Chemical stability of modern jet fuels

L A Vlasenkova, K V Shatalov, N M Likhterova
FAE "The 25th State Research Institute of Chemmotology of Ministry of defense of Russian Federation", Moscow, 10 Molodogvardeyskaya street, Russia
vlasenkova.l@yandex.ru

Abstract. The article shows the need to study the chemical stability of jet engine fuels containing components of deep oil refining and offers a method for studying the chemical stability of jet engine fuels. Based on this method, research was conducted on jet engine fuels of various production technologies and the influence of the hydrocarbon composition on the chemical stability of a mixture of individual hydrocarbons was studied. The inhibitory effect of aromatic hydrocarbons in a mixture with different content of naphthenic hydrocarbons has been studied. Using artificial aging of jet engine fuels, a low level of chemical stability of jet engine fuels based on hydrocracking of vacuum oil strips is shown.

1. Introduction
The current task of modern refining is to improve the quality of petroleum products by developing destructive processes for refining operations heavy oils and oil residues [1]. One such process is the hydrocracking of vacuum oil, which has recently been actively used by manufacturers to produce jet fuels.

Among the technologies for obtaining jet fuels (crude distillation and hydrotreated kerosene fractions), hydrocracking is the only process during which there is a radical transformation of the group hydrocarbon composition. In addition to the reactions of removal of heteroatomic compounds and hydration of olefin hydrocarbons (characteristic reactions for the hydrotreatment technology) hydrocracking process involves hydration of aromatic hydrocarbons, cracking high-molecular and naphthen compounds, dealkylation of cyclical structures and isomerization of paraffin hydrocarbons. In this way, isoparaphin-naphthene base with a low content of aromatic hydrocarbons is formed (5%) [2].

It is known that aromatic hydrocarbons inhibit the oxidation of naphthenes [3,4]. Accordingly, such a change in hydrocarbon composition would lead to increase the rate of fuel oxidation, reduce its chemical stability and storage life.

At the moment, the assessment of chemical stability in the scope of regulatory documentation requirements for the product is limited only to indirect physical and chemical indicators - the evaporation gum test, iodine test, acidity - which are point characteristics that do not allow us to assess the dynamics of changes in the chemical stability of jet fuels.

2. Chemical stability of jet fuels obtained by various production technologies
In FAE "The 25th State Research Institute of Chemmotology of Ministry of defense of Russian Federation" a method for assessing chemical stability was developed. The essence of method is to heating (100°C) fuel (75 cm³) in a closed space at elevated oxygen pressure (400 kPa) in the presence of 0.125 g initiator of oxidation (dicumyl peroxide) with continuous recording of temperatures, pressures...
and estimates (mass of oxygen absorbed $\Delta m_{O_2}$, maximum oxygen absorption rate $v_{max}$) [5]. The organization standard was developed for the method and its metrological certification was performed in accordance with GOST 8.563-2009 and GOST R ISO 5725-2002 [6].

The study of commercial fuels for jet engines of various production technologies using the developed method (table 1) made it possible to establish that fuels for jet engines based on kerosene fractions of hydrocracking have estimates of chemical stability ($\Delta m_{O_2} = 612.5…618.4 \mu g$, $v_{max} = 0.599…0.613 \mu g/min$) is 2-3 times worse than jet fuels obtained by hydrotreating kerosene fractions ($\Delta m_{O_2} = 173.8…386.5 \mu g$, $v_{max} = 0.186…0.354 \mu g/min$), and 6 times worse than fuels based on kerosene fractions of direct distillation oil ($\Delta m_{O_2} = 35.0…52.1 \mu g$, $v_{max} = 0.058…0.066 \mu g/min$).

| №  | Sample, fuel processing technologies                        | Chemical stability |                 |
|----|------------------------------------------------------------|--------------------|----------------|
| 1  | TS-1 jet fuel, straight-run KF (kerosene fraction)          | $35.0$             | $0.066$        |
| 2  | TS-1 jet fuel, straight-run KF                              | $39.6$             | $0.058$        |
| 3  | TS-1 jet fuel, straight-run KF                              | $52.1$             | $0.059$        |
| 4  | TS-1 jet fuel, demercaptanized KF, antioxidant additive, anti-wear additive | $24.0$             | $0.058$        |
| 5  | TS-1 jet fuel, demercaptanized KF, straight-run KF, antioxidant additive, anti-wear additive | $42.2$             | $0.058$        |
| 6  | TS-1 jet fuel, straight-run KF, hydrocracked KF, antioxidant additive, anti-wear additive | $30.1$             | $0.058$        |
| 7  | TS-1 jet fuel, straight-run KF, hydrotreated KF, antioxidant additive, anti-wear additive | $121.5$            | $0.109$        |
| 8  | RT jet fuel, hydrotreated KF, antioxidant additive, anti-wear additive | $173.8$            | $0.161$        |
| 9  | RT jet fuel, hydrotreated KF, antioxidant additive, anti-wear additive | $361.5$            | $0.203$        |
| 10 | RT jet fuel, hydrotreated KF, antioxidant additive, anti-wear additive | $386.5$            | $0.354$        |
| 11 | RT jet fuel, hydrotreated KF, antioxidant additive, anti-wear additive J | $357.8$            | $0.186$        |
| 12 | RT jet fuel, hydrotreated KF, antioxidant additive, anti-wear additive | $287.1$            | $0.301$        |
| 13 | TS-1 jet fuel, KF hydrocracked, antioxidant additive, anti-wear additive | $612.5$            | $0.613$        |
| 14 | RT jet fuel, KF hydrocracked, antioxidant additive, anti-wear additive | $695.6$            | $0.713$        |
| 15 | RT jet fuel, KF hydrocracked, KF hydrotreated, antioxidant additive, anti-wear additive | $621.7$            | $0.587$        |
| 16 | TS-1 jet fuel, KF hydrocracked, antioxidant additive, anti-wear additive | $618.4$            | $0.599$        |
The high chemical stability of jet engine fuels based on straight-run kerosene fraction is explained by the increased content of heteroatomic compounds in their composition, which are natural inhibitors of oxidation [7]. Hydrotreated jet engine fuels, which have content of natural oxidation inhibitors, are stabilized using an antioxidant additive [8].

The low level of chemical stability of fuels for jet engines obtained by hydrocracking of vacuum oil strips is explained by a change in the hydrocarbon medium of fuels of a similar composition compared to “traditional” fuels of crude distillation of oil and hydrotreating of kerosene fractions.

Chromato-mass spectrometric analysis of fuel samples from various production technologies (table 2) showed that straight-run and hydrotreated fuels contain ≈30% of normal alkanes, ≈20% of isoalkanes and ≈17% of naphthenes protected from oxidation by a high content of aromatic hydrocarbons (≈20%). Hydrocracked fuels are characterized by a low content of normal alkanes (≈15%), a high content of isoalkanes that are more prone to oxidation (≈33%), and a high content of naphthenes (≈46%) with a low content of monoaromatic hydrocarbons (≈4%) and polycyclic aromatic hydrocarbons.

Table 2. Hydrocarbon composition of jet engine fuels

| Groups of hydrocarbons | Straight-run jet fuel | Hydrotreatment technology | Hydrocracking of vacuum oil strips |
|-----------------------|-----------------------|---------------------------|-----------------------------------|
| Alkanes               |                       |                           |                                   |
| - linear alkane       | 33.47                 | 29.88                     | 15.04                             |
| - nonlinear           | 22.38                 | 20.51                     | 33.11                             |
| Naphthenes            |                       |                           |                                   |
| - monocyclic          | 17.00                 | 15.65                     | 35.92                             |
| - polycyclic          | 2.70                  | 4.42                      | 10.13                             |
| Aromatic hydrocarbons |                       |                           |                                   |
| - monocyclic          | 16.19                 | 21.87                     | 3.99                              |
| - polycyclic          | 0.70                  | 1.51                      | 0                                 |
| Unsaturated hydrocarbons | 0.69                 | 0.01                      | 0.95                              |

3. **Chemical stability of mixtures of individual hydrocarbons**

Using the developed method, mathematical models (1) and (2) were constructed, reflecting the relationship between chemical stability and individual hydrocarbon composition:

\[
\Delta m_{o_2} = 459.6 + 176.4x_1 - 56.9x_2 - 22.0x_3 - 87.7x_1x_2 + 19.7x_1x_3 - 35.2x_2x_3
\]

\[
v_{\text{max}} = 0.291 + 0.116x_1 - 0.028x_2 - 0.003x_3 + 0.003x_1x_2 + 0.003x_1x_3 - 0.015x_2x_3 + 0.016x_1x_2x_3
\]

where \(x_1\) is the content of naphthenes (from 30 to 70 % wt.), \(x_2\) is the content of bicyclic hydrocarbons (from 1 to 4% wt.), \(x_3\) is the content of monoaromatic hydrocarbons (from 5 to 15% wt.).

These mathematical models allowed us to study the inhibitory effect of aromatic hydrocarbons (figure 1, 2) and establish that, the chemical stability estimates are at a low level, when the content of naphthenic hydrocarbons in the mixture is more than 50%, regardless of the content of aromatic hydrocarbons, (\(\Delta m_{o_2} > 400 \mu g, v_{\text{max}} > 500 \mu g/\text{min}\)).
The inhibitory effect of bicyclic aromatic hydrocarbons is clearly manifested when the mixture contains 15% monoaromatic hydrocarbons. When the mixture contains 5% monoaromatic hydrocarbons, the inhibitory effect of polyaromatics appears only when the content of naphthenes is more than 50%.

4. Accelerated laboratory aging of jet fuels
The chemical stability of jet fuels has also been investigated under accelerated laboratory aging. Artificial storage in the laboratory was carried out for 30 days, keeping samples with fuel in a thermostat at a temperature of 100 °C (figure 3) and controlling the change in indicators “acidity” and “evaporation gum test” (table 3).
The rate of oxidation products accumulation for fuels based on kerosene fractions obtained by hydrocracking is 45 times higher in terms of "acidity" and 17 times higher in terms of "evaporation gum test" than the rate of oxidation products accumulation in fuels obtained by crude distillation and hydrotreating of kerosene fractions (table 3).

### Table 3. Results of accelerated laboratory aging of jet fuels

| Sample                                                                 | Chemical stability | Acidity (GOST 5985) | Evaporation gum test (GOST 8485) |
|------------------------------------------------------------------------|-------------------|---------------------|----------------------------------|
| - 100 % straight-run jet fuel                                          | 36.6              | 0.058               | 0.05                             |
| - 100 % hydrotreated kerosene fraction, antioxidant additive, anti-wear additive | 193.9             | 0.179               | 0.03                             |
| - 100 % hydrotreated kerosene fraction, antioxidant additive, anti-wear additive | 675.1             | 0.637               | 1.37                             |
| - 100 % hydrotreated kerosene fraction, antioxidant additive, anti-wear additive | 36.6              | 0.066               | 1.1                              |
| - 100 % hydrotreated kerosene fraction + 0.0034 % Agidol-1             | 0.058             | 0.051               | 0.512                            |
| - 100 % hydrotreated kerosene fraction + 0.0040 % Agidol-1             | 0.203             | 0.203               | 0.203                            |
| - 100 % hydrotreated kerosene fraction + 0.0040 % Agidol-1             | 0.559             | 0.559               | 1.2                              |

The output of estimated fuel indicators based on kerosene hydrocracking fractions beyond the limits specified in GOST 10227 is 5 times faster in relation to crude distillation fuel and 3.5 times faster in relation to hydrotreated fuel.

### 5. Efficiency of antioxidant additive Agidol-1 introduction

The estimation of efficiency of antioxidant additive Agidol-1 introduction (table 4) in kerosene fractions of hydrogenation processes by developed method showed that a demercaptanized kerosene fraction has high level of chemical stability without added antioxidant, at the level of straight-run fuel.

### Table 4. Efficiency of antioxidant additive Agidol-1 introduction

| Sample                                | θ_max (μg/min) | Additive efficiency coefficient |
|---------------------------------------|----------------|-------------------------------|
| Kerosene fraction of hydrodemercaptanization | 0,066          | 1,1                           |
| Kerosene fraction of hydrodemercaptanization + 0,0034 % Agidol-1 | 0,058          | 1,1                           |
| Kerosene fraction of hydrotreatment    | 0,512          | 2,5                           |
| Kerosene fraction of hydrotreatment + 0,0040 % Agidol-1 | 0,203          | 2,5                           |
| Kerosene fraction of hydrocracking     | 0,670          | 1,2                           |
| Kerosene fraction of hydrocracking + 0,0040 % Agidol-1 | 0,559          | 1,2                           |

The most effective is the introduction of Agidol-1 in the hydrotreated kerosene fraction. This allows to increase the chemical stability of the hydrotreated fraction by 2.5 times.

The introduction of Agidol-1 into the kerosene fractions of hydrocracking makes it possible to increase their chemical stability by only 1.2 times. Moreover, if you look at the curve of the dependence
of the maximum oxygen absorption rate on the time of the test (figure 4), you can see that regardless of the introduction of an antioxidant, the sample is completely oxidized.

![Graph]

**Figure 4.** The effect of antioxidant additives on the chemical stability hydrocracked kerosene fraction

It is known that the maximum storage period for jet fuels based on the kerosene fraction of crude distillation is 10 years, and fuels based on hydrotreated kerosene fractions is 7 years [9]. The guarantee period for storage of jet fuel is 5 years. Given that the chemical stability of jet fuel based on kerosene fractions of hydrocracking is two times lower than the chemical stability of hydrotreated jet fuel, it can be assumed that the storage life of hydrocracking fuels will be two times lower than that of hydrotreated fuels, i.e. 3,5-4 years.

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