization percentage of upgraded oil increased to 10.20%, 19.31%, and 22.56%, respectively. Furthermore, an increase in the desulfurization ratio indicates the capacity and efficiency of the catalyst in the hydrodesulfurization reactions that were formed as a result of the catalyst's higher capacity in the hydrogenation reactions [37]. Moreover, the C-S bonds are among the weakest chemical bonds found in crude oil, which are widely present in asphaltenes and resin compounds that were subjected to extensive splitting, resulting in a decrease in sulfur content [38], and this is consistent with all analyses performed. However, the presence of the catalyst in the hydrogenation processes caused a redistribution of carbon and hydrogen content, increasing the H content because of continuous breakage of the heavy hydrocarbon's weak C-C bonds [39], resulting in an increase in the H/C ratio from 1.644 to 1.706 at 300°C.

Table (4): Elemental analysis before and after upgrading with and without Mn-naphthenate.

Agent	C	H	N	S	H/C ratio	Sulfur removal (%)
Initial heavy oil sample	83.48	11.41	0.38	4.61	1.644	-
Non-catalytic - 200 °C	83.38	11.48	0.36	4.46	1.650	3.13
Non-catalytic - 250 °C	82.87	11.47	0.35	4.21	1.665	8.55
Non-catalytic - 300 °C	83.15	11.49	0.34	4.17	1.658	9.54
Catalytic - 200 °C	83.16	11.48	0.35	4.14	1.656	10.20
Catalytic - 250 °C	82.96	11.67	0.32	3.72	1.688	19.31
Catalytic - 300 °C	82.91	11.79	0.26	3.57	1.706	22.56

3.5. XR- Diffraction study of “Mn-naphthenate”

The chemical state of the catalyst manganese naphthenate and the mechanics of the reaction were evaluated through analysis of the XRD of the solid catalyst particles after the reaction at 300°C in the presence of water. X-ray powder diffraction (XRD) studies were carried out utilizing Debye-Scherer geometry on desktop MD-10 diffraction machines. A Fe Kα radiation tube with λ = 0.193728 was used. The phase was determined using the QualX 2.0 program. MnS (purple) reactions were observed in two stages. Thus, in the presence of a catalyst containing a high amount of naphthenate, which acts as a hydrogen donor, and in the presence of water, a very high percentage of desulfurized catalyst MnS was obtained. This indicates that the hydrodesulfurization reaction occurred significantly[40], which is consistent with the analysis of the evolved gases, which contained a high percentage of H_2S gas, and what was obtained from the elemental analysis. As demonstrated by the data, the catalyst works effectively in the hydrogenation, hydrodesulfurization, and cracking reactions.

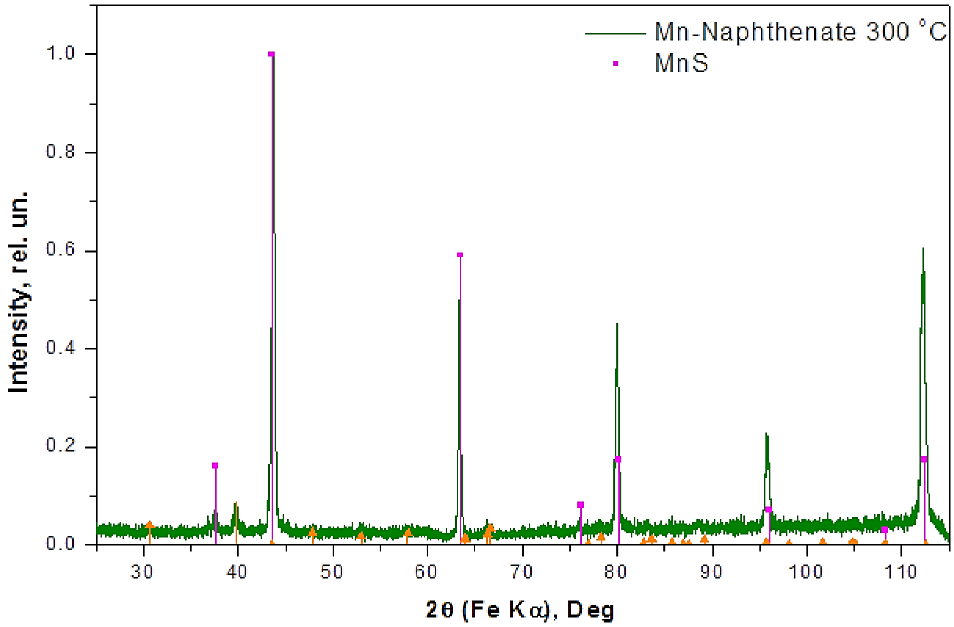

Fig. (5): X-ray diffraction patterns of coke containing Mn-naphthenate catalyst at 300 °C.

3.6. FTIR for Mn – naphthenate

The FTIR spectra of manganese naphthenate ($C_{22}H_{14}MnO_4$) could be analyzed by examining the typical absorption bands associated with various functional groups. This study employed a Vertex 70 FTIR spectrometer (Bruker, Germany) to identify the structure of the catalyst being studied [27]. Figure 6 displays the catalyst structure used for heavy oil upgrading. The presence of monomer compounds, namely methylene molecules, is indicated by the presence of CH_2 peaks inside the borders of the functional group area that covers the peaks approximately 2920 cm^{-1} and 2850 cm^{-1}, these peaks represent the CH stretching vibrations of the methylene groups ($-CH_2-$). The presence of these peaks indicates the presence of aliphatic hydrocarbon chains within the structure. According to FTIR analysis, the high and multiple CH_2 peaks are related to the content of organic bonds in the catalyst, which helps introduce the metal ion into the internal oil phase, enhancing the cracking ability of the catalyst. In addition, the results of FTIR analysis show peaks around 1600 cm^{-1} and 1450 cm^{-1}, where these peaks are related to the asymmetric and symmetric stretching vibrations of the carboxyl groups (-COO-). This is what characterizes metal carboxylates, which confirms the presence of the manganese naphthenate compound.

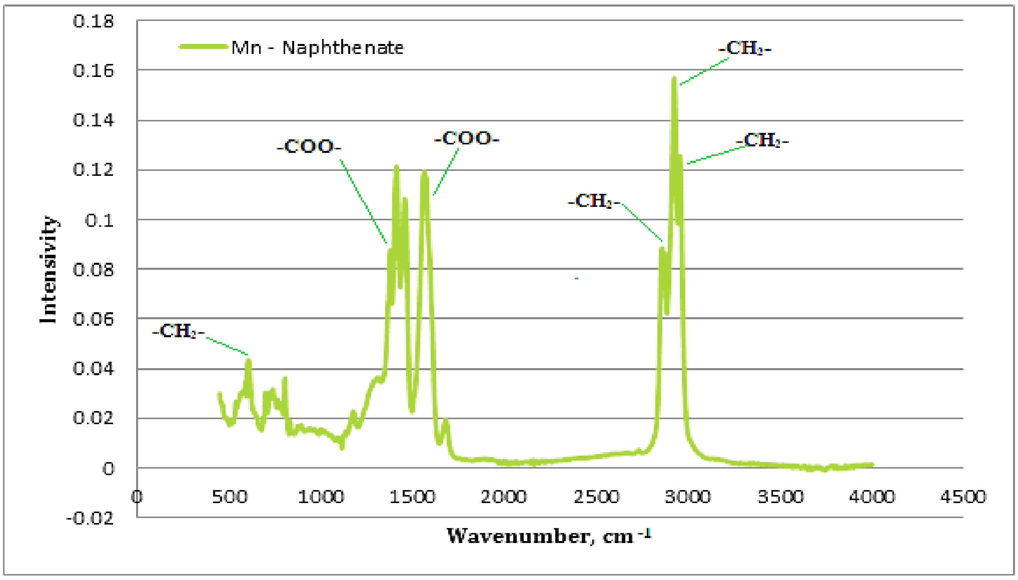

Fig. (6): FTIR spectra of the obtained Manganese naphthenate ($C_{22}H_{14}MnO_4$)

4. Conclusion

The mechanism ability of a Manganese naphthenate ($C_{22}H_{14}MnO_4$) oil - soluble catalyst was investigated in the upgrading of heavy oil from the Tatarstan oil field under steam conditions in this study. Experiments were carried out with and without the catalyst at three temperatures: 200, 250, and 300 °C. After the reaction at 300 °C in the presence of water, the XRD results of the solid particles of the catalyst revealed large amounts of MnS, indicating the catalyst's ability to hydro-desulfurization reactions. Furthermore, the oil-soluble catalyst's role in heavy oil upgrading is primarily manifested in the following aspects:

- Obtaining a significant reduction in viscosity (from 2802 to 1437 mPa.S), equivalent to a 51% reduction in viscosity.
- Light compounds (saturated and aromatic) increased in content from 72.92% to 80.76%, while saturated compounds increased in content from 28.75% to 47.045%.
- The content of heavy compounds (resins and asphalts) has dropped from 27.08% to 19.23%.
- During the reaction, high proportions of light gases (C1-C4) were obtained.

Furthermore, when heavy oil was upgraded with an oil-soluble catalyst, the content of saturated C10–C18 alkanes increased from 29% to 38% at 300°C. During the reaction, the H/C ratio increased, indicating that the oil-soluble manganese naphthenate catalyst performed well.

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References

[1] H. K. Abdel-Aal, M. A. Aggour, and M. A. Fahim, “Petroleum and gas field processing”, (1st ed.), *CRC press*, 2015. https://doi.org/10.1201/9780429258497.

[2] J. J. Conti, P. D. Holtberg, J. A. Beamon, A. M. Schaal, J. C. Ayoub, and J. T. Turnure, “Annual energy outlook 2014”, *US Energy Information Administration*, vol. 2, 2014.

[3] L. C. Castaneda, J. A. D. Munoz, and J. Ancheyta, “Current situation of emerging technologies for upgrading of heavy oils”, *Catalysis Today*, vol. 220-222, pp. 248–273, 2014. https://doi.org/10.1016/j.cattod.2013.05.016.

[4] A. E. Outlook, “With Projections to 2050 (US Energy Information Administration, 2017),” *Environmental Protection Agency, Washington, DC. https://www. eia. gov/outlooks/aeo*, 2017.

[5] K. Guo, H. Li, and Z. Yu, “In-situ heavy and extra-heavy oil recovery: A review”, *Fuel*, vol. 185, pp. 886–902, 2016. https://doi.org/10.1016/j.fuel.2016.08.047.

[6] D. Vartivarian and H. Andrawis, “Elayed coking schemes are most economical for heavy-oil upgrading”, *Oil & gas journal*, vol. 104, no. 6, pp. 52–56, 2006.

[7] E. Furimsky, “Catalysts for upgrading heavy petroleum feeds”, Elsevier, 2007.

[8] G. M. Dhar, G. M. Kumaran, M. Kumar, K. S. Rawat, L. D. Sharma, B. D. Raju, and K. S. R. Rao, “Physico-chemical characterization and catalysis on SBA-15 supported molybdenum hydrotreating catalysts”, *Catalysis Today*, vol. 99, no. 3–4, pp. 309–314, 2005. https://doi.org/10.1016/j.cattod.2004.10.005.

[9] T. N. Pham, D. Shi, and D. E. Resasco, “Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase”, *Applied Catalysis B: Environmental*, vol. 145, pp. 10–23, 2014. https://doi.org/10.1016/j.apcatb.2013.01.002.

[10] J. Alfadhli, A. Alhindi, A. Alotaibi, and D. Bahzad, “Performance assessment of NiMo/γ-Al2O3 catalysts for upgrading KEC-AR: An assessment of selected apparent kinetic parameters of selected hydrotreating reactions”, *Fuel*, vol. 164, pp. 38–45, 2016. https://doi.org/10.1016/j.fuel.2015.09.079.

[11] A. Al-Marshed, A. Hart, G. Leeke, M. Greaves, and J. Wood, “Effectiveness of different transition metal dispersed catalysts for in situ heavy oil upgrading”, *Industrial & Engineering Chemistry Research*, vol. 54, no. 43, pp. 10645–10655, 2015. https://doi.org/10.1021/acs.iecr.5b02953.

[12] A. Al-Marshed, A. Hart, G. Leeke, M. Greaves, and J. Wood, “Optimization of heavy oil upgrading using dispersed nanoparticulate iron oxide as a catalyst”, *Energy & Fuels*, vol. 29, no. 10, pp. 6306–6316, 2015. https://doi.org/10.1021/acs.energyfuels.5b01451.

[13] A. Yusuf, R. S. Al-Hajri, Y. M. Al-Waheibi, and B. Y. Jibril, “In-situ upgrading of Omani heavy oil with catalyst and hydrogen donor”, *Journal of Analytical and Applied Pyrolysis*, vol. 121, pp. 102–112, 2016. https://doi.org/10.1016/j.jaap.2016.07.010.

[14] A. Hart, J. Wood, and M. Greaves, “In situ catalytic upgrading of heavy oil using a pelletized Ni-Mo/Al2O3 catalyst in the THAI process”, *Journal of Petroleum Science and Engineering*, vol. 156, pp. 958–965, 2017. https://doi.org/10.1016/j.petrol.2017.06.067.

[15] C. Yuan, D. A. Emelianov, M. A. Varfolomeev, N. O. Rodionov, M. A. Suwaid, and I. R. Vakhitov, “Mechanistic and kinetic insight into catalytic oxidation process of heavy oil in in-situ combustion process using copper (II) stearate as oil soluble catalyst”, *Fuel*, vol. 284, p. 118981, 2021. https://doi.org/10.1016/j.fuel.2020.118981.

[16] F. Zhao, Y. Liu, Z. Fu, and X. Zhao, “Using hydrogen donor with oil-soluble catalysts for upgrading heavy oil”, *Russian Journal of Applied Chemistry*, vol. 87, no. 10, pp. 1498–1506, 2014. https://doi.org/10.1134/S1070427214100164.

[17] L. A. Rankel, “Hydrocracking vacuum resid with Ni W bifunctional slurry catalysts”, *Fuel processing technology*, vol. 37, no. 2, pp. 185–202, 1994. https://doi.org/10.1016/0378-3820(94)90015-9.

[18] H. Luo, W. Deng, J. Gao, W. Fan, and G. Que, “Dispersion of water-soluble catalyst and its influence on the slurry-phase hydrocracking of residue”, *Energy & Fuels*, vol. 25, no. 3, pp. 1161–1167, 2011. https://doi.org/10.1021/ef1014378.

[19] J. Cui, Z. Zhang, X. Liu, L. Liu, and J. Peng, “Analysis of the viscosity reduction of crude oil with nano-Ni catalyst by acoustic cavitation”, *Fuel*, vol. 275, p. 117976, 2020. https://doi.org/10.1016/j.fuel.2020.117976.

[20] M. Alaei, M. Bazmi, A. Rashidi, and A. Rahimi, “Heavy crude oil upgrading using homogenous nanocatalyst”, *Journal of Petroleum Science and Engineering*, vol. 158, pp. 47–55, 2017. https://doi.org/10.1016/j.petrol.2017.08.031.

[21] F. A. Aliev *et al.*, “In-situ heavy oil aquathermolysis in the presence of nanodispersed catalysts based on transition metals”, *Processes*, vol. 9, no. 1, pp. 1–22, 2021. https://doi.org/10.3390/pr9010127.

[22] M. A. Coronel-García, A. I. R. de la Torre, J. M. Domínguez-Esquivel, J. A. Melo-Banda, and A. L. Martínez-Salazar, “Heavy oil hydrocracking kinetics with nano-nickel dispersed in PEG300 as slurry phase catalyst using batch reactor”, *Fuel*, vol. 283, p. 118930, 2021. https://doi.org/10.1016/j.fuel.2020.118930.

[23] J. Ancheyta, “Modeling of processes and reactors for upgrading of heavy petroleum”, *CRC Press*, 2013.

[24] “Specification sheet.,” *Schmierungstechnik*, vol. 19, no. 2, 1988, pp. 61–63, 1988.

[25] X. D. Tang, X. D. Chen, J. J. Li, L. Y. Deng, and G. J. Liang, “Experimental study on homogeneous catalytic upgrading of heavy oil”, *Petroleum Chemistry*, vol. 57, no. 12, pp. 1018–1023, 2017. https://doi.org/10.1134/S0965544117120143.

[26] K. Chao, Y. Chen, H. Liu, X. Zhang, and J. Li, “Laboratory experiments and field test of a difunctional catalyst for catalytic aquathermolysis of heavy oil”, *Energy & Fuels*, vol. 26, no. 2, pp. 1152–1159, 2012. https://doi.org/10.1021/ef2018385

[27] C. W. Brown, P. F. Lynch, and M. Ahmadjian, “Applications of infrared spectroscopy in petroleum analysis and oil spill identification”, *Applied Spectroscopy Reviews*, vol. 9, no. 1, pp. 223–248, 1975. https://doi.org/10.1080/05704927508081491.

[28] A. A. Al-Muntaser, M. A. Varfolomeev, M. A. Suwaid, D. A. Feoktistov, C. Yuan, A. E. Klimovitskii, B. I. Gareev, R. Djimasbe, D. K. Nurgaliev, S. I. Kudryashov, E. V. Egorova, A. V. Fomkin, O. V. Petrashov, I. S. Afanasiev, and G. D. Fedorchenko, “Hydrogen donating capacity of water in catalytic and non-catalytic aquathermolysis of extra-heavy oil: Deuterium tracing study”, *Fuel*, vol. 283, p. 118957, 2021. https://doi.org/10.1016/j.fuel.2020.118957.

[29] T. Sato, S. Mori, M. Watanabe, M. Sasaki, and N. Itoh, “Upgrading of bitumen with formic acid in supercritical water”, *The Journal of Supercritical Fluids*, vol. 55, no. 1, pp. 232–240, 2010. https://doi.org/10.1016/j.supflu.2010.07.010.

[30] P. R. Kapadia, M. S. Kallos, and I. D. Gates, “A new reaction model for aquathermolysis of Athabasca bitumen”, *The Canadian Journal of Chemical Engineering*, vol. 91, no. 3, pp. 475–482, 2013. https://doi.org/10.1002/cjce.21662.

[31] S. K. Maity, J. Ancheyta, and G. Marroquín, “Catalytic aquathermolysis used for viscosity reduction of heavy crude oils: a review”, *Energy & Fuels*, vol. 24, no. 5, pp. 2809–2816, 2010. https://doi.org/10.1021/ef100230k.

[32] J. Li, Y. Chen, H. Liu, P. Wang, and F. Liu, “Influences on the aquathermolysis of heavy oil catalyzed by two different catalytic ions: Cu2+ and Fe3+”, *Energy & fuels*, vol. 27, no. 5, pp. 2555–2562, 2013. https://doi.org/10.1021/ef400328s.

[33] H. Jia, P.-G. Liu, W.-F. Pu, X.-P. Ma, J. Zhang, and L. Gan, “In situ catalytic upgrading of heavy crude oil through low-temperature oxidation”, *Petroleum Science*, vol. 13, no. 3, pp. 476–488, 2016. https://doi.org/10.1007/s12182-016-0113-6.

[34] J. Wang, T. Wang, X. Hou, and F. Xiao, “Modelling of rheological and chemical properties of asphalt binder considering SARA fraction”, *Fuel*, vol. 238, pp. 320–330, 2019. https://doi.org/10.1016/j.fuel.2018.10.126.

[35] Y. L. Chen, P. Li, Y. Q. Wang, and J. He, “Change of carbazole compounds in heavy oil by catalytic aquathermolysis and the catalytic mechanism of viscosity reduction”, *Journal of Fuel Chemistry and Technology*, vol. 39, no. 4, pp. 271–277, 2011.

[36] A. V. Vakhin, S. A. Sitnov, I. I. Mukhamatdinov, F. A. Aliev, S. I. Kudryashov, I. S. Afanasiev, O. V. Petrashov, M. A. Varfolomeev, and D. K. Nurgaliev, “Aquathermolysis of heavy oil in reservoir conditions with the use of oil-soluble catalysts: part III–changes in composition resins and asphaltenes”, *Petroleum Science and Technology*, vol. 36, no. 22, pp. 1857–1863, 2018. https://doi.org/10.1080/10916466.2018.1514413.

[37] W. L. Qin and Z. L. Xiao, “The researches on upgrading of heavy crude oil by catalytic aquathermolysis treatment using a new oil-soluble catalyst”, in *Advanced Materials Research*, Trans Tech Publ, 2013, pp. 1428–1432. https://doi.org/10.4028/www.scientific.net/AMR.608-609.1428.

[38] J. B. Hyne, P. D. Clark, R. A. Clarke, J. Koo, and J. W. Greidanus, “Aquathermolysis of heavy oils”, *Rev. Tec. INTEVEP;(Venezuela)*, vol. 2, no. 2, 1982.

[39] Y. Wang, Y. Chen, J. He, P. Li, and C. Yang, “Mechanism of catalytic aquathermolysis: Influences on heavy oil by two types of efficient catalytic ions: Fe3+ and Mo6+”, *Energy & fuels*, vol. 24, no. 3, pp. 1502–1510, 2010. https://doi.org/10.1021/ef901339k.

[40] A. A. Saraev *et al.*, “XAS study of Mo-based dispersed catalysts for upgrading of heavy oil”, *Radiation Physics and Chemistry*, vol. 175, 2020, https://doi.org/10.1016/j.radphyschem.2019.05.025.