Hydrodesulfurization and Hydrodearomatization of Kerosene over high metal loading Ni w/γ-Al_2O_3 Catalyst

ازالة الكبريت والمركبات العطرية بالهيدروجين من الكيروسين باستخدام عامل مساعد NiW/γ-Al_2O_3 ذو نسبة تحميل عالية

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Abstract

The present research investigates hydrodesulfurization (HDS) and hydrodearomatization (HAD) of raw kerosene with 0.364 wt. % sulfur and 16.498 wt. % aromatics supplied from Al-Dura Refinery. Hydrotreating reactions were carried out in one stage reactor over high metal Ni W/γ-Al_2O_3 prepared catalyst at different temperatures 275-350°C, pressures 32-62 bar, LHSV 1-4 hr^{-1}, and H_2/HC ratios 200-500. The prepared catalyst was pre-sulfided remarkably at low temperature and high pressure to avoid risky of sintering associated with gaining the active sulfide phase at high temperatures. Results showed an obvious differences between HDS and HAD rates due to difficulty of polyaromatics saturation compared with desulfurization. Sulfur and aromatics removal were achieved from 74.9% to 95.6% and from 1% to 12.8% respectively at different operating conditions. Advanced saturation conditions were promoted the hydrogenation reaction bath and played a significant role for achieving acceptable levels of HDS and HDA. In general, HDS and HDA increased with decreasing LHSV and increasing temperature, pressure, and H2/HC ratio. Burning quality, fire hazard, and aromatics content of kerosene were characterized by measuring of smoke point, flash point, and aniline point respectively. These properties were enhanced at different hydrotreating conditions due to the skeletal conformation change of kerosene hydrocarbons during reactions.

Keyword Hydrodesulfurization, Hydrodearomatization, Ni W/γ-Al_2O_3 catalyst, Kerosene, Burning Characterization.

Introduction

Kerosene is a mixture of liquid hydrocarbons usually obtained by distillation of petroleum and widely used as a jet fuel, cleaning solvent, and thinner. It consist from wide range of hydrocarbons and removing of undesired compounds represents a necessity to meet requirements for air pollution control. Hydrodesulfurization (HDS) is applied to reduce sulfur content and hydrodearomatization (HDA) to saturates the aromatics to produce fuel with outstanding burning qualities by using of highly active noble-metal catalysts permits the reactions to take place at mild conditions.[1, 2]

Deep desulfurization is required to remove of refractory sulfur aromatics compounds. However, these compounds are remaining in by conventional hydrodesulfurization process because of the inhibiting effects of co-existing polyaromatics and nitrogen compounds,[3] in the feed as well as H_2S in the product.[4]

Meet environmental objectives it also may be necessary to hydrogenate aromatic rings (aromatic saturation) followed by ring-opening to reduce aromatic content by converting aromatics to paraffins.[5, 6]

The presence of nitrogen and sulfur compounds which competitively approached the catalytic active sites tended to poison the catalyst and led to reduce the hydrogenation activity of the catalyst.[7] Nitrogen compounds and polyaromatic were adsorbed competitively with the sulfur species on the active catalytic sites at temperatures where the hydrodegnation step was proposed to be rate limiting.[8] Polyaromatics compete with sulfur compounds on the surface of hydrotreating catalyst, perhaps more for the flat chemisorption thereby influencing the hydrogenation and subsequent HDS.

Hydrodearomatization and hydrodesulphurization can be done in one stage that are suitable to treat feeds with relatively high sulfur content over transition metal-sulfide. Four NiMo catalyst,[9] supported on Al_2O_3 have been studied in the hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) of a Mexican straight run gasoil at three different temperatures 613, 633, and 653 K in one stage. The results of catalytic activity of these materials varied depending on dispersed MoS particles and pore distribution in final catalysts.

Pt-Pd/USY catalyst was used in the two stage process to achieve deep aromatics reduction using noble metal catalysts after HDS of the feed, [10-12] since the hydrogenation activity of these catalysts is decreased by the sulfur compounds and therefore this type of catalysts can only be applied in a second reactor where aromatics is reduced.

The purpose of this research is preparation active NiW/Al_2O_3 hydroteating catalyst with high metals oxides and gain the sulfide active phase at low pre-sulfiding temperature to avoid catalyst sintering associated at high temperatures. Our target is to carry out multi-reactions in one stage hydrotreating using unique bi-functional catalyst type with a very specific physical and chemical properties for proceeding HDA of difficult polynuclear aromatics to saturates and HDS of sulfur molecules at different operating conditions. Furthermore, improving burning characteristics of kerosene which are relevant to extents of hydrotreating reactions and measure the ability to burn steadily and cleanly.

Experimental Work

Materials

Kerosene fraction was supplied from Al-Dura Refinery with physical properties tabulated in Table (1). Formulated spherical shape gamma alumina (γ-Al_2O_3) was supplied from local resources with 201.12 m^2/g surface area, 0.24 cm^3/g pore volume, and 1.043 g/cm^3 bulk density. Nickel nitrate ($N_2NiO_6.6H_2O$) was supplied from Himedia lab. India with molecular weight 290.81 and purity of 97 % and ammonium Meta tungestate hydrate ($H_{26}N_6O_{40}W_{12}.XH_2O$) was supplied from Sigma –Aldrich Germany, 85 % WO_3 basis (gravimetric).

Table (1) Physical Properties of Kerosene Fraction

Property	Value
Density, g/cm^3	0.7973
Sulfur content, wt%	0.3641
Aromatic content, wt%	16.4986
Smoke Point, mm	27
Aniline Point, °C	64.4
Flash Point, °C	40

Preparation of NiW/γ-Al_2O_3 Catalyst

60 g γ-Al_2O_3 was dried in oven at 110oC for 2 h and then located in 250 ml flask for degassing under vacuum pressure for 10 min. Ni/γ-Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 in an aqueous solution of nickel nitrate prepared by dissolving 22.7 g nickel nitrate in 38 g distilled water; aqueous solution was added dropwise from separating funnel under vacuum and continuous shaking for 2-3 h at room temperature and left for 24 h under stilling. Catalyst was dried overnight and calcined for 4 h at 115oC and 450oC respectively. NiW/γ-Al_2O_3 was then prepared by degassing Ni/γ-Al_2O_3 catalyst under vacuum and impregnated with an aqueous solution of ammonium tungstate prepared by dissolving 17.07 g ammonium Meta tungstate hydrate in 45.02 gm distilled water; aqueous solution was added dropwise to the Ni/γ-Al_2O_3 catalyst particles under vacuum and shaking for 2-3 h at room temperature and left 24 h under stilling. Catalyst was dried overnight and calcined for 4 h at 115°C and 450°C respectively.

Catalyst Characterization

The physical and chemical properties of the prepared bi-metallic catalyst NiW/γ-Al_2O_3 are tabulated in Table (2).

Surface area

Surface area measurements for catalyst was carried out by BET method using [surface area analyzer, model Thermo Qsurf 9600, USA]. The data obtained from BET plot were used to calculate the specific surface area SA and monolayer capacity Vm as in Equations (1&2) [13].

$$SA = \frac{V_m \times a_{N2} \times N_A}{V_o \times W} \quad (1)$$

The monolayer capacity Vm is determined from Equation (2)

$$\frac{P_a}{V(P_o - P_a)} = \frac{1}{V_m * C_B} + \frac{C_B - 1}{V_m * C_B} \times \frac{P_a}{P_o} \quad (2)$$

Bulk density

Bulk density is determined by randomly placing 30 cm^3 of catalyst or supported particles in cylinder of 2 cm inside diameter. The difference in weight between the cylinder both filled with the catalyst and empty represents the weight of the catalyst. The bulk density is the ratio between the catalyst weights to the volume of the sample according to Equation (3) [14]

$$\rho_b = \frac{W_5 - W_4}{V1} \quad (3)$$

The bulk density is measured according to ASTM D- 4164 method using Autotap [by Quantachrom ,USA] located at Petroleum R&D Center

Real density

The real density is measured using Gas pycnometer under Helium Gas Pycnometry & vacuumed pressure of located at Petroleum R&D Center, model PMI, USA.

Crushing strength

The crush strength represents the resistance of the solid to compression, a property of paramount importance not only for industrial catalysts, but materials. In the case of catalysts it is noteworthy that many plant shutdowns occur due to mechanical failure of the catalyst, not to its loss of activity. Therefore an accurate measurement of catalyst mechanical properties is mandatory. Grain crushing strength is measured using CRUSH-BK located at Petroleum R&D Center according D4179 ASTM and this device produced from materials Technologies Company.

Flash point

This test was done at Duara refinery, model; ISL instrument, France, according to Abel IP 170 method.

Aniline point

This test was done at Duara refinery with kohler instrument, according to ASTM D-611.

Smoke point

This test was done at Duara refinery according to ASTM D 1322S with kohler instrument.

Aromatic content

Aromatic test was done in Dura refinery by using Agilent Technologies Instrument (7890 A, GC system, Wasson –ECE instrumentations, USA). The kerosene is introduced into a gas chromatograph equipped with an open tubular (capillary) column coated with the methyl silicone liquid phase modified with the capillary pre-column.

Sulfur content

sulfur content for kerosene was done in Dura refinery Labs according to ASTM D1266 (Lamp Sulfur) with Principle of Combustion in lamp and analysis, Model kohler instruments.

Chemical Composition

Metal deposited is determined using Atomic absorption at Ibn Sinaa Company. The physical and chemical properties of the prepared catalyst are tabulated in Table (2).

Table (2) Physical and Chemical Properties of Prepared NiW /γ-Al_2O_3 catalyst

Property	Value
Surface area, m^2 / gm	184.225
Pore volume, cm^3 / gm	0.215
Bulk density, gm / cm^3	1.043
Real density, gm / cm^3	3.6
Crushing strength, N	146.83
NiO ,wt %	5.33
WO_3 , wt %	22.42

Hydrotreating Unit

Continuous hydrotreating pilot plant unit (cata-test unit) as shown in figure (1). Model IFP design, Vinci Technologies Company, which is located at PRDC, was used for evaluation the activity of the prepared catalyst. The unit consists mainly of vertical tubular stainless steel reactor (17.5 mm I.D., 25.5 mm O.D. and 300 mm length) electrically heated in a two block oven, temperature controller, dosing pump, gas meter and high pressure separator. Hydrogen gas was supplied to the unit from a hydrogen cylinder.

(51g) of catalyst (catalyst layer length 23 cm) was charged in the mid-section of the reactor, upper and lower sections were packed with ceramic balls (ceramic layer length 3.5 cm). The unit was purged with nitrogen to ensure oxygen removal from the system; pressure increased gradually to (65bar) and kept for 3h to check leaks and reduced to (10bar). Hence, nitrogen was replaced by hydrogen 99.99% purity. Catalyst was pre-sulfided prior hydrotreating of kerosene to transform catalyst to sulfide form (active phase). Pre-sulfiding was performed at 310˚C, 30 bar, and 1ml/min using untreated light gas oil with 10000 ppm sulfur content for 12h. Hydrotreating of kerosene was carried out at different operating conditions (32-52) bar hydrogen pressure, (1 – 4) hr^{-1} LHSV, (275-350)˚C reaction temperature, and (200-500) l/l hydrogen to hydrocarbon ratio (H_2/HC). The liquid product was collected after stabilization period to attain a steady state.

Fig. (1) Front and back side of the hydro treating unit

Results and discussion

The major operating conditions which effect on the hydrodesulfurization, hydrodearomatization, and on upgrading physical properties of kerosene were studied at wide range, temperature (275-350)°C, pressure (32-62), liquid hourly space velocity (1-4) hr^{-1}, and H2/HC ratio (200-400) NL gas / L feed.

Effect of temperature

NiW /γ-Al_2O_3 prepared catalyst showed high desulfurization and low hydrodearomatization activity with temperature increase at constant pressure 32 bar, LHSV 1 hr^{-1}, and H_2/HC ratio 200 NL gas / L feed as shown in Figure (1). The desulfurization and dearomatizatiom were increased from 74.9% to 86.5% and from 4.2% to 6.1% respectively when temperature increased from 275°C to 350 °C. The results are relevant to the chemical composition of kerosene; sulfur, nitrogen, oxygen and polyaromatic molecules were competitively adsorbed on the catalyst active sites which restrict the activity toward the desired reaction. Low concentrations of nitrogen compounds are enough to hinder deep HDS and inhibit HDS reaction. [15, 16]

Supported tungsten catalyst can't be sulfide completely at commercial conditions and considerable amount of tungsten oxide is still [17]. The sulfidation degree of the W atoms dependent on the preparation procedure and the sulfidation conditions strongly influences the catalytic performance of NiW catalysts.[18, 19]

It was observed that enhanced support interaction through increased calcination temperatures leads to more difficult sulfidation of tungsten. Sulfidation at high pressure leads to increases the crystallinity of the catalysts as well-defined WS_2 structure at temperatures as high as 400°C in spite of increasing sulfidation with increase temperature to prevent crystals sintering. From above it can be concluded the reasons behind results; low catalyst calcination temperature 450°C and sulfiding conditions (high pressure 32 bar and low temperature 350°C) leads to high crystalline active phase catalyst WS_2 (Intercalated model). Hence, the active sites of hydrogenolysis is synthesized during sulfidation of catalyst independently from support while hydrogenation sites depends almost on the interaction between the oxide phase which sharply reduced and the support.[20] High sulfidation of tungsten explain the low hydrogenation and the high desulfurization rates which favors the direct desulfurization route. Anyway, thermodynamic equilibrium reached at higher reaction rates at higher temperature which leads to increase HDS and HAD with temperature increase.

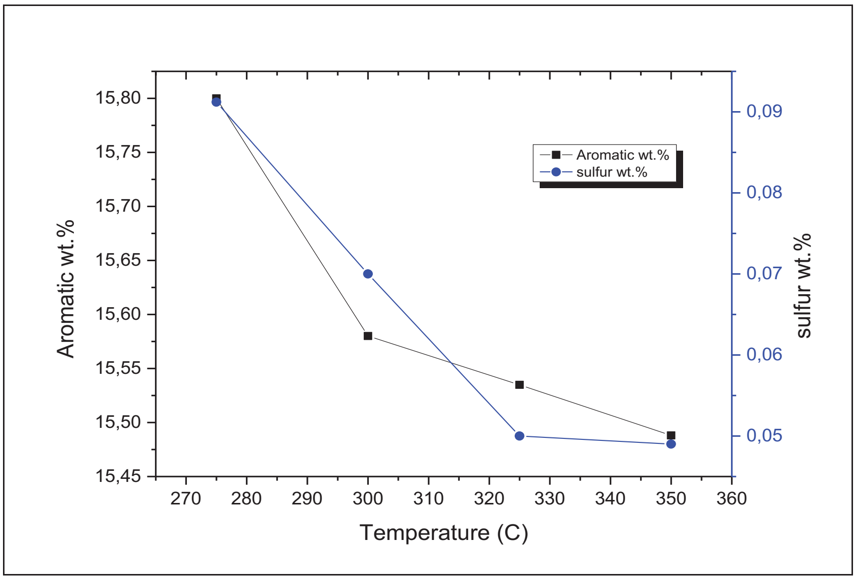

Fig. (2) Effect of Different Operating Temperatures on Aromatic and Sulfur Content of Treated Kerosene

Effect of Pressure

The effect of extended pressure range (32-62) bar was investigated on HDS and HDA at constant temperature 325^{o}C, LHSV 1hr^{-1}, and H_2/HC ratio 200 NL gas / L feed as shown in Figure (2). The desulfurization and dearomatizatiom were increased from 86.3% to 91.5% and from 5.8% to 8.3% respectively when pressure increased from (32 to 62) bar. In general, results show that pressure increase has a little effect on enhancement HDS and HAD, after (52) bar pressure there was no significant reduction in total sulfur and aromatics contents and reached to the stable pressure activity region. The effect of hydrogen pressure on HDS is relevant to feed boiling range and there exists a critical hydrogen pressure for above which is beneficial and below, HDS drops off rapidly. Moreover, at low partial pressures, hydrogen sulfide plays a useful role in retaining the sulfided phase of the hydrotreating catalysts. Hydrogen sulfide may in some cases enhance hydrogenation. This has been observed with HDS of dibenzothiophene on MoS_2 and $CoMo/Al_2O_3$ catalysts, [21, 22] and in the HDS of 4,6-dimethyldibenzothiophene over NiMo/C.[23, 24] Meanwhile, there is a necessity to suppress at high concentration due to its inhibiting complexion. Basically, high pressures attended to saturate the catalyst and slightly increase HDS and HDA activity.[25] Moreover, sulfur and aromatic molecules showed variation in reactivity with pressure change during hydrotreating process. The aromatics competed sulfur molecules with pressure increase, increase reaction rate between hydrogen and aromatics and nitrogen compounds in the feed leads to decrease sulfur conversion.[26] Hydrogen pressure has small effect on HDS and high pressures could change the sulfide phase and loss the active sites responsible for sulfur removal, high pressures favors hydrogenation rather than direct desulfurization.[27]

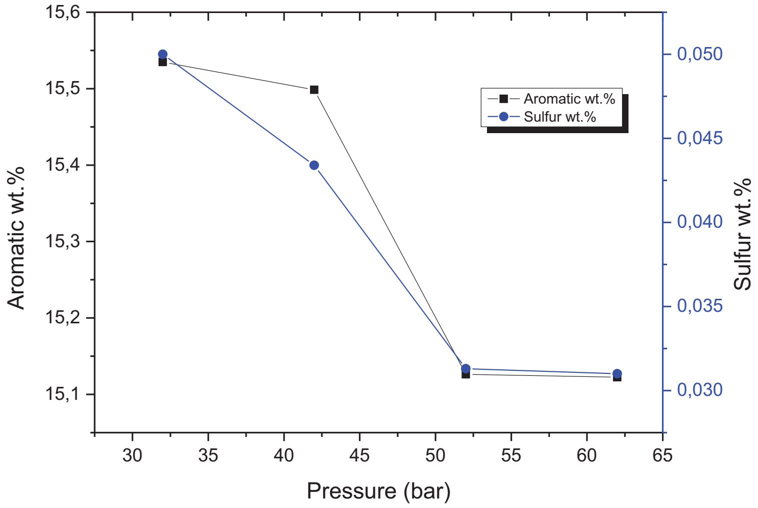

Fig. (3) Effect of Different Operating Pressures on Aromatic and Sulfur Content of Treated Kerosene

Effect of Space Velocity

The liquid hourly space velocity (LHSV) is considered an important parameter to specify effect of feedstock volumetric flow rate per unit volume of catalyst on reaction rates. In general, LHSV decrease results in developing of hydro treating reactions.

However, extremely low LHSV faces serious challenges in unit operation, [28] which depends on boiling point of feed stocks. Extreme decrease in LHSV leads to increase channeling which results into inferior contact between reactants and catalyst. Furthermore, operation at a very high LHSV leads to develop pressure drop through reactor bed and reduce contact time between reactants and catalyst. As long as capacity of production is relevant to LHSV, high space velocity is favored for economical demands in the commercial hydrotreating operation from 1 to 2.5 h^{-1} [29].

Figure (3) shows the effect of LHSV on HDS and HDA of kerosene at constant temperature 325°C, pressure 32 bar, and H_2/HC ratio 200 NL gas / L feed. The desulfurization and dearomatizatiom were decreased from 86.3% to 78% and from 5.8% to 1.0% respectively when space velocity increased from 1 to 4 h^{-1}.

Obviously decreasing LHSV improve HDS and HDA due to the sufficient residence time offered for reactant molecules to contact with catalyst active sites responsible for hydrotreating reactions whether the direct desulfurization or hydrogenation bath. Both reactions, desulfurization and dearomatization were highly influenced by LHSV and a sharp decline in reactivates was observed with increasing of space velocity.

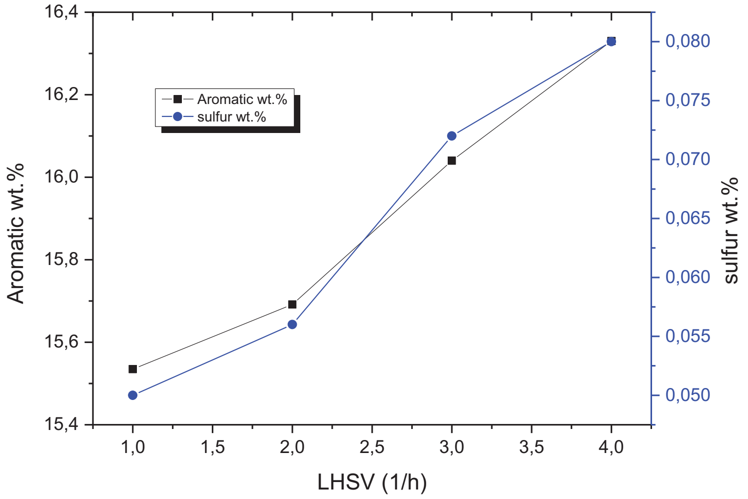

Fig. (4) Effect of Different Operating LHSV on Aromatic and Sulfur Content of Treated

Effect of Hydrogen to Hydrocarbon Ratio

The hydrogen flow rate in the hydroteating unit is administered by economical aspects. Increasing the recycle-gas rate increases H_2/oil ratio and maintain higher H_2 partial pressure assists reduce the start of run temperature of the reactor, which increases the catalyst life time.[30] However, there is a limit for H_2/HC ratio at which there is no significant increase in hydrogen partial pressure. Beside need to a certain H_2 rate, particular amount of H_2S in the gas stream is essential to maintain the sulfide phase of catalyst during hydrotreating process. High concentration of H_2S in the recycle gas stream leads to reduce H_2 purity and partial pressure.

Therefore, gas recycle is considered essential to maintain the H_2 partial pressure and offer adequate amount of hydrogen to reach high conversions during hydrotreating process. Figures (4) shows the effect of H_2/HC ratio on aromatic and sulfur content of kerosene studied at H_2/HC ratio range 200-500 NL gas / L feed with constant temperature 325°C, pressure 32 bar, and LHSV 1h^{-1}. The results show that sulfur and aromatic content decreased with increase H_2/HC ratio.

The desulfurization and dearomatization of kerosene increased from 86.3% to 95.6% and from 5.8% to 12.8% respectively when H_2/HC ratio increased from 200 to 500 NL gas / L feed. It is obviously that dearomatization and desulfurization were highly affected by H_2/HC ratio compared responding with the other variables, excess of hydrogen gives high opportunity for desulfurization of complex molecules and conversion of polyaromatics to monoaromatics and conversion the later to saturates. Maximum reduction was achieves at 500 NL gas / L feed.

Saturation of aromatics is an exothermic reversible reaction; high H_2 partial pressure achieved at high H_2/HC ratio shifts the reaction forward and surpass risk of backward reaction caused by temperature increase. It is desirable for HDA reactions to take place under kinetic control rather than thermodynamic. [31] Increasing of H_2 partial pressure leads to decrease H_2S partial pressure, thus reducing inhibition effect during hydrotreating. From foregoing, high removal limits of aromatics could be achieved besides acute decreasing in sulfur content with high H_2/HC ratio at moderate temperature, pressure, and low LHSV.

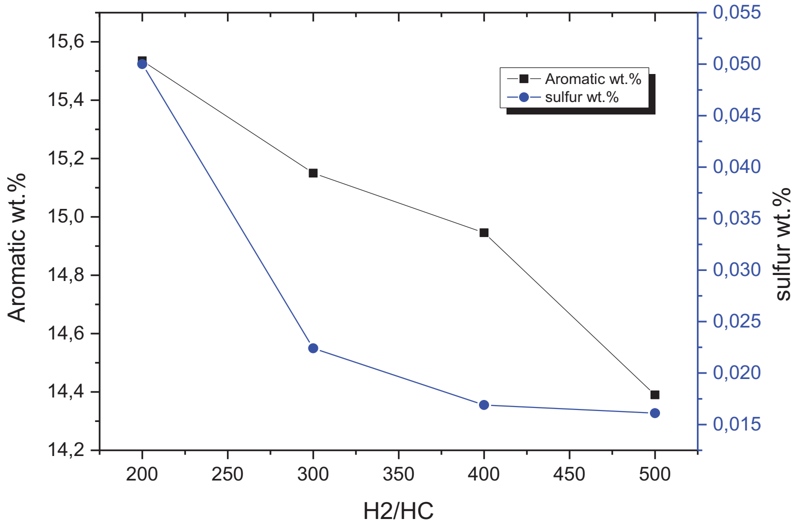

Fig. (5) Effect of Different Operating H_2/HC ratio on Aromatic and Sulfur Content of Treated Kerosene

Effect of Hydrotreating Conditions on Kerosene Properties

The hydrotreated kerosene was characterized by measuring physical properties like smoke point, aniline point, and flash point. In general, these properties are adequately reflects the nature of chemical configuration of petroleum fraction, properties change is largely relevant to the change of hydrocarbon molecules of kerosene during hydrotreating reactions. It is important to determine burning characteristics, fire hazard, and aromatic content of kerosene.

Lowest possible level of smoke during burning is required. Therefore, low proportions of aromatics, naphthenes, and unsaturated hydrocarbons are favorable due to burn with a reddish or even smoky flame. Smoke point is considered a test measures the burning qualities which defined as the maximum height in mm, of a smokeless flame of fuel. Smoke point of the hydrotreated kerosene was improved with decreasing LHSV and increasing temperature, pressure, and H_2/HC ratio as shown in Table (3). Smoke generation was decreased with reduction of aromatics content, maximum height 30 mm was achieved at high H_2/HC ratio and low LHSV where adequate H_2 amount and enough residence time was conducted respectively to gain deep hydrogenation. The dearomatization could evaluated by aniline point test, often this test used to estimate aromatics content of kerosene.

The lowest temperature at which an equal volume mixture of the petroleum oil and aniline are miscible is the aniline point. Hydrocarbons exhibits different aniline points and since aniline is an aromatic, aromatic compounds exhibit the lowest aniline points due to high miscibility in aniline at ambient conditions while paraffin compounds have the highest aniline points. Aniline point was increased with decreasing LHSV and increasing temperature, pressure, and H_2/HC ratio. It is clear that increasing of aniline point is due to conversion of poly aromatics in sequence to mono aromatics, naphthenic, and saturates. Maximum increase in aniline points (maximum aromatics reduction) was achieved at 500 H_2/HC ratio. Fire hazard considerations acquires high importance, flash point which is a guide to the fire hazard associated with the use of kerosene indicates to the explosion potential of fuel.

The flash point of a liquid distillate is the lowest temperatures at which sufficient vapors are generated and a spontaneous ignition can be occur if a spark is present. It is a significant feature for distillate fuels related to safety in storage and transport, low flash point fuel is a higher fire hazard. Results show that flash point increased with decreasing LHSV and increasing temperature, pressure, and H_2/HC ratio. It is clear that enhancement of flash point highly dependent on pressure and H_2/HC ratio, H_2 saturation conditions play an essential role in skeletal configuration change of kerosene hydrocarbons (polyaromatics to saturate) and reflects on evaporation condition of kerosene. A remarkable change observed at 500 H_2/HC ratio, flash point increased from 40°C to 46°C.

Table (3) Properties of Hydrotreated Kerosene at different Operating Conditions

Property	Feed	Hydrotreated Kerosene															
		Temperature (°C)				Pressure (bar)				LHSV (1/h)				H_2/HC			
		275	300	325	350	32	42	52	62	1	2	3	4	200	300	400	500
Smoke Point (mm)	27	28	28	29	29	28	28	29	29	30	29	29	28	29	29	29	30
Aniline Point (°C)	64.4	65	65.6	66.1	66.7	66.1	66.1	66.7	66.7	66.1	66.1	65.6	65	65.6	66.1	66.7	67.2
Flash Point (°C)	40	40.4	41.9	41.9	42.4	41.9	42	43.1	43.2	41.9	41.1	41.1	40.9	41.9	43.2	46	46

Conclusions

High metal oxide NiW/γ-Al_2O_3 catalyst is an effective catalyst for decreasing of sulfur and aromatics content of kerosene to an acceptable levels by employing HDS and HDA reactions in on stage fixed bed reactor, and improving smoke point, aniline point, and flash point of kerosene to meet the environmental requirements. This bi-functional catalyst showed an efficient reactivity toward middle distillates through adopting hydrogenation reaction bath in one stage reactor. The hydrotreating operating parameters had a different influence on improvement of kerosene, decreasing of space velocity and increasing of temperature, pressure and the H_2/Oil ratio led to deep sulfur removal and acceptable aromatic saturation levels.

Nomenclature

a_{N2}	Surface area of a N_2 molecule (16.2 $A^{\circ 2}$/molecule)
C_B	B.E.T. constant, Eq.2
N_A	Avogadro number ($6.022*10^{23}$ molecules/mole)
P_a	Equilibrium pressure (Pa)
P_o	Saturation pressure of the adsorbent gas at experimental conditions (Pa)
V	Volume adsorbed at equilibrium pressure
V_1	Volume of catalyst (cm^3)
V_m	Monolayer volume (cm^3)
V_o	Molar volume of the gas (22414 cm^3/mole)
W	Mass sample (g)
W_4	Weight of cylinder empty (g)
W_5	Weight of cylinder with catalyst (g)
ρ_b	Bulk density (g/cm^3)

Abbreviations

HDA	Hydrodearomatization
HDS	Hydrodesulfurization
HDN	Hydrodenitrogenation
LHSV	Liquid hourly space velocity
SA	Surface area

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