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Thermal Stability Study of Ras Lanuf Jet Fuel by NMR-Spectroscopy and Gas Chromatography Mass Spectrometry

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دراسة الثبات الحراري لوقود الطائرات المنتج بشركة رأس لانوف بواسطة جهازي الرنين النووي والكروماتوغرافية وتحديد الكتلة

جميل الحكيمي و صالح جبريل و إبراهيم رجب و إبراهيم التيجاني

تم دراسة الثبات الحراري لوقود الطائرات المنتج في شركة رأس لانوف لتصنيع النفط والغاز بواسطة جهاز الرنين النووي المغناطيسي والكروماتوغرافية وتحديد الكتلة. حيث تم تسخين الوقود عند درجات حرارة مختلفة 360، 380، 400، 240، درجة مئوية، كما تم تحديد الكم الحجمي لكل من المركبات الأورماتية والأليفياتية بواسطة جهاز الرنين المنغاطيسي ولوجظ أن بداية تكون المواد الولوفينية والأروماتية في درجات الحرارة العالية. كما لوحظ إرتفاع مفاجئ في كمية المواد الأروماتية في C_{12}، C_{11} يواكبه إنخفاض في كمية المواد الأليفاتية عند درجات الحرارة العالية (420، 440 درجة مئوية). أما التعرف النوعي على المواد الجديدة الناتجة فقد تم بواسطة جهار الكروماتوغرافية وتحديد الكتلة. وكانت بداية تكون مادة الكربون الصلب عند درجة حرارة 420 مئوية، وارتفعت هذه الكمية إلى 19.5% من الوزن الكلي عند درجة حرارة 440 مئوية.

Abstract: *Abstract The thermal stability of jet fuel produced by Ras Lanuf refinery was studied by nuclear magnetic resonance-spectroscopy (n.m.r.) and gas chromatography mass spectrometry (g.c-m.s.). The fuel was thermally stressed for 3 hours at different temperatures 360, 380,400.420 and 440 °C. The vol% of aromatics, olefins and paraffins was calculated by proton n.m.r. spectroscopy. The buildup of olefinic compounds started at 380 °C. GC analysis indicated that the formation of olefins and aromatics at high temperatures was accompanied by a decrease in C_{11} and C_{12} aliphatic fractions. Rapid increase of aromatics content was also observed at high temperatures (420-440 °C). Identification of the new formed compounds was carried out by g.c-m.s. The formation of solid carbonaceous deposits was firstly observed at 420 °C. Its content reached 19.5 wt% at 440 °C.*

INTRODUCTION

The development of new high speed aircraft generation required a fuel with high thermal stability. The fuel for such aircrafts would have to withstand temperatures in the range of 400-500 °C for several hours and the pyrolytic degradation of the jet fuel at this speed may be much more important than autoxidation. The possibility of the fuel pyrolysing and forming solid carbonaceous deposits in the fuel delivery system is of particular concern because of deposition of such materials in fuel lines or burner nozzles could lead to catastrophe. Jet fuels are mixtures with a huge number of hydrocarbons that became an extraordinarily complex chemical composition following thermal stressing at elevated temperatures. The distribution of molecular

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species broadens as cracking and transformation reactions produce a myriad of aliphatic and aromatic molecules of varying structures and molecular weights[1].

Conventional jet fuels are limited to maximum heating temperature of about 300 °C. Thermal oxidation stability of jet fuels at 100 to 300 °C in presence of oxygen has been researched for several decades[2-8]. For the development of fuel that will resist degradation by thermal stressing, the scientist should understand how the molecular structure of the fuel affects the thermal stability and what the molecular mechanisms that lead to the formation and accumulation of carbonaceous solids are. Many studies of fuel thermal stability were carried out. The principal indication of thermal instability was found to be the amount of solid carbonaceous deposit that forms during thermal stressing in a closed reactor[9]. The other important indicator was the formation of gaseous products. The change of the jet fuel composition can be followed by different methods. N.M.R-spectroscopy has been widely used to characterize petroleum oils and fractions[10-15]. The use of n.m.r. spectroscopy offers distinct advantages over other spectroscopic methods since it can be recorded in relatively short times, and it provides detailed compositional characteristics of the oil fraction that are unobtainable by other methods. The g.c-m.s technique has also contributed greatly to the analysis of various petroleum fractions[16,17].

In this work, the change of the chemical composition of jet fuel at different temperatures (360, 380, 400 and 420 °C) was followed by means of n.m.r. spectroscopy and g.c-m.s. The structure parameters obtained by the spectra are discussed and the composition change of the jet fuel at different temperatures is presented. The new formed compounds are separated and identified by g.c-m.s. This paper represents the first step of a research programme in the RASCO laboratory for investigating the compositional factors that affect the thermal stability of jet fuel.

EXPERIMENTAL

The jet fuel fraction was received from Ras Lanuf refinery (distillation temperature 150-204 °C). The fuel was heated for 3 hours in a stainless steel autoclave designed in the RASCO workshop. N.M.R. spectra was obtained by Bruker 100 Mhz spectrometer in 5 ml probe. Tetramethyl silane was used as an internal standard and deuterated chloroform as a solvent.

The integration and treatment of the obtained spectra was carried out on the Bruker data station with the WINNMR program. For g.c-m.s analysis a UNICAM series 610 Automass instrument, equipped with a 105 m Fison DB-1 (d=0.25 mm) capillary column, operating temperature programmed (150 °C for 25 min, rate 5 °C/min up to 300 °C with helium as a carrier gas. GC analysis had been performed using Carlo Erba Instrument 4100 equipped with 105 m Fison DB=1 (d=0.25mm) capillary column, operating temperature programmed (150 °C for 25 min, rate 5 °C/min up 300 °C with helium as a carrier gas.

RESULTS AND DISCUSSION

Theory of the n.m.r calculation:

The n.m.r. method is based on calculating the relative number of carbon atoms, classified as aromatics, paraffinis, or olefins in jet fuel from n.m.r. integral spectrum. The calculation of the composition of aromatics, paraffins and olefins by volume is given by the following equations[18, 19]:

$$\text{Aromatics, vol \%} = \frac{1.279.\,(A + C/3)}{1.279.\,(A + C/3) + (D - 2B + E/2 + F/3) + 2.5.\,B} \times 100 \quad (1)$$

$$\text{Paraffins, vol \%} = \frac{(D - 2B + E/2 + F/3)}{1.279.\,(A + C/3) + (D - 2B + E/2 + F/3) + 2.5.\,B} \times 100 \quad (2)$$

$$\text{Olefins, vol \%} = \frac{2.5.\,B}{1.279.\,(A + C/3) + (D - 2B + E/2 + F/3) + 2.5.\,B} \times 100 \quad (3)$$

A = aromatic carbons

B = olefinic carbons

C = CH_2 and CH_3 substituted to aromatic ring

D = aliphatic tertiary C-atoms

E = aliphatic methylene groups

F = aliphatic methyl groups

Some carbon atoms go uncounted for because they are completely substituted and give no n.m.r signal. Other carbons are erroneously counted as belonging to a given hydrocarbon class. Their protons resonate in the regions of n.m.r. spectrum where other hydrocarbon types normally appear. The densities of the light paraffins and aromatics are different, therefore, correction factors for these effects are carried out. The densities of aromatic compounds are significantly greater than paraffins. The aromatic terms in equation (1) through (3) need to be multiplied by a constant to correct the density differences. For these purposes, a quantitative determination of individual compounds in kerosene was carried out by gas chromatography. The weighted average density for each hydrocarbon class was calculated by the following equation[19]:

$$\text{weighted average density} = \frac{\Sigma\,[\,\text{vol\%}_{(i)}]\,[\text{density}_{(i)}]}{\Sigma\,[\,\text{vol\%}_{(i)}]} \qquad (4)$$

The weighted average density for aromatics was found to be 0.8662 g/ml and for paraffins 0.7592g/ml. The aromatic term (A+C/3) must, therefore, be multiplied by 0.8765 to correct the density differences.

In the n.m.r. spectroscopy, the full substituted carbon atoms give no signal. Correction factor for this phenomena was also calculated for individual compounds in kerosene fraction. The following equation was applied[19]:

weighted average ratio
(carbon counted/carbon uncounted) =

$$\frac{\Sigma\,[\,\text{vol\%}]\,(i)\;\dfrac{\text{no. carbon counted (i)}}{\text{no.carbon uncounted (i)}}}{\Sigma\,[\,\text{vol\%(i)}]} \qquad (5)$$

The correction factor for aromatics in kerosene fraction was found to be 0.6843. The aromatic term in the equations mentioned above (1,2 and 3) must be multiplied by 1.46. That means the overall constant to multiply the aromatic term with is 1.2796.

Correction factors of weighted average density and weighted ratio (carbon counted/carbon uncounted) for olefins were also calculated. The weighted average density for olefins was found to be 1.1704 and the weighted ratio (carbon counted/carbon uncounted) 2.14. The overall constant to be applied to the olefinic term is 2.5.

For paraffins, no density correction was necessary because the aromatics and the olefins were normalized to the paraffins density. Weighted average ratio for paraffins was calculated only. Its value was 1.

n.m.r. analysis:

The proton n.m.r. spectra for the base kerosene fractions obtained from the RASCO refinery and for the thermally stressed kerosene samples are indicated in Figures (1-3) and Table 1. The integral values for the regions were obtained from the spectra and were calculated by the above mentioned equations. The n.m.r. spectra were divided into the regions of interest based upon the chemical shifts of specific proton types. These areas are illustrated in Table 2.

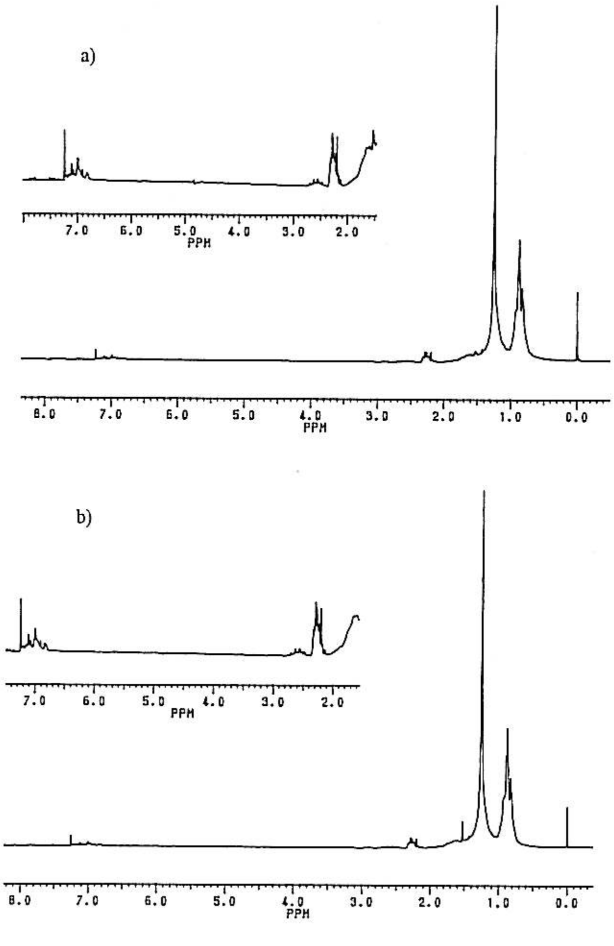

Fig. 1. ^{1}H-NMR spectra of a) base kerosene without heating and b) for kerosene heated for 3h at 360 °C, $CDCl_3$ as solvent and TMS as standard.

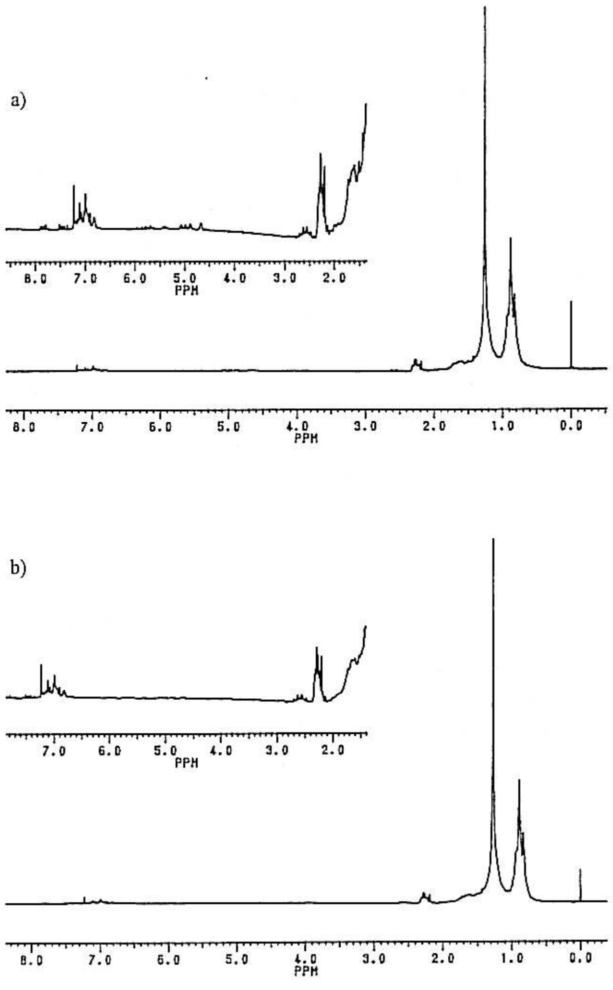

Fig. 2. ^{1}H-NMR spectra of a) thermally stressed kerosene at 400 °C and b) thermally stessed kerosine at 380 °C, CDC1$_3$ as solvent and TMS as standard.

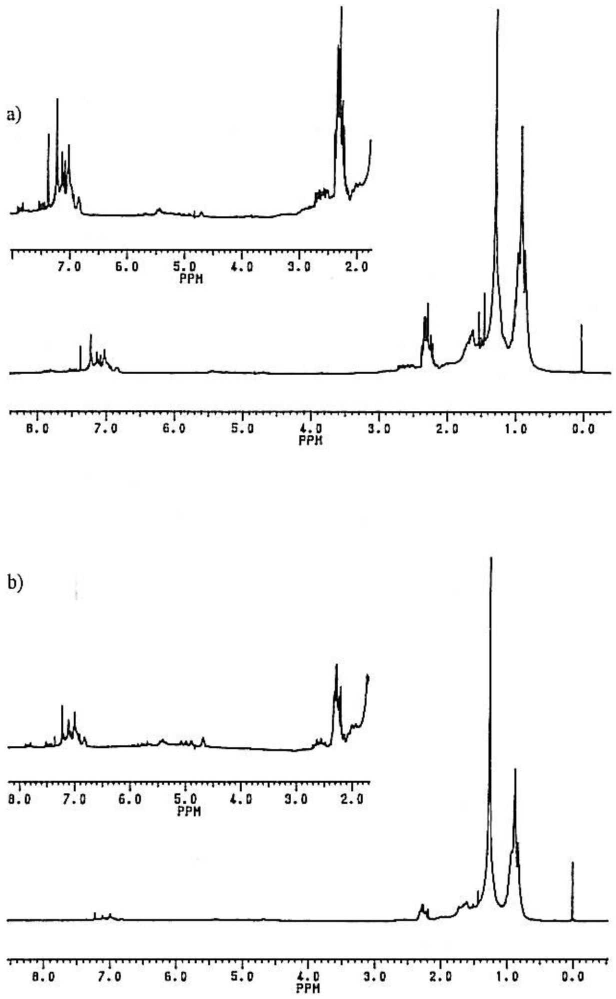

Fig. 3. ^{1}H-NMR spectra of a) thermally stressed kerosene at 440 °C and b) thermally stressed kerosene at 420 °C, CDC1$_3$ as solvent and TMS as standard.

Table 1: Properties of the RASCO base kerosene

Specific gravity	0.7855
Density g/ml	0.7853
API gravity	48.64
Freezing point, °C	-55
total sulphur, wt%	0.0023
Smoke point, mm	29

Table 2: Proton n.m.r assignments for functional groups of interest in kerosene[21,22]

Chemical shift region (ppm)	Proton type
0.6 to 1.0	hydrogen atoms of CH$_3$ in aliphatics and CH$_3$ in γposition and more distance to aromatic ring
1.0 to 1.5	CH in aliphatics and CH, CH$_3$ in β position to aromatic ring
1.5 to 2.151.5	CH in aliphatics and CH$_2$ to double bounds
2.15 to 3.0	CH, CH$_2$ and CH$_3$ in α-position to aromatic ring
4.5 to 6.0	CH to olefins
6.6 to 8.0	CH to aromatic ring

The increase of temperature up to 360 °C showed no change in the kerosene composition. By temperature at 380 °C a value of 2.8 vol% of olefinic compounds was obtained. At this temperature, formation of solid carbonaceous deposits was not observed. The colour of the kerosene remained unchanged. Table 3 shows that at high temperatures (T-400-440 °C), the paraffinic carbons are extensively converted to olefins and aromatics. The colour of the kerosene becomes yellow at these temperatures. Building up of carbonaceous solids started at 420 °C and the olefins and aromatics quantities go up to 14.9 vol% and 12.9 vol% respectively. A rapid increasing in the formation of carbonaceous solids was observed at 440 °C. At this temperature, 19.5 wt% carbonaceous solid was found. The aromatic content was increased to 57.4 vol%. The n.m.r. results indicated that the primary pathways to form carbonaceous solid are firstly, formation of olefins and secondly, cyclization to aromatics. This conclusion is derivable from the n.m.r. results shown in Table 3.

Table 3: Composition of thermally treated jet fuel by n.m.r spectroscopy and carbonaceous solid formation

Temperature/°C	Aliphatics (vol%)	Olefinics (vol%)	Aromatics (vol%)	Carbonaceous solid (wt%)
150-204	88.32	—	11.58	0.00
360	88.17	—	11.83	0.00
380	85.3	2.8	11.9	0.00
400	84.16	3.84	12	0.00
420	72	12.97	14.99	0.02
440	28.76	13.8	57.44	19.50

These tests show that the determinated kerosene can be thermally stressed up to 400 °C without any significant change in its composition. The value of olefinic compounds formed at this temperature lies in the internationally accepted limit, 5% of olefins is allowed to be contained in the jet-A kerosene[20]. On the other hand, the undesired carbonaceous solid could firstly be observed at 420 °C.

g.c -m.s analysis:

g.c -m.s analysis of the thermally unstressed kerosene was carried out. C_{11}, C_{10}, C_{12} and C_9 were found as main compounds in the RASCO kerosene respectively. None of olefinic compounds could be indicated in the base kerosene. At 380 °C, small amounts of light olefins were observed (*e.g.* ethylene and propylens). Increasing the temperature to 400 °C leads to a build up of olefins with higher molecular weights. The main compounds formed were methyl 1-butene, trans-2-pentene, 2-methyl-2-buttene, 2-methyl-1-pentene, 2-methyl-2-pentene, 4,4-dimethyl-1-pentene and methyl hexene. Bifunctional olefins or olefins with higher molecular weight were not observed. The appearance of oxygenated compounds like carboxylic acids, alcohols or ketones were not observable. It seems that these compounds are not stable enough for long periods of time (3h) at high temperatures. The g.c and g.c-m.s analysis implied that the C_{11} aliphatic fraction is the main cracking feed. By starting of formation of olefins at 380 °C, the C_{11} content decreases from 20 vol% to 17.1 vol%. The C_{12}, C_{10}, and C_9 values remained unchanged. At 420 °C the cracking process was observed in C_{12}, C_{11}, C_{10}, and C_9. Table 4 illustrates the vol% of these four fractions at different treatment temperatures. It seems from the g.c-m.s analysis that the C_{11} fraction negatively affects the thermal stability of kerosene.

Table 4: Comparison of the vol% of the main aliphatic compounds in kerosene at different temperatures

T/°C	C_9 (vol%)	C_{10} (vol%)	C_{11} (vol%)	C_{12} (vol%)
150-204	1.6	9.5	20	3.80
360	1.6	10	18.2	4.40
380	1.84	10.4	17.1	3.88
400	1.6	9.7	16.1	3.60
420	1.64	6.66	9.97	2.15

CONCLUSION

The n.m.r. spectroscopy and g.c-m.s analysis showed that the Jet fuel produced by Ras Lanuf is thermally stable up to 400 °C. The thermal degradation starts at 380 °C which leads to trace amounts of olefinic compounds. The g.c analysis indicated that the formation of new olefinic and aromatic compounds is mainly at the expense of the C_{11} aliphatic fraction. The production of carbonaceous deposits was firstly observed at 420 °C.

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