ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 2, August 2013

Production and Evaluation of some Gas Oil Fractions from Taq-Taq Crude Oil and Their Structural Group Analysis

Abdulsalam R. Karim, Luqman O. Hamasalih

***Abstract*- Three different boiling range fractions of gas oil were produced from Kurdistan Taq-Taq crude oil. Their percentage yield were estimated to be (F1= 34.12, F2= 15.6,F3= 25). Full physical and chemical analysis for all fractions were achieved and compared to Iraqi marketing specifications, then the structural group analysis for the three fractions were determined using n-d-M method.**

Key words: **crude oil, gas oil, group analysis, sulfur content, ASTM distillation, PONA.**

I. INTRODUCTION

Gas oil is a fraction of crude oil obtained by atmospheric or vacuum distillation with boiling range between 225-337^{o}C (light gas oil) or 320-426^{o}C (heavy gas oil) [1],[2]. Gas oil consists of a large number of hydrocarbon mixture containing straight-chain alkenes (paraffin's), saturated cyclic structures (naphthenes) and aromatics [3],[4]. It contains some heterogeneous compounds rather than carbon and hydrogen such as sulphur, nitrogen and oxygen as well as traces of metallic constituents such as iron, copper, nickel and vanadium [2]. One of the recent challenges in the petroleum refineries is the reduction of sulfur content of gas oil to the new low limits (50 ppm). As sulfur compounds cause many problems when exist in petroleum fractions, they cause environmental pollution, because they emit poisonous emissions such as SO2 and H2S when the fuel is burned. Sulfur compounds are poisonous to catalyst and they are corrosive to metallic parts of diesel fuel engines [5]. Several methods for the determination of sulfur compounds have been reported, including colorimetric titration, chromatographic, iodimetric, X-ray fluorescence spectrometry and ultraviolet fluorescence [6]. The conventional method for reducing sulfur is catalytic hydrodesulphurization (HDS) under severe conditions. Many other methods for desulfurization have been reported [7]-[11], among them selective adsorption, biodesulfurization, and oxidation/extraction (oxidative desulphurization) etc. for removing these refractory sulfur compounds from petroleum products [12]. Knowing hydrocarbon classes' proportion in petroleum fractions is another necessity in gas oil studies to indicate the influence on the whole fuel properties, such as density, freezing point, thermal stability, combustion quality. For the determination of the hydrocarbon classes proportion, chromatography is currently widely used. Another determination method is *structural group analysis*, where the composition is expressed as weight percentage of carbon in Aromatic, Parafinic and Naphtenic structures, and also takes into account the number of cycles in aromatic and naphtenic structures [13]. In this study several types of gas oil with different boiling ranges where produced from Taq-Taq crude oil and their physical properties, S-contents and chemical properties determined using n-d-M method, which is a simple and easy method of structural group analysis.

II. MATERIAL AND METHOD

A. Gas oil Samples and ASTM tests

The three samples of gas oils were produced from Taq-Taq crude oil/Kurdistan region- North of Iraq. Several physical properties of gas oils were determined according to the ASTM standard methods such as, Specific gravity and API gravity-ASTM D-1298, Flash point-ASTM D-92, Pour point-ASTM D-97, Diesel index- IP-21, Cetane number IP-218, Ash content ASTM D-482, Viscosity ASTM D-445, distillation ASTM D-86 and determination of total sulfur content by XRF- technique ASTM D-2622.

B. N-d-M procedure

Refractive index, density and molecular weight of gas oil samples were measured, then value of PONA were estimated using the following equations.

A-Calculate ν and w.

$$\nu = 2.5\,(n-1.4750) - (d-0.8510)$$
$$w = ((d-0.8510) - 1.11(n-1.4750)$$

(i) If ν = + ve $\% CA = 430\,\nu + (3660/M.wt)$

If ν = - ve $\% CA = 670\,\nu + (3660/M.wt)$

(ii) If w= + ve $\% CR = 820\,W + (10000/M.wt)$

If w = - ve $\% CR = 14110 + (10600/M.wt)$

(iii) $\% CN = \% CR - \% CA$

(iv) $\% CP = \% 100 - \% CR$

B- Calculate number of aromatic rings

If ν = + ve $RA = 0.44 + 0.055\,M\,\nu$

If ν = - ve $RA = 0.44 + 0.08\,M\,\nu$

C-Calculate of total ring number

If w= + ve $RT = 1.33 + 0.146\,M + (w - 0.005)$

If w = - ve $RT = 1.33 + 0.180\,M + (w - 0.005)$

D- Calculate number of naphthenic rings

$RN = RT - RA$

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 2, August 2013

Table (1) General properties and test results of Taq-Taq Crude Oil

Test	Method	Results	Unit
density@15°C	ASTM D 5002	791.5	Kg/m3
Specific gravity@60/60°F	conversion	0.7919	
API gravity@ 60°F	calculated	47.2	API
B.S.& Water	ASTM D 4007	0.05	%vol.
Water Content	ASTM D 4006	<0.05	%vol.
Vapour Pressure	ASTM D 5191	28.1	kpa
Total Acid Number	ASTM D 664	0.11	MgKOH/g
Flash Point(Abel)	IP 170	Below – 30	°C
Pour Point	ASTM D 5853	Below - 42	°C
ASTM Colour	ASTM D 1500	Darker than 8.0	
Sulphur Content	ASTM D 4294	0.672	% Wt.
Salt Content	IP 265	11.1	Mg/L
Total Nitrogen	ASTM D 4629	259	Mg/kg
Ash Content	ASTM D 482	0.005	% Wt.
Wax Content	UOP 46	<5.0	% Wt.
Kinematic Viscosity@40°C	ASTM D 445		Mm^2/S
Kinematic Viscosity@50°C			
Kinematic Viscosity@70°C			
Kinematic Viscosity@80°C			
UOP K Factor	UOP 375 / Calc	12.3	
Micro carbon Residue	ASTM D 4530	1.07	% Wt.
Conradson Carbon Residue	ASTM D 189	1.04	% Wt.
Gross Calorific Value	ASTM D 240	44.81	Mj/kg
Mercury	UOP 938	<1	ppb Wt
Asphaltene	IP 143	0.14	% Wt.
Distillation	ASTM D 86		
Metal			
Sodium	ICP	1	Mg/kg
Potassium		<1	
Copper		<1	
Lead		<1	
Iron		5	
Nickel		1	
Vanadium		2	
Arsenic Content	UOP 387	<5	Ppb Wt

B. *Yield and Properties of diesel fuel and gas oil fractions:*

Three different gas oil fractions, with various boiling point ranges, were obtained by fractional atmospheric distillation of Crude Oil and results are shown in table (2).

II. RESULT AND DISCUSSION

A. *Crude oil property*

Gas Oil fractions, were obtained from fractionation of Taq-Taq Crude Oil (Kurdistan Region-North of Iraq) with general properties and test results shown in table (1).

Table (2) the yield percentage of gas oil fractions

Fraction No.	Boiling point range **°C**	Yield %v
F1	171- 300 **°C**	34.12
F2	241- 300 **°C**	15.60
F3	241- 360 **°C**	25

Each gas oil fraction was analyzed according to the standard ASTM methods, and compared to the Iraqi marketing specification of gas oil. Results are shown in table (3).Table 3 is shown in Appendix.

As indicated from the results of table (3), flash point of the fraction with boiling range (171-300 °C) is less than the minimum permissible flash according to the regulated Iraqi specification, which means that this fraction cannot be stored and handled without serious fire hazard, and it need to be striped with steam to improve its flash point to the minimum required Iraqi marketing specification of 54 °C. On the other hand the two other fractions (F2 and F3) have higher pour points than the minimum permissible according to the Iraqi marketing specification, so, they must be dewaxed or there is a need for adding some pour point depressant additives for the improvement of pour point , which is an indication of the lowest temperature at which a gas oil can be stored and still be capable of flowing under gravitational forces. Gas oils with higher pour point are permissible, where heated storage and adequate piping facilities are provided. All other properties listed in table (3) are in fulfillment with the requirements of Iraqi marketing specification of gas oil.

C. *ASTM D-86 DISTILLATION OF THE FRACTIONS*

Boiling point of pure component is a useful guide for identification of the substance, but mixtures do not have a single boiling point. They boil over a range of temperature depending on pressure, composition and the nature of the apparatus used to carry out the experiment. Relatively simple apparatus of distillation with ASTM designation D-86 applied to all three fractions obtained from Taq-Taq crude oil, this type of distillation is the best known non-fractionating distillation and it is frequently called an ASTM and sometimes an Engler distillation which is widely used before. The distillation test shows the volatility of the fuel and the ease with which it can be vaporized. Distillation temperature is not directly significant to operation of gas turbines designed for grades 3-GT and 4-GT. In other gas turbines that are most susceptible to carbon deposition and smoke formation, the more volatile fuels may provide better performance. Tables (4), (5) and (6) show ASTM distillation data for the three gas oil fractions.

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 2, August 2013

In this distillation there is no deliberate attempt to fractionate, and accordingly the vapor temperature does not represent the true or actual boiling point of the material situated at that percentage in the crude oil.

CI. STRACTURAL GROUP ANALYSIS USING N-D-M METHOD

n-d-m Method is a method of structural group analysis depend on several physical parameters like refractive index, density, and molecular weight, that is used to statistical distribution of petroleum fractions to their components, especially the amount of aromatic, paraffinic, and naphthenic compounds. Any petroleum fractions contain different amount of aromatic and paraffinic compounds, the presence of aromatic or paraffinic compounds directly affected the physical and chemical properties. Three different ranges of gas oil which obtained from Taq-Taq crude oil, that different in boiling point ranges were used in this research which they vary in their composition. the knowledge of n-d-m method get the important characteristics on petroleum products and petroleum properties as the amount of its components. For each fraction refractive index and density were determined and molecular weight was estimated by two method.

I- Estimate of molecular weight of petroleum fractions as a function of Characterization factor.

II- Estimate of molecular weight of petroleum fractions as a function of API gravity.

Estimated the molecular weight of fractions using these two figure below

The results in table (7) show that three fractions of gas oil have different Molecular weight which mean that the fractions have different chemical composition and n-d-M method used to determine the exact amounts of aliphatic, naphthenic and aromatic carbons in these fractions, also the number of rings of naphthenic and aromatic in the structure of fractions, by using the equations which were described in detail in section (2).

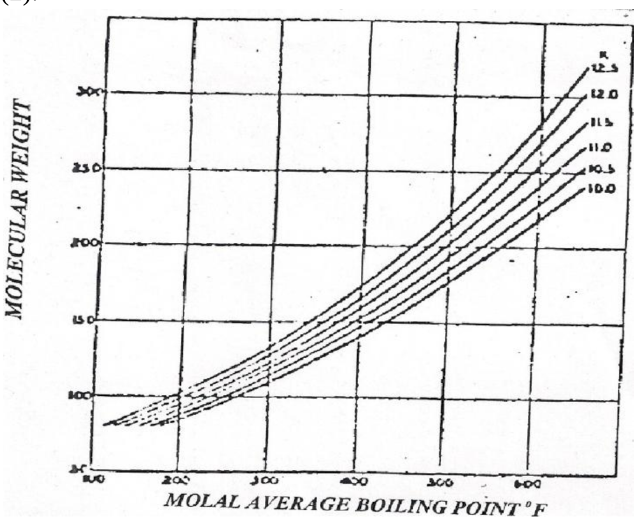

Fig. (1) Petroleum fraction as a function of boiling point and characterization factor

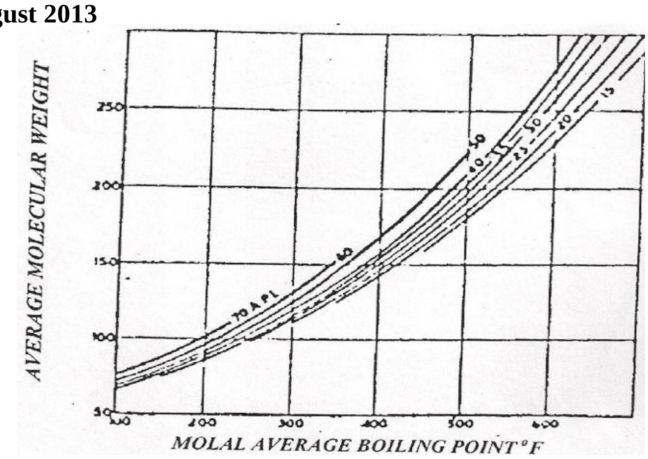

Fig. (2) Petroleum fraction as a function of boiling point and specific gravity Molecular weight estimated from the two methods above show in table (7)

According to the n-d-M method the percentage of aliphatic, naphthenic and aromatic carbon with total ring and ring of naphthenic and aromatic were estimated, the results shown in table (8), (9) which used molecular weight estimated by molal average boiling point and characterization factor and (10), (11) which used molecular weight estimated by molal average boiling point and API gravity. Because of the wide boiling range of Fraction (1), it contains a greater percentage of both aromatic and paraffin compounds is much than the others two Fraction, while in Fraction (3) has more amount of aromatic percentage than the Fraction (2) , because the Fraction (3),is heavier than Fraction (2) as it contain more amount of heavy compounds [end point of fraction (3) extended to 360°C, while it is only 300°C for fraction (2)]. This difference in the amount of aromatic and paraffinic composition effect on the suitability of each fraction, and appear clearly in some properties and characteristics such as specific gravity, API-gravity, viscosity, flash point, pour point, aniline point…etc. Gas oils with high paraffinic content and low aromatic content are preferred as they are of higher quality.

REFERENCES

[1] Rafiqul.A. B., Md. Rabiul I. S., and Md. Riaz P. Production of diesel fuel from used engine oil, International Journal of Mechanical & Mechatronis Engineering, 10 (2), 1-6, 2010.

[2] Ahmad M. A. Development of NiW-Zeolite-based catalysts for hydrocracking of gas oil: synthesis, characterization, activity and kinetics studies. Ph.D. thesis, 2007, Universiti Sains Malaysia.

[3] Praveen Ch, Shishir S. Novel method for estimation of kinetic parameters in VGO cracking. Petroleum & Coal, 51(3) 193-195, 2009.

[4] Ulf N. Ring-opening catalysts for cetane improvement of diesel fuels. Ph.D. thesis, 2005, KTH – The Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Technology SE-100 44 Stockholm, Sweden

[5] Saeid Sh., Mahdi A. and MortezaT. Production of ultra low sulfur diesel: simulation and software development. Petroleum & Coal, 49 (2), 48-59, 2007.

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 2, August 2013

[6] Zlatotsvet T., Dobromir Y., Aleksandar D. and Petko P. Estimation of measurement uncertainty for the determination of the total sulfur in petroleum and petroleum products in UV-fluorescent analysis. Petroleum & Coal, 54 (1) 14-23, 2012.

[7] Dehkordi AM Sobati MA and Nazem MA. Oxidative desulfurization of non-hydro treated kerosene using hydrogen peroxide and acetic acid. Chin J Chem Eng. t7:869-874, 2009.

[8] Ali SH, Hamad DM, Albusairi BH and Fahim MA. Removal of dibenzothiophenes from fuels by oxy-desulfurization. Energy Fuels, 23:5986-5994, 2009.

[9] Al-Shahrani F, Xiao TC, Llewellyn SA, Barri S, Jiang Z, Shi HH, Martinie G and Green MLH. Desulfurization of diesel via the H2O2 oxidation of aromatic sulfides to sulfones using a tungstate catalyst. Appl Catal B –Environ 73:31t-316, 2007.

[10] Zhou X, Tan Q, Yu G, Chen L, Wang J and Novaro O. Removal of dibenzothiophene in Diesel oil by oxidation over a promoted activated carbon catalyst. K inet Catal. 50:543-549, 2009.

[11] de Souza WF, Guimaraes IR , Guerreiro MC and Oliveira LCA. Catalytic oxidation of sulfur and nitrogen compounds from diesel fuel. Appl Catal A –Gen. 360:205-209, 2009.

[12] Yordanka Ts. Tasheva, Petko St. Petkov and Isay D. Lazarov. Method of decreasing unlikely compounds in gasoline. Petroleum & Coal 52 (1):56-61, 2010.

[13] Anca I. D., Claudia I. K., Ancaelena E. S. and Anisoara A. N. Jet fuel characterization using structural group analysis. Ovidius University Annals of Chemistry, 21 (2) 2:.147-151, 2010.

APPENDIX

Table (3) properties of gas oil fractions

Tests	standard methods	Result (171-300°C)	Result (241-300°C)	Result (241-360°C)	Iraqi Specification
Specific gravity@ 15.6°C	ASTM D-1298	0.7929	0.8288	0.8448	(0.84)(Max)
A.P.I gravity	ASTM D-1298	46.94	39.2287	35.978	(37) (Min.)
Flash point °C (C.O.C)	ASTM D- 92	52 °C	85 °C	90 °C	54(Min.)
Viscosity.@ 37.8 °C /Cst	ASTM D - 445	1.7153	3.3165	5.1041	6(Max)
Viscosity.@50°C /Cst	ASTM D - 445	1.4141	2.6298	3.8653	5 (Max)
Pour point °C	ASTM D - 97	Under -20 °C	-6°C	3 °C	-9 (Max)
Sulphur content	ASTM D - 336	0.4	0.5	0.65	1(Max)
Diesel .Index	Ip- 21	75.432	65.1588	63.97244	55(Min.)
Cetane Number	Ip- 218	54.311	46.914	46.06015	53(Min.)
Calorific value (Kcal/Kg)	ASTM D-2382	11079.5	10957.5	10900.9	10800(gross)
Distilled at (350 °C) (%v)	ASTM D- 86	100%	100%	90%	85%(Min.)
Aniline point °C	ASTM D- 611	71.5 °C	74.5 °C	81 °C	Record
%product from crude oil	……………..	34.12%	15.60%	25%	Record

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 2, August 2013

Table (4) show ASTM distillation of F1

Boiling point Range F1 (171 - 300°C)	
Dist. %v/v	Temp. °C
I.B.P	156
5%	162
10%	171
20%	180
30%	190
40%	199
50%	209
60%	220
70%	232
80%	249
90%	271
95%	284
97%	286

Table (5) show ASTM distillation of F2

Boiling point Range F2 (241 - 300°C)	
Dist. %v/v	Temp. °C
I.B.P	198
5%	214
10%	224
20%	236
30%	244
40%	253
50%	263
60%	273
70%	284
80%	300
90%	321
93%	322
…	….

Table (6) show ASTM distillation of F3

Boiling point Range F3 (241 - 360°C)	
Dist. %v/v	Temp. °C
I.B.P	215
5%	240
10%	250
20%	264
30%	275
40%	284
50%	295
60%	306
70%	318
80%	334
90%	349
95%	355
96%	356

Table (7) Molecular weight estimated by the two methods

Fractions	Sp.gr.	Molecular weight gm/mol estimated from Molal average boiling point and characterization factor	Molecular weight gm/mol estimated from Molal average boiling point and API gravity
F1	0.7929	168.75	166.66
F2	0.8288	217.187	213.5
F3	0.8448	240.6	233.33

Table (8) Percentage of aliphatic, naphthenic, aromatic and total ring carbon in the fractions

compositions	F1	F 2	F3
%Aliphatic carbons	76.815	63.25	60.27
%Naphthenic ring carbons	9.972	27.537	27.26
%Aromatic carbons	13.213	9.213	12.47
%Total ring carbons	23.185	36.75	39.73

Table (9) Number of total ring, naphthenic ring and aromatic ring in fractions

Number of Rings	F 1	F 2	F 3
Total Rings	0.458	0.945	1.128
Naphthenic rings	0.189	0.703	0.766
Aromatic rings	0.269	0.242	0.362

Table (10) Percentage of aliphatic, naphthenic, aromatic and total ring carbon in the fractions

compositions	F1	F 2	F3
%Aliphatic carbons	76.03	62.40	58.90
%Naphthenic ring carbons	10.47	28.10	28.16
%Aromatic carbons	13.48	9.50	12.94
%Total ring carbons	23.97	37.60	41.10

Table (11) Number of total ring, naphthenic ring and aromatic ring in fractions

Number of Rings	F 1	F 2	F 3
Total Rings	0.469	0.952	1.124
Naphthenic rings	0.198	0.705	0.760
Aromatic rings	0.271	0.247	0.364