

Uncovering the Hydrocracking Efficiency of Iron-Based Catalysts: A Novel Approach to Asphaltene Transformation in Iranian Heavy Oil

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Article History Received: 25 Oct 2023 Accepted: 13 Nov 2023 Published: 25 Jun 2024 Research Article **Abstract** – In the quest for optimal asphaltene conversion, this study investigated a range of cost-effective and easily accessible catalyst precursors, targeting both high yields of lighter products and minimal coke formation. The hydrocracking experiments were conducted within a 10 ml bomb-type reactor equipped with a reciprocating stirrer operating at a reciprocation rate of 200 times per minute. The experiments were performed at a temperature of 425°C for a duration of 90 minutes, with an initial hydrogen pressure of 100 bar. The outcomes of each experiment were assessed in terms of liquid products, coke production and C5- gas products. To analyze the Iranian heavy asphaltene, Nuclear Magnetic Resonance (¹H NMR), Gel Permeation Chromatography (GPC) and elemental analysis were employed. Gas products were characterized using Gas Chromatography (GC). The investigation aimed to identify the catalyst precursor mixture that would maximize asphaltene conversion while minimizing coke production. A series of catalyst precursors, encompassing FeSO₄·H₂O, its binary mixtures with metal oxides (Fe₂O₃, Al₂O₃, CaO, SiO₂), and combinations of Fe₂O₃, Al₂O₃, and SiO₂ with elemental sulfur, were evaluated. The experimental results demonstrated that the toluene-soluble fraction (TSF), which includes the middle distillate portion, could be increased to a maximum of 56% while concurrently reducing the coke yield to 19%, down from the initial 36.9% when no precursor was used.

Keywords - Asphaltene, hydrocracking, iron-based catalyst, optimization

1. Introduction

The global energy landscape has long been shaped by the vast reservoirs of heavy oil blends, prominently featuring the Iranian Heavy Oil. Processed extensively in regions such as China, India, Japan, and the Mediterranean countries, this blend is characterized by its significant asphaltene content, a challenging component to refine due to its complex molecular structure and propensity to lead to coke formation [1].

In recent times, the shift towards heavier crude sources has been noted, with these sources containing a high concentration of contaminants like sulfur, nitrogen, metals, and asphaltenes, which significantly affect the quality of the residual oil post distillation [2]. Asphaltenes, in particular, pose a significant challenge in heavy oil refining due to their interference with hydroprocessing which is pivotal in achieving higher liquid oil yields [3].

One of the major challenges in refining heavy oils, particularly those high in asphaltenes, is their inherently low yield of valuable distillates. Asphaltenes are known for their high Conradson carbon residue value and the presence of heteroatoms that poison catalysts, making their effective conversion into low-boiling products

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imperative yet challenging [4]. Historically, several methodologies have been tested to improve the cracking of asphaltenes, with catalytic hydrocracking standing out due to its efficiency. The increasing emphasis on refining heavy crude oil demands the development of novel upgrading techniques to produce high-value products. Both hydroconversion and thermal cracking have been recognized as pivotal processes for the distillation of heavy oil fractions and residues, specifically focusing on comprehending the molecular transformations of asphaltenic compounds subsequent to upgrading [5].

Recent studies have shown the promising results of various catalysts, such as NiMo/c-Al2O3, in enhancing the reactivity of asphaltenes [6]. Further adding to this body of work, [7] have demonstrated the efficacy of transition metal-based catalysts in the catalytic upgrading of heavy oil, suggesting that such catalysts could be particularly beneficial for the Iranian Heavy Oil context. The pivotal role of catalysts in heavy oil hydroprocessing is highlighted by the temperature-driven cracking reactions and the acidity of the catalyst support, both of which act as the primary drivers for the refining process [3]. However, the high cost of catalysts can be a limitation, as seen in methods like the catalytic oxidation reaction of asphaltene, where the cracking reaction rate was found to increase at temperatures above 180°C, albeit with a concurrent rise in coke generation rate [8].

Advancements in catalyst technology have led to the emergence of soluble dispersed catalysts. These catalysts display superior catalytic activity compared to finely powdered counterparts, primarily because of the in situ generation of exceedingly small active metal sites that boast high surface-area-to-volume ratios [9]. Recent technologies have reviewed the utilization of dispersed catalysts in heavy oil upgrading, shedding light on the advancements in catalyst systems that could potentially improve the hydrocracking process of heavy oils and asphaltenes. Furthermore, slurry-phase hydrocracking has gained attention, with the development of catalysts for this process undergoing two phases: homogeneous dispersed catalysts and heterogeneous solid powder catalysts. Homogeneous dispersed catalysts are subdivided into water-soluble dispersed catalysts and oil-soluble dispersed catalysts, each offering unique advantages for heavy oil hydrocracking [10].

Given the escalating demand for petroleum-derived products, the upgrading of heavier quality crude oil and petroleum residues is inevitable. [11] provide insights into the effectiveness of different ligand-based catalysts, which could be key to improving the upgrading process while maintaining cost-effectiveness. Hydroprocessing, a preferred process for heavy oil upgrading, is orchestrated with the presence of a catalyst, underscoring the vital role catalysts play in this process [12]. However, there remains significant scope for identifying and exploring alternative catalyst systems that are not only effective but also economically viable. In light of the growing scarcity of other energy sources, unconventional feedstocks like heavy vacuum residue (VR) have been explored for the production of high-value transportation fuels, and advancements in catalytic hydrocracking have been pivotal in enhancing the quality of these feedstocks [9,13].

In this context, iron-based catalysts present a compelling option. Drawing on the insights from [7] and [14], the present study explores the feasibility of using similar oil-soluble catalysts for Iranian Heavy Oil, aiming to improve the refining efficiency and quality of the end products. Iron, being abundant and relatively inexpensive, offers a sustainable alternative to more scarce and costly metals. Moreover, iron catalysts, especially in conjunction with other metal oxides, might provide unique catalytic properties that can boost asphaltene conversion rates and reduce coke formation.

A study showcased the use of ferrocene-based catalysts, including Magnetite (Fe_3O_4) and Iron Sulfide (FeS), which acted as active forms of catalysts to accelerate the hydrothermal conversion of heavy crude oil and its heavy fractions including resins and asphaltenes. These transformations were authenticated using X-ray

Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX), and Mössbauer analyzing techniques [15,16]. In parallel, research by [16] delved into the potential of catalysts crafted from activated carbon amalgamated with iron. Their methodology either involved iron impregnation onto the carbon, subsequently transforming it into iron sulfide in situ, or combining it with pyrite. When subjected to semi-batch autoclave hydrocracking tests under modest hydrogen pressures (7–10 MPa), these catalysts showcased a commendable capability in curbing coke formation during vacuum residue hydrocracking. In a different study, another inquiry focused on the nuances of asphaltene conversion, specifically with 10 wt.% Fe catalysts, characterized by average pore diameters oscillating between 4.5–15 nm. Findings indicated that conversion escalated with pore diameter expansion up to 12 nm, approximating a 70% conversion rate. Beyond this threshold, the rate plateaued. Moreover, maltene yield seemed to be intrinsically tied to pore diameter, with an apex yield of 40% being observed in the 12–15 nm range [17]. Amplifying the scope of enhancing thermal recovery efficiencies, [18] embarked on a study aimed at the catalytic hydrothermal treatment of heavy oil. Their objective was to pare down the presence of dense constituents such as resins and asphaltenes. This research leaned on the use of an iron tallate catalyst during a hydrothermal simulation executed on a bituminous sandstone sample sourced from the Ashal'cha reservoir.

Despite the various strides made in employing iron-based catalysts for asphaltene hydrocracking, the literature still presents a gap in understanding the nuanced behavior and performance metrics of these catalysts, particularly in the context of Iranian Heavy Oil. The majority of the studies focus on generic heavy oils or different types of crude, which may have distinct compositional and reactive properties compared to Iranian Heavy Oil. The specific exploration of FeSO₄.H₂O and its binary mixtures with metal oxides (Fe₂O₃, Al₂O₃, CaO, SiO₂) alongside combinations with elementary sulfur in the hydrocracking reactions has been scant. This creates an avenue for a detailed investigation to fathom the synergies between these materials and the asphaltene content in Iranian Heavy Oil. Furthermore, the precise impact of these catalyst systems on the yield of valuable distillates and the mitigation of coke formation remains to be thoroughly elucidated. The extant literature also lacks a systematic comparison of the performance metrics of these iron-based catalyst systems relative to other metallic and non-metallic catalysts under similar operational conditions. This underscores the imperativeness of the present study, which aims to bridge these knowledge gaps through a meticulous exploration of the performance of specified iron-based catalysts in the hydrocracking of asphaltenes derived from Iranian Heavy Oil. Through this endeavor, the study aspires to unveil new insights that could potentially revolutionize the refining practices for heavy oils rich in asphaltenes, thereby contributing to the broader endeavor of enhancing the efficiency and sustainability of heavy oil processing. Furthermore, [14] highlight the importance of continued research into in-situ upgrading and catalysis, which is especially pertinent for the types of heavy oils addressed in this study.

The present study delves deep into the performance of iron-based catalysts, specifically $FeSO_4$. H_2O , its binary mixtures with metal oxides (Al₂O₃, Fe₂O₃, SiO₂,CaO) and combinations with elementary sulfur, in the hydrocracking reactions of asphaltenes derived from Iranian Heavy Oil. Through a systematic exploration, the study aims to identify the potential of these catalysts in transforming the refining landscape of heavy oils rich in asphaltenes.

2. Materials and Methods

2.1. Resid Analysis

The feedstock employed for the slurry phase hydrocracking reactions in this study was sourced from TUPRAS and consisted of Iranian heavy vacuum residue (VR). This vacuum residue was derived during the processing of 100% Iranian Heavy crude oil, specifically originating from ASRFO and HVGO according to ASTM D1160, with a 95% cut point temperature at 550 °C. The VR exhibited a specific gravity of 1045.0 Kg/m³ at 15 °C, corresponding to an API gravity of 3.9 as per EN-ISO-3675 standards.

2.2. Asphaltenes Isolation

The feedstock utilized in this investigation was Iranian Heavy Vacuum Residue (IHVR) acquired from TUPRAS. Notably, IHVR exhibited a pour point above room temperature, necessitating pre-treatment in an oven at 120 °C for 30 minutes to enhance its flowability. Following this, the residue was subjected to a precipitation process by combining it with n-heptane at a weight ratio of 1/40, after preheating. The emerging mixture was stirred at 60°C and subsequently cooled with consistent stirring for six hours. Post-stirring, the solution was kept overnight, leading up to a filtration step. The filtrate was then processed to extract maltenes by evaporating the n-heptane. For the isolation of asphaltene, the technique of Soxhlet extraction was employed.

In total, ten separate experiments were conducted to obtain asphaltene from Iranian heavy vacuum residue, yielding asphaltene content variations ranging from 13% to 13.5%. The comprehensive analysis of these experiments revealed that the average asphaltene content for Iranian heavy oil residue stands at approximately 13.28%.

2.3. Materials

For the catalyst experiments, high-purity chemicals were utilized. These comprised 99.5% FeSO4:7H₂O and 99% Al₂O₃ from Merck. Additionally, >99% Fe₂O₃, 98% CaO, and 99% SiO₂ were procured from Sigma-Aldrich. Elemental sulfur with a purity of 99.8% was sourced from TUPRAS for the studies. In assessing the coke yield, reagents of elevated purity, like 99% n-heptane and >99.5% carbon disulfide from Merck, and >99.7% toluene from Sigma-Aldrich, were employed. For molecular weight assessments, 99% tetrahydrofuran, obtained from Merck, was used. Soxhlet extraction was conducted using cellulose cartridges measuring 28x80 mm provided by Macherey Nagel.

2.4. Structural Analysis

Elemental characterization was performed using the Thermo Finnigan Flash EA 1112 Series Elemental Analyzer. In this procedure, helium served as the carrier gas, while a 2 mg sample was combusted in the presence of oxygen at 1000 °C. The outcomes from this analysis are detailed in Table 1.

Table 1. Iranian asphaltene analysis									
Elemental Analysis	C (%) H	I (%) S (%	%) N ((%) O(%)					
	75.52	7.39 4,8	6 1.	18 1,05					
GPC Analysis	Mn (g/mol)		Mw (g/mol)						
	1422		3826						
SARA Analysis	Saturates (%)	Aromatic (%)	Resin (%)	Asphaltene (%)					
	25	45	17	13					

For molecular weight assessments, the Agilent 1200 series Gel Permeation Chromatography (GPC) instrument was employed. A Zorbax column measuring 300 x 7.5 mm, packed with mixed gel, was employed, and refractive index detection was utilized. Tetrahydrofuran served as both the solvent and carrier phase, and the analysis involved injecting 20 μ l of the sample at a volumetric rate of 1 ml/min, as detailed in Table 1.

For the ¹H-NMR analysis, a Varian UNITY INOVA 500MHz NMR spectrometer was utilized. A 0.5 ml solution of chloroform (CDCl3) was employed as the solvent for dissolving 5 mg of the IRHV sample, as shown in Figure 1.



Figure 1. ¹H-NMR analysis of Iranian asphaltene

2.5. Methods

2.5.1. Pre-treatment

 $FeSO_4 \cdot 7H_2O$ underwent a drying procedure for an hour at 120 °C in an oven. Following this, the metal oxides and $FeSO_4 \cdot 7H_2O$ were combined in a 1:1 weight ratio and transferred to a Retsch PM 400 ball mill for blending. After approximately 20 minutes of milling, the mixtures were subjected to sieving via a Retsch AS 450 analytical sieve shaker. Catalyst precursor materials that were within the 50-325 mesh size range, corresponding to 45 microns to 300 microns, were preserved in sealed desiccators for subsequent use in hydrocracking reactions. Additionally, elemental sulfur was milled using the Retsch PM 400 ball mill.

2.5.2. Reactors

The hydrocracking reactions were conducted within 10 ml batch tubing bomb reactors, each consisting of two distinct sections. The upper section was equipped with a D-Pro high-pressure needle valve, linked to 1/4 inch stainless steel Swagelok tube fittings. For effective mixing of the reaction contents, a metal ball with a diameter of 9.5 mm was placed inside the reactor, achieving a stirring speed of 200 rpm.

2.5.3. Reactions Procedure

The reactors were conventionally loaded with 0.5 g of Iranian heavy oil asphaltene along with 0.025 grams of catalyst precursors. Before commencing the reaction, the reactor was subjected to a purging procedure,

consisting of five cycles alternating between nitrogen and hydrogen. Following this, the reactor was pressurized with hydrogen to reach 100 bars and the shut-off valve was secured. Subsequently, the complete reactor setup was submerged in a Yigitsan fluidized sand bath pre-set at 425°C.

Once the reaction had proceeded for 90 minutes, the reactor was promptly removed from the sand bath and rapidly cooled by immersing it in cold water for about 10 minutes. After this rapid cooling, the reactor setup was left to stabilize at ambient temperature for around 30 minutes.

Precise measurements of the reactor's weight were undertaken, and gas yield was ascertained upon opening the high-pressure needle valve, followed by re-weighing. The gas products underwent analysis using Gas Chromatography. A Soxhlet extraction was performed employing 28x80 mm cellulose cartridges, utilizing toluene as the extracting solvent. The residual solid, comprising both coke and the catalyst, was weighed. The toluene-soluble fraction was computed by deducing the weights of the gas and solid residues from the starting weight of the reaction mixture.

3. Results and Discussion

3.1. Structural Analysis Results

The spectral analysis reveals distinctive regions associated with various structural elements. The area encompassing chemical shifts up to 1 ppm is indicative of approximately 11.57% methyl groups. Within the range of 1 to 1.7 ppm, the spectrum reflects a substantial presence of methylene branching, accounting for approximately 34.1% of the structural composition. Furthermore, the region spanning from 2.1 to 2.4 ppm suggests the prevalence of α -methyl branching, constituting approximately 40.56% of the structural features. Signals within the chemical shift range of 2.4 to 3.5 ppm correspond to the presence of CH and CH₂ methylene groups proximate to aromatic ring structures. In the higher chemical shift region, specifically between 7 and 8 ppm, signals correspond to the existence of two and three-ringed structural motifs.

3.2. Catalyst Performance Results

The mixing ratios of the precursors used in the study are shown in Table 2. Table 3 provides a comprehensive overview of the masses of reactants and the percentages of products. This encompasses the initial mass of the mixture containing resid and catalyst precursors, the amount of H₂ consumed, and the weight percentages of the resultant coke, gas, and the toluene-soluble fraction (TSF) products. It is noteworthy that the utilization of the $FeSO_4 \cdot H_2O + SiO_2$ mixture as a catalyst precursor yields the lowest coke yield, with a noteworthy achievement of a 10% coke yield.

Table 2. Mixing ratios of the precursors									
Reaction No	Precursor Used	Asphaltene (g)	Asphaltene / Precursor	Precursor (g)					
1	Without precursor	0.5	-	-					
2	FeSO ₄ .H ₂ O	0.5	20	FeSO ₄ .H ₂ O:0.025					
3	FeSO ₄ .H ₂ O+Fe ₂ O ₃	0.5	20	FeSO ₄ .H ₂ O:0.0125; Fe ₂ O ₃ :0.0125					
4	FeSO ₄ .H ₂ O+Al ₂ O ₃	0.5	20	FeSO ₄ .H ₂ O:0.0125; Al ₂ O ₃ :0.0125					
5	FeSO ₄ .H ₂ O+CaO	0.5	20	FeSO ₄ .H ₂ O:0.0125; CaO:0.0125					
6	FeSO ₄ .H ₂ O+SiO ₂	0.5	20	FeSO ₄ .H ₂ O:0.0125; SiO ₂ :0.0125					
7	$Fe_2O_3+Al_2O_3+S$	1.0	10	Fe2O3:0.02; Al2O3:0.02; S:0.06					
8	$Fe_2O_3{+}Al_2O_3{+}SiO_2{+}S$	1.0	10	Fe ₂ O ₃ :0.025; Al ₂ O ₃ :0.025; SiO ₂ :0.025; S:0.025					
9	Maltene+Fe ₂ O ₃ +S	1.0	10	Maltene:1.00; Fe ₂ O ₃ :0.02; S:0.08					

Reaction No	Precursor Used	Asphaltene + Precursor Mass (g)	H ₂ mass (g)	Coke (%)	Gas (%)	TSF (%)				
1	Without precursor	0.500	0.140	36.9	11.0	52.1				
2	FeSO ₄ .H ₂ O	0.525	0.140	33.0	30.0	37.0				
3	FeSO ₄ .H ₂ O+Fe ₂ O ₃	0.525	0.120	25.1	26.0	48.9				
4	FeSO ₄ .H ₂ O+Al ₂ O ₃	0.525	0.130	36.5	44.3	19.2				
5	FeSO ₄ .H ₂ O+CaO	0.525	0.140	25.4	53.0	21.6				
6	FeSO ₄ .H ₂ O+SiO ₂	0.525	0.100	23.0	62.5	14.5				
7	$Fe_2O_3{+}Al_2O_3{+}S$	1.100	0.130	27.0	41.0	32.0				
8	$Fe_2O_3{+}Al_2O_3{+}SiO_2{+}S$	1.100	0.140	19.0	25.0	56.0				
9	Maltene+Fe ₂ O ₃ +S	2.100	0.140	37.3	54.1	8.6				

Table 3. Asphaltene slurry hydrocracking reactions products

The existing literature provides accounts of hydrocracking reactions involving heavy oil fractions that transpire under diverse sets of conditions. These conditions encompass a wide spectrum of temperature, pressure, and residence time, and the reactions are typically carried out using catalysts like NiMo/Al₂O₃, CoMo/Al₂O₃, and NiW/SiO₂-Al₂O₃ in tubular fixed-bed reactors or continuous stirred-tank reactors (CSTRs). The range of hydrocracking temperatures investigated spans from 340 to 500°C, while the associated pressures have been explored within the range of 70 to 125 bars. Moreover, the residence times have been observed to range from 10 minutes to 3 hours.



Figure 2. Slurry hydrocracking reactions products

In many commercial hydrocracking facilities, the primary feedstock is HVGO, and the heavier components of the crude oil often remain uncracked. In this research, asphaltene derived from Iranian heavy oil residue was subjected to experimentation within a laboratory-scale batch slurry reactor. The primary objective was to identify the most efficient, cost-effective, and easily prepared catalyst. Several precursor options were explored, including FeSO₄·H₂O, its binary mixtures with metal oxides (Fe₂O₃, Al₂O₃, CaO, SiO₂), and combinations of Fe₂O₃, Al₂O₃, and SiO₂ with elemental sulfur. The slurry hydrocracking reactions products are shown in Figure 2. The resulting product mixture was systematically separated into its gas, liquid, and solid components, and the yields of each product category were quantified individually. Remarkably, the lowest coke yield was achieved when using Fe₂O₃+Al₂O₃+SiO₂+S as a precursor.

In typical commercial hydrocracking processes, the focus is on producing middle distillate products such as kerosene and diesel from HVGO, and coke formation is rarely observed during these reactions. In the context of residue cracking, however, coke formation poses a significant challenge due to its potential to obstruct

reactor systems, even though it is the least valuable product. Asphaltene, as a primary constituent, is recognized as a key factor contributing to coke formation. Consequently, the primary aim of this study was to minimize coke formation, while the secondary goal was to maximize the yield of middle distillate fractions. The experimental results demonstrated that the toluene-soluble fraction (TSF), which includes the middle distillate portion, can be increased to a maximum of 56% while concurrently reducing the coke yield to 19%, down from the initial 36.9% when no precursor was used.

4. Conclusion

In exploring the hydrocracking of asphaltenes from Iranian heavy oil residue, this research illuminated the profound impact of precursors on both product yield and the reduction of by-products, specifically coke. Using a lab-scale batch slurry reactor, the experimentation shed light on the advantages of strategically choosing and combining precursors. Remarkably, the combination of Fe₂O₃, Al₂O₃, SiO₂, and elemental sulfur yielded the most optimal results, minimizing coke formation to a significant degree. Given the inherent challenges associated with coke, which can hinder reactor operations and offers limited economic returns, this outcome is particularly noteworthy. Furthermore, the study also highlighted the potential to elevate the yield of the toluene-soluble fraction (TSF), which includes the desired middle distillate fractions. The peak achievement was a boost in TSF to an impressive 56%, while simultaneously slashing the coke yield from its initial 36.9% (without precursor) to 19%. These findings, therefore, not only further the understanding of asphaltene hydrocracking dynamics but also suggest a potential pathway to optimizing commercial hydrocracking processes, emphasizing the judicious choice of catalysts and precursors.

Author Contributions

The first and second authors conducted statistical evaluations, gathered the data, and authored the manuscript. The third author formulated and planned the analysis. This paper is derived from the second author's master's thesis, supervised by the third author.

Conflicts of Interest

All the authors declare no conflict of interest.

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