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REVIEW

Kurdistan crude oils as feedstock for production of aromatics

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Abstract Crude oils from various locations in Iraqi Kurdistan were fully evaluated, so that enables refiners to improve there operation by selecting the best crude oil that yields high naphtha content to be used as a catalytic reforming feedstock after determination of total sulfur content and then de sulfurizing them, then cyclizing or reforming these sweet naphtha cuts to produce aromatic fractions which can be splitting into benzene, toluene, and xylenes.

Contents

Abbreviations: DNO, Det Norske Oljeselskap (Norwegian Oil Company); Casco/Ascom, also named (Komet) this is oil and gas operating company working in Kurdistan; TQ, Taq–taq; K, Kirkuk.

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1. Introduction

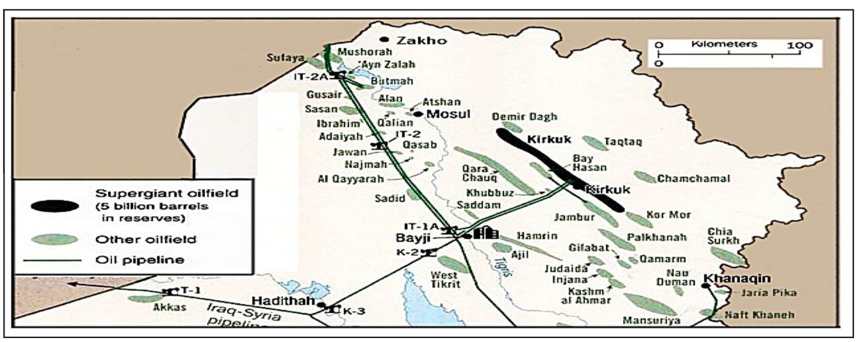
The petrochemicals refinery processes crude oil to produce feedstock for chemical plants. The most important process are: (1) The production of aromatics and (2) the production of olefins. The aromatics referred here are: benzene, toluene, ethyl benzene, and xylenes, the production of aromatic feed stocks originates with the catalytic reforming of a refinery stream of heavy naphtha range 50–215 °C and rich in naphthenes (David et al., 2006). Atypical stream that meets these criteria would be a naphtha stream from a hydrocracker, or the straight run naphtha from atmosphere distillation but still the aromatic components are too low and it must be increased through reforming process.

There are numerous parties interested in participating Iraqi Kurdistan's oil production and refining industry, and the following entities are attempting to establish or complete oil refineries (Robert Nall, 2008).

1-Taq taq petroleum refining company limited 2-KAR Group

3-WZA Petroleum Company limited 4-Casco/Ascom 5-DNO

There are several feed stocks with widely varying characteristics, ranging from light low sulfur ''sweet'' crudes produced by Taq–taq to the much heavier crude oil produced by (DNO), with Kirkuk blend being in the middle. There is no '' one size fit all '' approach that will work for all the crude oils. The refineries must be tailored to the unique characteristics of the oil that will be refined. Attempting to do otherwise will result in unites with shortened operating lives, increased operating costs, reduced capacity and excess capital costs. Thus there is a need for the crude oil assay which is a compilation to laboratory and pilot plant data that define the properties of the specific crude oil, and this is our aim in this research study for some of Kurdistan crude oils. (please see the map)



2. Experimental part

2.1. Chemical reagents

Alumina powder, sulfuric acid (%98), lead(II) acetate tri hydrate (%99), cupric chloride dehydrate (%99.5), propane thiol(%98), Methyl 2-propane thiol(%99), 1-butane thiol%99, 1-octanethiol%97, 2-propane thiol%98, 2-methyl thiophene%98, 3-methyl thiophene%99, 2-ethyl thiophene%99, purchased from across organics.

Four different crude oils were used: two of them taken from Taq taq region near Koya town, which are named TQ1 and TQ2, the third sample was taken from the combination of all wells in the Kirkuk city and named K, the fourth sample was taken from Zakho.

2.2. Apparatus and instruments

1- True boiling point apparatus consists of: distillation flask, electrical heating mantel, fractional column, condenser, temporary receiver, graduated receiver, ice bath with water re-cyclization pump.

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2- Quick digital portable Octane analyzer of Zeltex Inc. (ZX-101C, 130 western Maryland parkway, Hager's town, MD21740, USA).
3- Gas chromatography of CP-3800 from Varian, equipped with 8200 auto sampler and micro liter syringe, 1177 injector, and pulsed flame photometric detector (PFPD) operated in sulfur mode. The capillary column of 30 m in length, 0.25 mm(mm) internal diameter, and 0.25 μm thick films of %50 phenyl and methyl silicon stationary phase of Varian equivalent. CP-Sil, 24-CB, CP7821.
4- Hydromerers, Muffle furnace, Digital electric thermo state shaker, Digital sensitive balance.
5- Spectro phoenix II, bench top XRF analyzer from AMETEX material analysis division.

2.3. Procedures

2.3.1. Atmospheric fractional distillation

The fractional distillation achieved for all crude oils and the following fractions collected:

(i) From initial boiling point to 150 °C was taken and named as natural gasoline (N.G).
(ii) From 80 to 180 °C was taken and named heavy naphtha (H.N).

2.3.2. Procedure for gas chromatographic analysis

(i) The DB-17 column 30 m in length, 0.25 mm internal diameter and 0.25 μm thick film of %50. Phenyl and %50 methyl Silicone stationary phase Varian equivalent: CP-Sil 24CB, CP7821, which is a specific type column for separation of sulfur compounds, was programed from 35 to 220 °C, with the rate of 10 °C/min heating following 2 min as an initial hold, 10 min as final hold. Therefore the total run time becomes 30.5 min.
(ii) The temperature of the rear injector (1177) was adjusted at 220 °C, the split ratio 1:100, and PFPD detector were adjusted at 300 °C, which is a type selective detector for sulfur compounds.
(iii) The flow rate of gasses, Air 1 was 17 ml/min, Air 2 was 10 ml/min. and H_2 was 13 ml/min. Helium used as carrier gas was 1.3 ml/min. Gases' Pressure was as follows: Air was (60) Psi, H_2 was (42) Psi, and He was (80) Psi.
(iv) 1 ml of sample was injected by micro-siring, then run and waited for getting the chromatogram of each run.

3. Results and discussions

3.1. Evaluation of crude oils

Although all crude oils contain the same composition of carbon, hydrogen, nitrogen, oxygen, sulfur, besides they are all composed of paraffin, naphthene, olefin and aromatic, rarely there are two crude oils with the same characteristics, and that is because every crude oil regardless of its geographical sources contains various compounds in different quantities that make up its composition (Kevin and Giles, 2002). The following table summarizes some of the crude oils from various locations in Kurdistan (Table 1). Worthy of note in (Table 1) is the difference in the character of various crudes that enable refiners to improve their operation by selecting the best crude or crudes that meet their product marketing requirements, For example; where a refining product slate demands a high quantity of "no lead" gasoline and modest outlet for fuel oils then crude feed such as Taq–taq would be a prime choice. Its selection provides a high naphtha yield with a high naphthene content as a catalytic reforming feed stock, fuel oil in this case also is less than 20% of the barrel. The Kirkuk crude would be a contender, in the case of a good middle of the road crude, Kirkuk crude or Zakho crude oil offers a reasonably balanced product slate with good, middle, or distillate quality and yields (Speight, 2007).

For bitumen manufacture and lube oil manufacture the TQ2 crude oil is a formidable competitor.

3.1.1. The crude oil assay

The crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil. At a minimum point the assay should contain a distillation curve, a specific gravity curve, and also some data on pour point, sulfur content, viscosity, and many other properties (Table 2). Engineering companies use this assay data in preparing the process design of petroleum plants they are bidding on.

3.1.2. The process common to most energy refineries

In refining the crude oil is first broken into those raw stocks which are the basis of the finished products. This breakup of the crude is achieved by separating the oil into a series of boiling point fractions which meet the distillation requirements and some of the properties of the finished products (Table 3 and Table 4).

Table 1 Kurdistan crude oil from various locations.

Properties	TQ1	TQ2	Kirkuk	Zakho
Specific gravity@15.6 °C	0.7904	0.9115	0.8464	0.8914
A.P.I gravity (degree)	47.52	23.74	35.64	27.24
Sulfur content %W	0.6	2.1	2.0	1.92
Natural gasoline (IBP-150 °C) vol.%	31	4.5	14.5	10
Kerosene (150–240 °C) vol.%	22.6	10.5	20	20
Gasoil (240–350 °C) vol.%	25.6	14.5	23	30
Long residue (> 350 °C) vol.%	20.74	70.5	39.5	40

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Table 2 Kurdistan crude oils assay.

Properties	TQ1	TQ2	Kirkuk	Zakho
A.P.I gravity (degree)	47.52	23.74	36.05	29.08
Pour point °C	L-40	−27	−24	−30
Water content %V	Nil	Nil	Nil	O.O9
Flash point °C (C.O.C)	Flammable	Flammable	Flammable	40
Water and sediment %V	< 0.05	0.08	0.2	0.3
Ash content %W	0.047	0.058	0.009	0.015
Salt content (ppm)	0.0024	0.02	5.0	0.0095
Viscosity@37.8 °C/cst	1.93	67.28	5.20	13.24
Viscosity@50 °C/cst	1.66	40.48	3.92	9.57

Table 3 General properties of different boiling point fractions obtained from various crude oils from Kurdistan.

Tests	Taqtaq TQ1		Kirkuk		Zakho		TQ2	
	N.G	H.N	N.G	H.N	N.G	H.N	N.G	H.G
Sp.gr.@15.6 °C	0.7025	0.7239	0.7110	0.7490	0.7234	0.7134	0.7338	0.7541
A.P.I (degree)	69.91	63.96	67.51	57.41	64.10	66.84	61.33	56.14
Vis.@40 °/Cst	0.61	0.76	0.57	0.70	0.68	0.71	0.71	0.84
Octane number								
RON	75.5	72.9	77.3	74.6	73.6	72.6	750	74.4
MON	70.9	68.1	72.1	69.0	68.9	67.8	71.2	69.6
R + M/2	73.2	70.5	74.7	71.8	71.3	70.2	73.1	72
Distilled@100 °C %V	55	10	45	8	40	9	33	3.5
Distilled@145 °C %V	95	77	85	61	80	58	70	5
Final b.p °C	153	174	154	174	150	180	167	185
Calorific value (kcal/kg)	11360	11278	11338	11221			11296	11206

Table 4 Evaluation of crude oils according to IP-method.

Temp. range °C	Vol.%				Relative density at 15.6 °C			
	TQ1	TQ2	Kirkuk	Zakho	TQ1	TQ2	Kirkuk	Zakho
IBP-150	33.4	5.9	17	12	0.7120	0.8007	0.7100	0.7149
150–300	40.2	26	32	26	0.7957	0.8123	0.8000	0.8156
Residuum > 300	26.4	64.9	51	62	0.8965	0.9920	0.9150	0.9259

3.2. Determination of total sulfur content

Total sulfur content of crude oils used in this work, and the naphtha fractions obtained from them, were determined using spectro phoenix II (which uses the XRF technique). The results are listed in Table 5 which indicate clearly the low sulfur content of the crude oil from TQ1 and the naphtha fraction obtained from it in comparison with the others. This result combined with results of crude evaluation indicates that the crude oil of Taq–taq field is a light nearly sweet crude oil.

Table 5 Determination of total sulfur.

Crude oil	Naphtha fractions (b.p range °C)	Sulfur %w	Sulfur content of whole crude %w
TQ1	IBP-90	0.001	0.61
	90–125	0.0025	
	125–180	0.0133	
TO2	IBP-90	0.0350	2.20
	90–125	0.0460	
	125–180	0.0500	
K	IBP-90	0.1100	1.99
	90–125	0.0700	
	125–180	0.1310	
Zakho	IBP-90	0.0050	2.70
	90–125	0.0080	
	125–180	0.0210	

3.3. Doctor test (qualitative test) for identification of hydrogen sulfide, mercaptans, and elemental sulfur in naphtha fractions obtained from TQ1, TQ2, K, and Zakho crude oil

Table 6 shows the qualitative test (doctor test) for identification of hydrogen sulfide (H_2S), mercaptans, and elemental sulfur of naphtha fractions obtained from the various crude oils used in this work, the results indicate that all samples give positive test for mercaptan, and negative test for elemental sulfur; while for hydrogen sulfide TQ2 and Zakho samples give positive test but samples of TQ1 and K are giving negative test. Therefore, we conclude that naphtha fractions obtained from

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Table 6 Doctor test for naphtha fractions.

Crude oil	Naphtha fractions (b.p range °C)	Hydrogen sulfide	Mercaptan	Elemental sulfur
TQ1	IBP-90	−Ve	+ Ve	−Ve
	90–125	−Ve	+ Ve	−Ve
	125–180	−Ve	+ Ve	−Ve
TO2	IBP-90	+ Ve	+ Ve	−Ve
	90–125	+ Ve	+ Ve	−Ve
	125–180	+ Ve	+ Ve	−Ve
K	IBP-90	−Ve	+ Ve	−Ve
	90–125	−Ve	+ Ve	−Ve
	125–180	−Ve	+ Ve	−Ve
Zakho	IBP-90	+ Ve	+ Ve	−Ve
	90–125	+ Ve	+ Ve	−Ve
	125–180	+ Ve	+ Ve	−Ve

Table 7 Retention times and peak areas of sulfur compounds.

Sulfur compounds	Tr (minute)	Peak area (count)
2-Propanthiol	3.414	1824608
2-Methyl-2-Propanthiol	3.543	426983
1-Propanthiol	3.600	0493042
1-Butanthiol	4.813	3737536
1-Octanthiol	11.771	278477
2-Methyl thiophene	6.970	1026810
3-Methyl thiophene	7.053	578454
2-ethyl thiophene	8.739	2108168

TQ1 and K do not need caustic treatment prior to any catalytic conversion processes, while naphtha fractions obtained from TQ2 and Zakho must be treated with caustic prior to catalytic conversion processes to avoid any catalytic poisoning

These sulfur compounds will cause foul odor and are corrosive to metals, in addition may cause oxidative deterioration as well as inhibit the performance of various additives such as tetra ethyl lead (TEL), and anti oxidants in finished products.

Therefore it is necessary to remove them by extraction processes or convert them into less dangerous sulfur compounds by conversion processes.

3.4. Gas chromatographic analysis using PFPD

The PFPD detector is a special type of GC-detectors which is used for the detection of sulfur or phosphorous containing compounds and does not respond to the normal hydrocarbon compounds. Thus chromatograms of sulfur compounds present in these naphtha fractions, compared with retention time of some standard sulfur compounds, shown in Table 7 were very useful to indicate the effect of some chemical treatments such as treatments with H_2SO_4, Na_2PbO_2, $CuCl_2$, and Al_2O_3 which are used to remove or alter the sulfur compounds in petroleum products in processes called sweetening processes, the success of these processes is depending on oxidation, mercaptan dissolving, and hydro-de-sulfurization processes (Wendt and Diggs, 1924; Krause, 1952; Birch and Norris, 1929; Youtz and Perkins, 1927; Salem, 1994; Lien et al., 1949; Thompson et al., 1955; Zinnen, 1999; Drushel and Sommers, 1967; Vogh and Dooley, 1975).

Figs. 1–4 are examples of these chemical effects which show that they do not remove the sulfur compounds but convert them to other sulfur compound types (mercaptans readily oxidize to corresponding disulfides, and hydrogen sulfide oxidize to elemental sulfur (Wood et al., 1924).

This means it is necessary to desulfurize these naphtha fractions by hydro treating (HDS) methods to obtain proper feedstock for catalytic reforming unit.

Table 8 PIONA test for light and heavy naphtha fractions.

%Vol.	TQ1			K		
	C5–80 °C	80–125 °C	125–175 °C	C5–80 °C	80–150 °C	150–190 °C
Total paraffin	95.1	77.80	68.50	92.0	59.7	52.3
Total olefins	< 0.001	0.160	0.40	–	–	–
Total naphthenes	4.75	20.0	12.40	7.5	31.3	24.7
Total aromatics	0.07	1.60	16.30	0.1	9.0	23.0

%Vol.	C5-80 °C	80–150 °C	150–175 °C
TAWKE-3			
Iso paraffins	14.50	42.80	35.30
Total olefins	< 0.05	0.07	0.12
Total naphthene	13.30	20.80	19.0
Total aromatics	0.45	1.90	8.70

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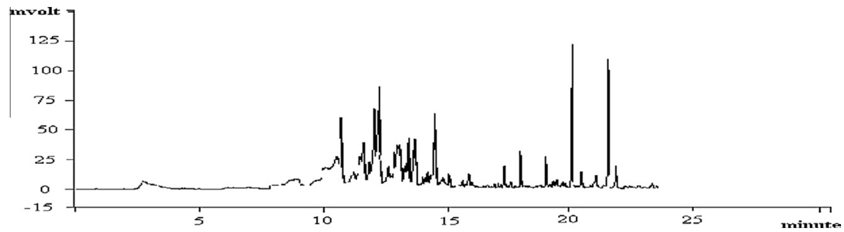

Figure 1 Chromatogram of H.N TQ1 before treatment.

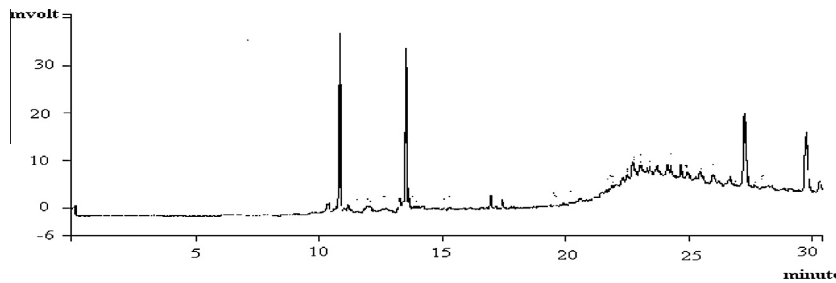

Figure 2 Chromatogram of H.N TQ1 after treatment by concentrate H_2SO_4.

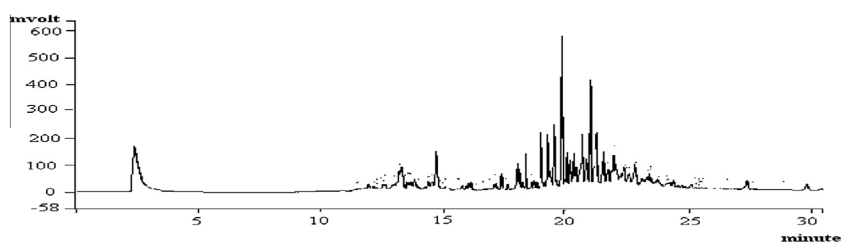

Figure 3 Chromatogram of H.N TQ1 after treatment by $CuCl_2$.

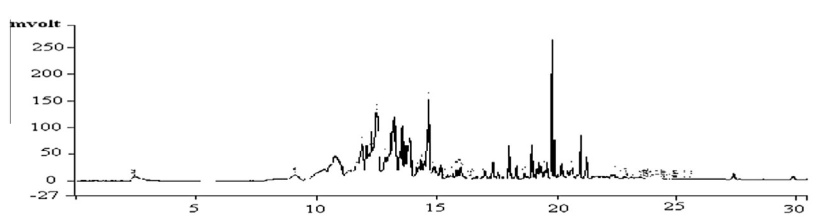

Figure 4 Chromatogram of H.N TQ1 after treatment by Al_2O_3.

3.5. Reformer feed quality

3.5.1. Chemical composition of the feed

The reforming feed is usually defined by its (PIONA): analysis which gives the contents of basic hydrocarbon types (paraffin, Iso paraffin, olefin, naphthene, aromatic).

As the fastest reaction of catalytic reforming is the dehydrogenation of naphthenic into aromatic hydrocarbons, the value of a specific feed is characterized by the initial concentration of naphthenic and aromatic hydrocarbons.

Table 8 shows the (PIONA) analysis of light and heavy naphtha fractions obtained from the various crude oils used in this research work.

A forming index of gasoline can be defined as N + 2A, obtained by adding twice the aromatic content to the naphthenic content, the higher the number the easier it is to get a product of given quality. In other words, if one uses in an existing unit a feed with an index N + 2A higher than some other well defined case, the reformate will have the same Octane number, at a lower average temperature and with a smaller amount of catalyst. This change will lead to a higher yield and a higher concentration of hydrogen in the recycle gas.

3.5.2. Distillation ranges

The catalytic reforming feed is made up of the light fraction of the crude oil with an initial boiling point of around 70 °C and a

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final boiling point of 160 °C. At the first sight it looks advantageous to feed the reforming unit with heavy fractions because their naphthenic and aromatic content is higher than that of light cuts; it thus gives better yields and easier operating conditions for a given product. However heavy cuts also contain stable compounds that lead to coke formation and deactivation of the catalyst; and to decrease the coke formation, one would have to increase the hydrogen recycle rate.

4. Conclusions

1- It was found that TQ1 crude oil has low sulfur content, and also light distillate fractions obtained from TQ1 contain fewer amounts of sulfur compounds if they are compared with those obtained from other crude oils.
2- Qualitatively all light fractions contain mercaptans (thiols) which are very harmful due to their bad odor, instability, corrosion problems, and lead to susceptibility effect, therefore they must be removed by HDS units.
3- Crude oil from TQ1 contains a high ratio of light fractions compared with other crude oils used in this research work.
4- Due to the rule (N + 2A), the light fraction boiling between 100 and 200 °C obtained from crude oil of TQ1 is suitable to be a feed to reformer unit to produce a rich aromatic content reformate, which is suitable to produce aromatic compounds.

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