JET FUELS DEGRADATION UNDER SEVERE THERMAL LOADS

DEGRADACJA PALIW LOTNICZYCH W WARUNKACH WYSOKICH TEMPERATUR

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Abstract: Paper presents research results of jet fuels thermal degradation exposed to different thermal loads. This problem is especially important as it influences safety of aircraft operation. Jet fuel in modern engines is used in heat transfer and cooling of different construction elements. Together with new engines' construction and materials used thermal loads affecting jet fuel become more severe, and thus in aircraft fuel system not well understood phenomena occur, resulting with plugging injectors, valves and affecting elastomers. They affect engine operation and should be well and carefully described and understood to prevent them. Research results presented here are the first data in Poland dealing with jet fuels' thermal degradation problem. Article is aimed to present the mechanism of jet fuel thermal degradation under different temperatures. The project has been funded by National Science Centre granted with decision no. DEC-2011/01/D/ST8/06567.

Keywords: jet engine, jet fuel, thermal stability, oxidation, thermal degradation

Streszczenie: Artykuł dotyczy problemu degradacji termicznej paliw lotniczych w warunkach oddziaływania wysokich temperatur. Jest to istotne zagadnienie z uwagi na jego bezpośredni wpływ na bezpieczeństwo eksploatacji statków powietrznych. W silnikach lotniczych paliwo wykorzystywane jest nie tylko do zasilania, ale także uczestniczy w odprowadzaniu ciepła oraz chłodzeniu elementów konstrukcyjnych. Należy zwrócić uwagę, iż w związku z intensywnym rozwojem konstrukcji lotniczych elementy silników pracują w warunkach coraz wyższych oddziaływań cieplnych, a obecnie stosowane paliwo lotnicze jest wykorzystywane do zasilania konstrukcji lotniczych już od ponad 30 lat. Dlatego też w eksploatacji coraz częściej obserwowane są nie w pełni wyjaśnione zjawiska zatykania dyszy wtryskiwaczy, blokowania zaworów oraz negatywnego oddziaływania na uszczelnienia i elastomery. Wyniki zaprezentowane w niniejszym artykule są efektem pierwszych w Polsce badań związanych z problemem degradacji termicznej paliw lotniczych. Projekt badawczy został sfinansowany ze środków Narodowego Centrum Nauki przyznanych na podstawie decyzji numer DEC-2011/01/D/ST8/06567.

Słowa kluczowe: silnik turbinowy, paliwo lotnicze, stabilność termiczna, utlenianie, degradacja termiczna.

1. Introduction

Modern jet engines operate at high temperatures for increased efficiency, and therefore generate more heat that needs to be removed. As jet fuel serves not only for power generation during combustion, but also as a coolant - may be exposed to high temperatures before being burned in the engine. Thermal loads in the fuel delivery system of advanced aircraft can reach even 500°C. Such high temperatures accelerate the reactions of hydrocarbons in jet fuel and as a result carbonaceous deposits can form in bulk fuel or on metal surfaces.

It is worth to notice that today the same fuel is used to power jet engines that had been used over 30 years ago all over the world. In Polish aviation Jet A-1 fuel was implemented in 1990s as a replacement of light fuels used to power Russian aircrafts. As aviation industry develops new constructions, today situation is that new and advanced aircrafts and engines are powered with the same fuel that aviation has been using for years. But – except from fuel – almost everything has changed: materials, design, construction, thrust etc. Please also note that in today's aviation both advanced and old technique is being operated on the same fuel. These are the reasons that during new aircrafts operation some not well known, described and understood phenomena are observed, resulting with clogging the filters and injector nozzles, changing spray pattern and temperature distribution in combustion chamber, blocking valves, damaging elastomers and seals in fuel systems. Most of them are effects of thermal loads that jet fuel is exposed to.

Jet fuels specifications are still changing [1-3]. Every year new editions are being issued. Some modifications are minor and do not influence fuels' operational properties. Others – like eligibility of FAME content up to 50 ppm or acceptance of synthetic components up to 50% (V/V)- however technically approved - may impact fuels' properties during storage or in aircrafts operation. New components will have impact on chemical reactions within the fuel under different conditions, will also result with phenomena not well described or recognized.

In Poland jet fuels are used commonly in civil and military aviation, but no detailed studies have been done on their operational parameters and changes in fuels' properties under severe conditions occurring in real jet engines – fuels have been adapted together with new aircrafts implemented from 1990s. There is a clear reason for research in this area, both for knowledge of conventional Jet A-1 fuel behavior and for good understanding of future fuels' behavior and phenomena that will surely occur after those fuels' implementation in aviation.

The subject of presented research is to investigate mechanisms of conventional jet fuel breaking down and changing chemical structure in conditions similar to those occurring in real jet engine – high system pressure and temperatures exceeding 150°C.

2. Experimental set-up

To investigate some aspects of jet fuels' thermal degradation, special test stand has been developed and built in the Air Force Institute of Technology. The rig has been described in [4], general view is presented below.

Fig. 1 General view of experimental test stand to investigate jet fuels' thermal degradation, with different sections: Pumping section – red; Heating section - yellow; Cooling section - blue; Data acquisition section – white.

Commercially available jet fuels from different production processes (Hydrotreatment and Merox) have been obtained and their chemical composition has been determined. Prior to thermal stressing approx. 1000ml sample of each fuel have been prepared. Both samples have been filtered through 0,45 μ m membrane filter to remove any solid contaminants. To test the fuel as much as possible similar to the fuel delivered to aircrafts, samples have not been deoxygenated.

Test plan assumed that approx. 720ml of each fuel will be stressed in wide range of temperatures (samples stressed from 200 to 500°C), with constant pressure value of 3,5MPa in the test stand and constant fuel flow speed of 3ml/min.

As solids and peroxides forming in fuel may be the evidence of thermal degradation (oxidation or thermal decomposition) and may influence other properties, after each thermal stressing following parameters have been measured and compared:

- Solid contaminants content on 0,8 μ m membrane filter according to ASTM D5452;
- Hydroperoxide number according to ASTM D3703;
- Total acid number according to ASTM D664;
- Conductivity according to ASTM D2624.

Results of research are presented below.

3. Experimental results and discussion

Chemical composition of both fuels is presented on fig. 2.

Fig. 2 Chemical composition of fuels being tested

As it can be clearly seen, both fuels have similar content of hydrocarbons groups (n-paraffins, naphtenes, iso-paraffins, aromates), but difference in distribution of C atoms number in hydrocarbons is an evidence, that their chemical composition (individual hydrocarbons content) is different – especially for C12-C15 hydrocarbons).

Thermal stressing of both fuels allowed for:

- observation of thermal degradation process:
- comparison, how differences in chemical composition resulting from different production processes affect both fuels' thermal degradation process.

Results are presented below on fig. 3-6. Values of each parameter have been normalized to [0, 1] range.

Fig. 3 Hydroperoxide number of thermally stressed jet fuels (flow speed 3ml/min, pressure 3,5MPa)

Hydroperoxides and peroxides are early precursors in the oxidative degradation of hydrocarbons. In Merox fuel, as compared with Hydrotreated, peroxides formed at lower temperatures, and rate of their formation was much higher. It was observed, that with increase of stressing temperature and thus increase of dissolved oxygen consumption for oxidation process:

- peroxides decompose to form radicals to continue oxidation process;
- as dissolved oxygen is still present in the fuel, peroxides continue to oxidize;
- with increasing temperature (above 200°C for tested Merox fuel, and above 250°C for Hydrotreated fuel) increased decomposition rate of hydroperoxides outstrips its formation rate and this depletes the hydroperoxide population before they can participate in the autooxidation chain;
- For temperatures 400-450°C the rate of hydroperoxides formation decreases significantly as almost total dissolved oxygen has been consumed for autooxidation mechanism and hydroperoxide thermal decomposition rate in this range of temperatures is high;
- at higher temperatures (450°C and above) autooxidation mechanism resulting from peroxides formation and decomposition is negligible.

Fig.4 (below) presents quantity of solids formed in tested fuels after their thermal stressing in wide range of temperatures.

Fig. 4 Solid contaminants formed in thermally stressed jet fuels (flow speed 3ml/min, pressure 3,5MPa)

Some differences are clearly visible, especially for higher (above 450°C) temperatures:

- in lower temperatures for both fuels maximum similar value of solids formed was observed (250°C). In Merox fuel particulates form rapidly around 250°C as in Hydrotreated fuel their formation took place in wider range of temperatures (200-250°C);
- for temperatures between 350°C and 400°C decrease in solids formed in fuels was observed;
- from 450°C and above significant increase in solid particulates formed was observed, with much higher rate for Hydrotreated fuel.

On fig. 5 (below) changes of Total Acid Number (TAN) values are presented.

*Fig. 5 Total Acid Number (TAN) values of thermally stressed jet fuels
(flow speed 3ml/min, pressure 3,5MPa)*

Changes of acidity of both fuels are similar, but some differences can be distinguished:

- up to 250°C continuous increase of acidity is observed, with maximum for 250°C, suggesting formation of weak organic acids. In this range those acids accumulate due to the oxidation of fuel hydrocarbons;
- temperatures between 250°C and 400°C – as temperature increases, oxygen is consumed and weak acids are thermally decomposed;

- temperatures of 400°C and above – non radical products (solids and gums) containing acidic substances are formed, and sulfur compounds present in fuel are involved in this process. The increase of acidity is much higher for Merox fuel as it contained significantly more total sulfur (0,2% m/m) than Hydrotreated fuel (0,03% m/m).

Fig. 6 (below) presents changes in conductivity of both fuels. Comparing data presented on fig. 6 clear statement can be made, that conductivity changes for both fuels are identical. The reason of that phenomena is the same static dissipater additive (SDA) contained in both fuels, with toluene as major ingredient. As temperature increases, toluene is oxidized and decomposed, and thus SDA is depleted resulting with decrease of fuels' conductivity. As it comes out from literature [6], in approx. 350°C toluene completely decomposes into H₂O and CO₂, via fragments of ethylene, butane, propene and butadiene – and results obtained in this project clearly present it. Additionally, during oxidation of toluene – as dissolved oxygen is still present in the fuel below 350°C – weak organic acid is formed (benzoic acid C₆H₅COOH), being one of factors influencing acid number increase in the range of temperatures below 350°C (see fig. 5).

Fig. 6 Conductivity of thermally stressed jet fuels
(flow speed 3ml/min, pressure 3,5MPa)

4. Summary and conclusions

Jet fuels' thermal degradation process is a complex phenomena, comprising different aspects and mechanisms. However – even as jet fuels' chemical composition can vary depending on a batch, production process, oil refinery and additives [5] - some general conclusions on the basis of research presented here can be made.

Jet fuels' thermal degradation can be divided into three major stages:

- below 350°C - autooxidation stage;
- between 350 °C and 400 °C - transition regime;
- above 400 °C - pyrolytic regime.

Autooxidation stage is based on free radical chain mechanism and dissolved oxygen present in the fuel. Hydroperoxides are the principal primary auto-oxidation products however, they decompose at higher temperatures to form radicals which auto accelerates the oxidation process. Hydroperoxides may also react with other heteroatomic species in fuels, e.g., sulfides and disulfides, to form non-radical products that may be deposit precursors. Oxidation of fuel hydrocarbons leads to formation of weak organic acids as well as may lead to formation of other oxygenated products (ketones, alcohols, aldehydes, carbonyls), resulting in increased acidity. These products continue to oxidize (as oxygen is present) and form insoluble gums, which lead to deposits formation in autooxidation stage.

As temperature is increased and oxygen dissolved in fuel is consumed, oxidative deposition decreases because increased thermal decomposition rate of hydroperoxides outstrips its formation rate. This depletes the hydroperoxide population before hydroperoxides can participate in the autooxidation chain reaction mechanisms.

After oxygen is almost fully consumed, approx. at 350°C, there is a region of little deposition activity.

Around 400°C pyrolytic region begins. At this stage critical factor seems to be initial composition of the fuel (individual hydrocarbons) and sulphur content. Fuel thermal degradation is characterized by the breakdown of the hydrocarbon chemical bonds by pyrolytic cracking, with long paraffinic chains cracked into smaller alkanes and alkenes, that further develop into aromatic compounds and solid deposits. Detailed analysis of the fuels is required to predict thermal decomposition, as different hydrocarbons groups have individual resistance to pyrolysis. But - as deposits are formed in fuel by nucleation and growth, and compose mostly of sulphur, carbon, oxygen and nitrogen - this results in rapid increase of acidity and fuel becomes a highly corrosive agent. It is supposed that long exposure of metal elements or elastomers on particulate solids formed during pyrolysis stage will result with their degradation and corrosion of metal surfaces.

Visually process of jet fuels' thermal degradation can be presented on following graph (fig. 7). Term “products of thermal degradation” used to describe vertical axis is a general description comprising different products of jet fuels' thermal degradation, mostly solids, gums and acidic substances.

Fig. 7 Stages of jet fuel thermal degradation

5. References

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