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AL – Mansuriya gas fields associated liquid and its role to increase the potential capacity of gasoline fuel in Daura oil refinery.

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1-Introduction:

Hydrotreating processing is commonly used to remove platforming catalyst poisons from straight run or cracked naphthas prior to charging to the platforming Process unit. It can be seen that the primary function of the naphtha Hydrotreating Process can be characterized as a "Clean up" Operation. The catalyst used in the Naphtha Hydrotreating Process is composed of an alumina base impregnated with compounds of cobalt or nickel and molybdenum. The catalyst is insensitive to most poisons which affect dehydrogenation reactions. A relatively high percentage of carbon on the catalyst does not materially affect its sensitivity or selectivity. Volumetric recoveries of products depend on the sulfur and olefin contents [1].

The Naphtha Hydrotreating Process is a catalytic refining process employing a selected catalyst and a hydrogen-rich gas stream to decompose organic sulfur, oxygen and nitrogen compounds contained in hydrocarbon fractions. In addition, hydrotreating removes organo-metallic compounds and saturates olefinic compounds.

Organo-metallic compounds, notably arsenic and lead compounds, are known to be permanent poisons to platinum catalysts. "The complete removal of these materials by Hydrotreating processing gives longer catalyst life in the platforming unit.

Sulfur, above a critical level, is a temporary poison to platforming catalysts and causes an unfavorable change in the product distribution. Organic nitrogen is also a temporary poison to platforming catalyst. It is an extremely potent one, however, and relatively small amounts of nitrogen compounds in the Platformer feed can cause large deactivation effects, as well as the deposition of ammonium chloride salts in the platforming unit cold sections.

Oxygen compounds are detrimental to the operation of a Platformer. Any oxygen compounds which are not removed in the hydrotreater will be converted to water in the platforming unit, thus affecting the water/ chloride balance of the platforming catalyst. Large amounts of olefins contribute to increase coking of the platforming catalyst. Also, olefins can polymerize at platforming operating conditions which can result in exchanger and reactor fouling.

The Naphtha Hydrotreating Process makes a major contribution to the ease of operation and economy of platforming. Much greater flexibility is afforded in choice of allowable charge stocks to the platforming unit. Because this unit protects the platforming catalyst, it is important to maintain consistently good operation in the Hydrotreating Unit.

In addition to treating naphtha for Platformer feed, naphthas produced from thermal cracking processes, such as delayed coking and visbreaking, are usually high in olefinic content and other contaminants, and may not be stable in storage. These naphthas may be hydrotreated to stabilize the olefins and to remove organic or metallic contaminants, thus providing a marketable product.

Keywords: AL – Mansuriya; Hydrotreating; platforming; naphtha, CCR, hydrogenolysis.

1-Purpose of the research:-

1.1. Increase the potential capacity of raw naphtha (light and heavy).

1.2. Provide extra sweet heavy naphtha for CCR unit.

1.3. Provide extra sweet light naphtha to isomerization unit to produce maximum allowable motors fuels.

1.4. Prevent accumulation of associated liquid in gas field.

The unit installed at Daura refinery in Baghdad is designed to process raw straight run distillate on high quality aircraft gas turbine fuel or well burning illuminating kerosene, in kerosene hydrotreating process.

Kerosene hydrotreating is a hydro-desulfurization process in complete vaporize phase employing cobalt-molybdenum catalyst. Hydrogen rich gas is supplied for the operation from the powerformer unit and is circulated by the compressors in the predicted design ratio to liquid feed.

Our work is to use kerosene hydrotreating unit (KHT) to hydrotreat AL – Mansuriya gas fields associated liquid, by keeping all the unit equipment as it is, and determining the appropriate feed capacity, amount of hydrogen required, operating conditions and equipment size for the new feed (AL – Mansuriya).

3-Experimental work:-

3.1. Results analysis of associated liquids for AL-Mansuriya gas fields, in summer and winter time consequently [2].

Table (1): Composition of associated liquids for AL-Mansuriya gas fields.

Composition	Base case, mol%		Composition	Base case, mol%	
	Summer	Winter		Summer	Winter
H_2O	0.0000	0.0000	n-Octane	15.6877	15.6306
H_2S	0.0288	0.0265	E-Benzene	0.0000	0.0000
N_2	0.0000	0.0000	p-Xylene	0.3402	0.3394
CO_2	0.0000	0.0000	m-Xylene	0.2723	0.2717
Methane	0.0000	0.0000	o-Xylene	0.2725	0.2719
Ethane	0.0084	0.0077	n-Nonane	21.7798	21.6991
Propane	1.7906	1.7615	n-Decane	16.4016	16.3400
i-Butane	1.8149	1.8477	n-C_{13}	4.3881	4.3711

n-Butane	4.4890	4.4892	M-Mercaptan	0.0617	0.0618
i-Pentane	4.1615	4.3130	E-Mercaptan	0.1351	0.1357
n-Pentane	5.0963	5.2262	n-P-Mercaptan	0.0736	0.0738
n-Hexane	9.9501	9.9512	t-B-Mercaptan	0.0541	0.0545
Benzene	0.5007	0.5011	COS	0.0042	0.0042
n-Heptane	12.0637	12.0249	CS_2	0.0000	0.0000
Toluene	0.5980	0.5972			
			Total	100.00	100.00
			Mercury, ppm	0.0422	0.0415

3.2. True boiling point and ASTM distillation tables for associated liquid which is calculated by Hysys simulation program according to the above compositions.

Table(2): TBP and ASTM of associated liquids for AL-Mansuriya gas fields.

	Cut point, Vol%	TBP, ºC	ASTM [D86], ºC
Light Naphtha	0.00	-60.58	-0.76
	1.00	-10.95	31.60
	2.00	-4.86	36.02
	3.50	1.09	40.16
	5.00	8.12	44.86
	7.50	26.03	56.11

	10.00	33.70	60.71
	12.50	35.49	61.77
	15.00	38.47	63.53
	17.50	57.56	74.82
	20.00	66.68	80.33
	25.00	68.35	81.36
	30.00	75.40	85.77
	35.00	85.49	92.70
	40.00	98.08	101.71
	45.00	99.47	102.74
	50.00	114.55	114.03
Heavy Naphtha	55.00	123.06	120.67
	60.00	129.76	125.95
	65.00	136.08	130.93
	70.00	146.37	139.00
	75.00	149.72	141.58
	80.00	153.98	144.84
	85.00	159.74	149.21
	90.00	168.46	155.72
	92.50	175.52	158.27

	95.00	188.46	162.94
Kerosene	96.50	194.42	165.09
	98.00	209.65	170.58
	99.00	230.32	178.04
	100.00	351.70	221.82

3.3. Physical properties.

Table(3): Physical properties of associated liquids for AL-Mansuriya

Properties	Base case	
	Summer	Winter
Density, Kg/m^3	666.36	666.27
Viscosity, cP	0.3164	0.3161
Sulfur content, wt%	0.35	0.35
M.Wt.	101.16	101.09
Thermal conductivity,W/m-K	0.110	0.1099
Specific heat, Kj/Kg-^{o}C	2.260	2.260
Surface tension, dyne/cm	16.21	16.20

3.4. Results of technological calculations of AL- Mansuriya hydrotreating process flow chart of Iraqi oil.

- Hydrogen required for AL- Mansuriya hydrotreating is calculated according to the following sulfur components analysis.

Table(4): sulfur components analysis.

Sulfur components	Wt%
Mercaptan	100
Aliphatic sulfide	0.00
Aromatic sulfide	0.00
Disulfide	0.00
Thiophene	0.00
Total	100

Hydrogen consumption in hydrotreating process will be divided in to:-

1) Hydrogenolysis of organic sulfur compounds;

2) Hydrogenation of unsaturated hydrocarbons;

3) Loss of hydrogen with the effluent (treated liquid and off gases).

Hydrogen consumption for the hydrogenolysis of organic sulfur compounds G_1, wt%, in feed:

$G_1 = \sum mi \times \Delta Si,$

Where: ΔSi- amount of sulfur (Mercaptan) removed by hydrotreating, wt%, in feed;

mi- Coefficient depending on the nature of the sulfur compounds and their hydrogenolysis flowchart [3,4].

Coefficient *m* reflects conversion depth sulfur compounds and equal to;

$mi = \frac{M_{H2} \times n_{H2}}{M_S \times n_{Si}}$,

где: M_{H2} – molecular weight of H_2 , $M_{H2} = 2$;

Ms - molecular weight of feed, Ms = 32;

n_{H2} - number of hydrogen molecules, involved in hydrogenolysis reactions;

n_{Si}- number of sulfur molecules,

For mercaptan.

$RSH + H_2 \xrightarrow{\qquad} RH + H_2S$;

$mi = \frac{2 \times 1}{32 \times 1} = 0.0625$

$G_1 = 00625 \times 0.35$

$= 0.022$ wt%

AL- Mansuriya = 10,000 bbl/day @ density = 666.36 Kg/m^3

= 44141.5 Kg/hr

Total H_2 required = 0.00022 × 44141.5

= 9.71 Kg/hr

= 0.22 Kg/Ton (feed)

$H_2S = \Delta Si \times \frac{Mwt, H2S}{Mwt, S}$

$H_2S = 0.35 \times \frac{34}{32} = 0.372$ wt%

= 0.372×44141.5 = 164 Kg/hr

- Determination the suitable feed capacity (AL- Mansuriya liquid) for the existing kerosene hydrotreating to avoid equipment overloading.

We performed much iteration by simulation program HYSYS and we found that the suitable feed of AL-Mansuriya liquid to avoid any bottleneck in any equipment in the existing kerosene hydrotreating unit is between (7,000-8,000) bbl/day, due to heat duty of overhead condenser (CW-1) limitations, as illustrated in the table below.

Table (5): Equipment sizing determination for three feed flow rates.

Equipment	Required duty by HYSYS (7000 bbl/D) MKcal/hr	Required duty by HYSYS (10,000 bbl/D) MKcal/hr	Original design duty MKcal/hr
H-1	1.15	1.668	6.0
H-2	0.5	0.65	2.87
E-1	1.30	1.81	3.13
E-2	5.2	7.4	10.22
A-1	0.223	0.32	2.0
W-1	0.125	0.18	0.97
CW-1	**1.23**	**1.73**	**1.3**

4-Expected products quantity:

Table (6): expected products from AL-Mansuriya liquids.

Feed, Kg/hr	
AL-Mansuriya Naphtha	44141.5
H_2	9.71
	44151.21
Products, Kg/hr	
Sweet Naphtha	39290
Off gases	4697.21
H_2S	164
Total	44151.21

4-Expected products quality:

Table (7): Physical properties of expected products.

Properties	
Density, Kg/m^3	686.7
Viscosity, cP @ 43 °C	0.41
Sulfur content, ppm	0.5
M.Wt.	109.5
Thermal conductivity,W/m-K	0.12
Specific heat, Kj/Kg-°C	239
Surface tension, dyne/cm	18.91

Conclusions

Containing only (Mercaptans) in Al-Mansuriya associated liquid make the hydrotreating process less severity due to absence of other sulfur compounds which are mentioned in table 4.

Using the existence kerosene hydrotreating unit (KHT) to hydrotreat Al-Mansuriya associated liquid will ensure production of sweet naphtha suitable for reforming and CCR units, and increasing the potential capacity of gasoline fuel.

Efficiency of hydrotreating (sulfur removing) process will be better because of the amount of catalyst in (KHT) is higher than the amount of catalyst used in our ordinary naphtha hydrotreating unit (NHT).

The suitable unit capacity for Al-Mansuriya associated liquid feed is between (7,000-8,000) bbl/day to avoid any bottleneck in any equipment in the existing (KHT) otherwise we have to resize some equipment.

References

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