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Jet fuel characterization using structural group analysis

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Abstract. This paper deals with the applicability of a structural method of analysis (the aniline point method) for light petroleum fractions like kerosene and jet fuel. As aniline point method requires, mixtures of pure hydrocarbons were used- typical for the corresponding classes of hydrocarbon within the same range of boiling points, thuse mimicking the petroleum fractions. The structural groups method n-d-M was applied further and the results were compared with those obtained by aniline point method. Results on hydrocarbon mixtures were compared with those for real petroleum fractions. It was demonstrated that chemical composition of kerosene and jet fuel can be determined either by aniline point method with good accuracy or with n-d-M method, both methods having the advantage to be cheap and fast. These methods can be used for intermediate products (raw or hydrogenated) but not for additivated finished products

Keywords: aniline point method, hydrocarbon class analysis, jet fuel composition , n-d-M method

1. Introduction

Kerosene and jet fuel are medium petroleum fractions and complex mixtures consisting of different types of hydrocarbons. Most of hydrocarbons are members of the parrafin, naphtene or aromatic classes with a carbon distribution between 8 and 16. The chemical composition depends on the petroleum's source [1].

Knowing hydrocarbon classes proportion in petroleum fractions is necessary because it influence sthe properties of whole fuel, such as density, freezing point, thermal stability, combustion quality [2,3]. For the determination of the hydrocarbon classes proportion, chromatography is currently used [4,5,6] but more rapid is the determination of composition by hydrocarbon class analysis.

Structural analysis of hydrocarbons from petroleum products is based on physical and chemical methods of separation. This analysis involve correlation between chemical composition and some physical properties that are liniar functions by composition. In this analysis, four types of molecules are considered: aromatics, olefins, parafins and naphtenics [1].

Another method to establish the composition of petroleum fractions is the structural groups analysis where the composition is expressed as % wt. carbon in aromatic, parafinic, naphtenic structures, but it also takes into account the number of cycles in aromatic, parafinic and naphtenic structures.

The aim of this study was to develop a rapid and cheap method for structural analysis of light petroleum fractions (kerosene, jet fuel): the aniline point method. The original method was elaborated for gasoline and its application to the heavy fractions is questionable [1]. Also structural groups' method n-d-M developed for gas oil and oils can be used expecting good results since the fractions analyzed here (kerosene, jet fuel) are lighter than gas oil.

2. Theoretical aspects

Through the aniline point method [7], the composition of a petroleum fraction on hydrocarbon classes can be easily determined with the equations 1 and 2:

$$\%\ \text{vol. aromatics} = K_A\,(T_2 - T_1) \qquad (1)$$

$$\%\ \text{vol. naphthenes} = K_N\,(T_P - T_2) \qquad (2)$$

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where:
T_P is the aniline point for the pure parafins;
T_1- the aniline point of the petroleum fraction;
T_2- the aniline point of the raffinate (petroleum fraction without aromatics);

K_N, K_A- constants depending on the boiling temperature range; these constants are determined experimentally with standard hydrocarbons as explained in the Section 3.

The structural groups' method n-d-M (refractive index-density-molecular weight) was developed for oil and gas oil [8] but it is expected to be applied even easier to lighter fractions such as kerosene and jet fuel. The method consists in determining just three physical properties and correlating them with the structural parameters: $\%C_A$ (% carbon in aromatics structures); $\%C_R$ (% C in cyclic structures: aromatic and naphthenic); $\%C_N$ (% C in naphthenic structures) and $\%C_P$ (% C in paraffinic structures. Composition is expressed in %wt.

Also, the number of cycles in the average molecule (R_T- total number of cycle; R_A- number of aromatic cycles and R_N- number of naphthenic cycles) can be calculated, but this wasn't of interest in the present study.

The equations used for determinations of these parameters are [4]:

$\Delta n = n_d^{20} - 1.4750$ (3) $V = 2.51\Delta n - \Delta d$ (5)
$\Delta d = d_4^{20} - 0.8510$ (4) $W = 2.51\Delta d - 1.11\Delta n$ (6)

For $V>0$ $\%C_A = 430V - 3660/M$ (7)
$V<0$ $\%C_A = 670V + 3660/M$ (8)

For $W>0$ $\%C_R = 820W - 3S + 10000/M$ (9)
$W<0$ $\%C_R = 1440W - 3S + 10600/M$ (10)
$\%C_N = \%C_R - \%C_A$ (11)
$\%C_P = 100 - \%C_R$ (12)

In Eq.9 and 10, S means the sulfur content (%wt.). The method applies up to 2% wt. sulfur.

The method can be applied to real petroleum fractions or to the same mixtures obtained from pure hydrocarbons used at the aniline point method.

3. Experimental

3.1. Materials and reagents

All used reagents (H_2SO_4, aniline, hydrocarbons: dodecane, decahydronaphthalene, and biphenyl) were of analytical grade (Fluka and Merck). The properties of pure hydrocarbons are presented in **Table 1**.

Table 1. The properties of pure hydrocarbons

Hydrocarbon	**M**	**d_4^{20}**	**n_d^{20}**	**Boiling point [^{0}C]**
Dodecane	170.33	0.7487	1.41952	216.28
Decahydronaphthalene	138.24	0.8971	1.4810	195.7
Biphenyl	154.20	0.9712	1.58728	255.55

The density was determined with the Bingham pycnometer; the molecular weight was determined by the graphical correlation between the density and mean distillation point on standard distillation curve ($t_{50\%\ STAS}$) [6] and the refractive index was determined by the refractometer Abbe [9,10,11]. The samples analysed in this study are unrefined jet fuel and kerosene samples from an atmospheric distillation plant (sampling at different dates) with distillation limits 140° -200 °C and 154° -210 °C respectively, with sulfur content of 0.15% wt and 0.21% wt respectively. The relative density d_4^{20} of jet fuel was 0.790 and kerosene's was 0.815.

3.2. Work procedure

The experiment started with the determination of constants K_N and K_A from the equations 1 and 2 needed for the estimation the % of different classes of hydrocarbons in petroleum products. Mixtures of pure hydrocarbons representatives for parafins (dodecane), naphthenes (decahydronaphthalene) and aromatics (biphenyl) were made-up. All these hydrocarbons are known to be present in kerosene.

First a parafin and a naphthenic are mixed in different proportions (0%-25%-50%-75%-100% v/v). Further a 50-50% v/v of this mixture is mixed with an aromatic hydrocarbon in a concentration (4%- 11%-13%-17% vol. aromatic). Aniline point is determined for each mixture with a standard procedure [12] and variation of aniline point with the proportion of hydrocarbons is established (see **figures 1** and **2**, in Section 4). Usually, the correlation between the composition and the aniline points is linear (Eq.1 and 2) and the constants K_N and K_A can be calculated from the slope of the line.

Then, the two large fractions of kerosene with distillation limits 154° -210 °C and 140° -200 °C were cut at 195°C in two fractions in a TBP column according standard procedure [13].

For all fractions, the proportion of parafins, naphtenes and aromatics was determined by the aniline point method. This method states that narrower fractions are analyzed with better results than larger ones.

The aniline point method involved the determination of aniline point for the petroleum fraction sample. Then, the aromatics were removed completely from the fraction with dehydrated sulfuric acid obtained from H_2SO_4 (94-98%) treated with P_2O_5. After the extraction of aromatics, the fraction was neutralized, washed many times and dried with $CaCl_2$. The aniline point of the "raffinate" (fraction without aromatics) is determined and Eq.1 is applied to find the percent of aromatics. The difference to 100 represents parafins + naphthenes. The Eq.2 is then applied to find % naphthenes and % parafins separately. The aniline point of pure parafins (T_p from Eq.2) was experimentally determined on dodecane and was 94°C.

3. Results and Discussions

Following the determination of aniline points of dodecane- decahydronaphthalene mixtures, it was drawn the curve for the variation of aniline point for parafins-naphthenes mixture with boiling point in the range of jet fuel and kerosene fractions, as seen in **Fig.1.**

Then, by adding biphenyl in different proportions to a 50-50% v/v dodecane-decahydronaphthalene mixture, the curve for the variation of aniline point with % vol aromatics was drawn (**Fig.2**). The slopes of these curves are in fact $1/K_N$ and $1/K_A$, so the constants are: $K_N = 2.11$.and $K_A=1.03$.

In **Table 2** and **Fig.3 a** comparison is done between the real composition of a synthetic mixture (a solution as it was made-up in the laboratory) and the results from applying the calculations of the n-d-M to the same solutions.

The results presented in the **Table 2** and **Fig.3** demostrate that there is a good accordance between the real and the calculated concentrations (standard deviation is 2.8%), so trials of n-d-M method to the petroleum fraction can proceed. The results obtained when applying the aniline point analysis compared with those obtained from n-d-M method applied to the petroleum fractions are shown in **Table 3**. Results of PA method were expressed as % wt in order to allow comparison with n-d-M method.

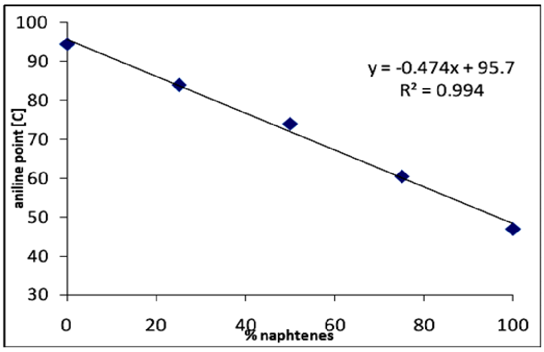

Fig.1. The variation of aniline point with % vol. naphtenes in the dodecane-decahydronaphthalene mixtures

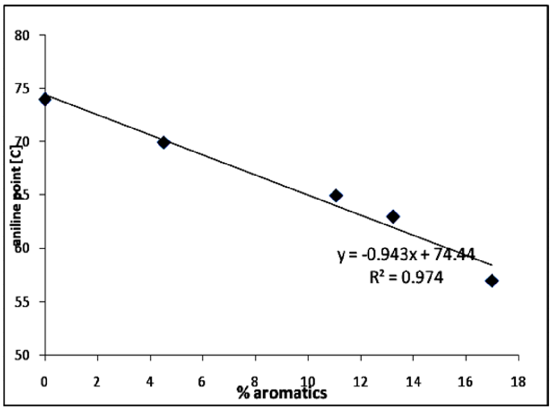

Fig.2. The variation of aniline point with % vol. aromatics in the biphenyl-dodecane-decahydronaphthalene mixtures

Table 2. Results obtained by n-d-M method for synthetic mixtures

Sinthetic mixture			Results according n-d-M method		
% wt P	% wt N	% wt A	%wt P (%C_P)	%wt N (%C_N)	%wt A (%C_A)
77.68	11.23	11.09	76.19	14.4	9.41
68.12	22.14	9.74	58.74	29.48	11.78
58.81	32.78	8.41	55.29	37.9	6.81
49.76	43.14	7.10	46.64	46.05	7.31
40.93	53.23	5.84	32.34	61.4	6.26

Table 3. Experimental data of aniline point method (AP) compared with results from n-d-M method for kerosene and jet fuel fractions

Kerosene						
Hydrocarbon class	**Light fraction**		**Heavy fraction**		**Large fraction**	
	AP	**n-d-M**	**AP**	**n-d-M**	**AP**	**n-d-M**
% wt aromatics	14.2	17.2	15.5	16.5	14.7	16.8
% wt naphtenes	36.0	36.9	37.2	37.7	36.9	37.2
% wt parafins	49.8	45.9	47.3	45.8	48.4	46.0
Jet fuel						
Hydrocarbon class	**Light fraction**		**Heavy fraction**		**Large fraction**	
	AP	**n-d-M**	**AP**	**n-d-M**	**AP**	**n-d-M**
% wt aromatics	10.3	9.6	13.5	14.3	12.6	13.5
% wt naphtenes	43.9	39.9	41.2	40.8	42.9	40.5
% wt parafins	45.8	50.5	45.3	44.9	45.5	46.0

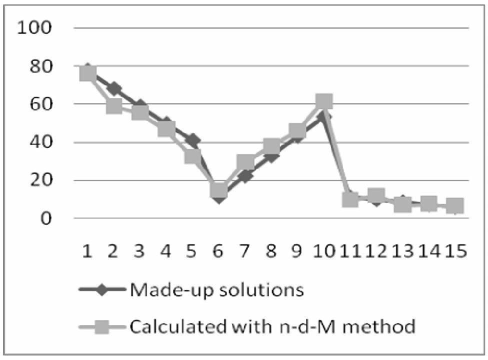

Fig.3. Comparison between the real composition of the synthetic mixtures and calculated with n-d- M method. **Legend**: Parafins %wt (1to 5), Naphthenes % wt (6 to10), Aromatics %wt (11 to 15)

Good results were obtained (standard deviation is 1.2%). One can observe in Table 3 that in general, the aromatic content determined by n-d-M method exceeds content determined by the aniline point method. This can be explained by errors introduced by differences between the model hydrocarbons used here and actual hydrocarbons in the petroleum fractions, which can contain: mono and di- substituted aromatics or aromatics with condensed cycles (derivatives of naphthalene).

4. Conclusions

The goal of this work was to develop a method for structural analysis of light petroleum fractions (kerosene, jet fuel) by aniline point method; for this, there were determined the values of the constants used in the equations pending on the method. The values obtained from experimental data are: K_A=1.03 for aromatics and K_N = 2.11 for naphtenes.

Using these values for constants on narrow and large fractions analysis comparable results were obtained with the data obtained by n-d-M method, and it proved that the values of the constant K_A, K_N are valid for the entire range of distillation.

These simple and cheap methods are preferable to the chromatography since for fractions with an end point over 195 ^{o}C, the chromatographic method can introduce bigger errors.

5. References

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