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Toward an optimal formulation of alternative jet fuels: Enhanced oxidation and thermal stability by the addition of cyclic molecules

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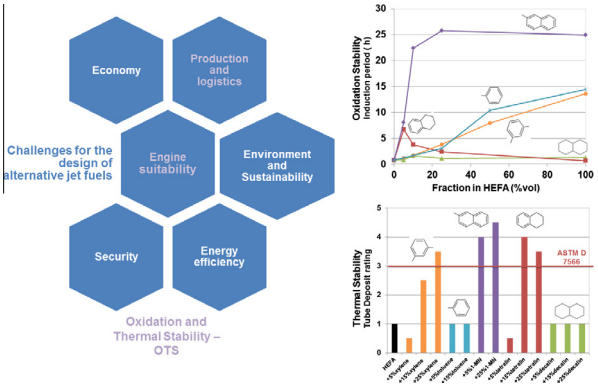
HIGHLIGHTS

- Thermo-oxidative stability is a key concern for alternative jet fuels development.
- Alternative biofuels used in jet fuels can have poor stability.
- The addition of Decalin and Tetralin improved the stability of alternative jet fuels.
- The addition of several alkylbenzenes improved the stability of alternative jet fuels.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidation and thermal stability (OTS) are key concerns for the development of alternative jet fuels, as they imply complex physical and chemical phenomena such as autoxidation, pyrolysis, cooxidation reactions and transfer-limitation. The OTS of an alternative aviation fuel was characterized using PetroOxy test from 120 to 160 °C and JFTOT test at 325 °C. The alternative jet fuel is a Synthetic Paraffinic Kerosene produced from Hydroprocessed Esters and Fatty Acids (HEFA-SPK). Results showed a high thermal stability of HEFA-SPK. However, a low oxidation stability was also observed. The oxidation stability of 8 model cyclic molecules was evaluated. Results allowed to estimate the influence of the molecular structure of cyclic molecules on liquid phase reactivity involving the number and the hydrogenation of the aromatic rings and the number and chain-length of the aromatic alkyl groups. The addition of several alkylbenzenes increased almost linearly the induction period of HEFA-SPK. Tetralin and decalin acted as inhibitors of the radical chain mechanism at low concentration, although having inherently low oxidation stability. Besides offering a better oxidation stability, the addition of specific low fractions of several alkylbenzenes, tetralin and decalin to HEFA-SPK allowed to achieve a good thermal stability as well. These molecules represent good candidates to improve OTS of HEFA-SPK. This work opens the way for the development of future fit-for-purpose formulations of alternative jet fuels with an increased fraction of renewables.

Background

Alternative jet fuels are receiving considerable attention for their potential to diversify energy sources and to reduce the impact of air transport on environment [1,2]. National and International

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Organizations have launched initiatives to increase their use in the coming years. The Biofuels Flight path project of the European Union aims to produce two million tons per year of aviation biofuels by 2020, corresponding to 3–4% of total jet fuel use in Europe. In Germany, AIREG targets 10% of alternative aviation fuels by 2025. The International Air Transport Association (IATA) estimates a realistic target of sustainable second generation bio jet to be near 3% by 2020.

The present study focuses on the oxidation and thermal stability (OTS) of a Synthetic Paraffinic Kerosene produced from Hydroprocessed Esters and Fatty Acids (HEFA-SPK) approved as synthetic blending component for alternative jet fuels. The current legislation allows its incorporation up to 50 vol% in alternative jet fuels and a minimum aromatic content of 8 wt% in the final blend (ASTM D7566) to ensure material compatibility. However, this level is conservative and does not take into account the influence of the molecular structure of aromatics on both material compatibility and OTS. For example, alkylnaphthalenes impact more significantly O-Nitrile rubber seal swell than alkylbenzenes [3]. Aromatics may produce an oxidation promoting or retarding effect [4]. They also influence the thermal stability (or deposit formation at high temperature), which is a function of the molecular structure and the concentration of reactants as well as of the temperature regime [5].

In this study, we investigated the OTS of HEFA-SPK and evaluated the influence on OTS of the addition of several pure cyclic compounds naturally present in conventional jet fuels. In the course of the work, oxidation stability and thermal stability measurements were carried-out using PetroOxy from 120 to 160 °C and JFTOT test at 325 °C, respectively. Results were analyzed and compared with previous literature work in order to improve the understanding of the oxidation and cooxidation kinetics of cyclic molecules and to define the best candidate molecules to improve OTS of paraffinic fuels.

1. Materials and methods

1.1. PetroOxy test

The PetroOxy test is a widely used measurement for the oxidation stability of diesel and biodiesel [6]. Recently, it has been successfully employed for jet fuel oxidation stability studies [7,8]. The oxidation status is monitored through oxygen uptake by the fuel. A small sample (5 ml) of a fuel is introduced in a closed and heated test cell under 7 bar of oxygen pressure. The decrease of oxygen pressure, measured continuously in the test cell, reflects oxygen consumption by the oxidation process. The induction period (IP) is defined by the time necessary to reach 10% of the pressure drop as illustrated in Fig. 1. At the IP, oxygen remains sufficiently in excess within the test cell [8] permitting the use of the obtained data for global kinetics assessment. The repeatability error, calculated from 25 different samples tested at different temperatures repeated 2–3 times each, is related to IP according to: $\tau_{IP} = 0.014\text{-}IP + 1.229$, indicating a relative error of about 2%. This value is in agreement with the level indicated in PetroOxy standard for middle distillate fuels (ASTM D 7545) as well as previously published results by Araujo et al. [9]. Tests were conducted from 120 to 160 °C for individual reagents, at 140 and 160 °C, for HEFA-SPK/cyclic molecules mixtures, and at 140 °C for n-decane/cyclic molecules mixtures.

1.2. Jet fuel thermal oxidation tester – ASTM D3241

The Jet Fuel Thermal Oxidation Tester (JFTOT) is a standard test procedure used to assess the thermal stability of conventional and alternative aviation fuels. The details of this method are provided elsewhere [10]. JFTOT rates jet fuels stability utilizing two metrics: filterable liquid particulates are monitored by pressure drop through a filter (*dP* filter), and surface deposits on the test tubes are assessed by visual rating after the test. Tests were carried on at 325 °C meeting the specification of HEFA-SPK (ASTM D 7566 – 11 a).

1.3. Fuel matrix

The reagents tested in this study were a commercial fossil Jet A-1, three alternative paraffinic Hydroprocessed Esters and Fatty Acids (HEFA-SPK) and their blends with Jet A-1 at 25% and 75 vol %. Besides, several model cyclic molecules were evaluated individually and in mixture with HEFA-SPK and n-decane, to better assess the complex interaction of cyclic molecules present in fossil jet fuel with alternative fuels composed mainly of linear and branched alkanes.

1.3.1. Conventional Jet A-1

The conventional Jet A-1 is a hydrotreated ultra-low sulfur jet fuel supplied by Total. In accordance with the regulation for hydrotreated jet fuels, an antioxidant additive was added. The GC2D of Jet A-1 indicates a carbon chain-length distribution ranging from C8 to C16 and centered on C10. It contained 17 wt% normal alkanes, 27 wt% branched alkanes, 30 wt% cyclic alkanes and 25 wt% aromatics as summarized in Table 1. Aromatics are composed of C8–C11 mono-aromatics, namely, xylene (and/or ethylbenzene) at 3.9 wt%, propyl-, butyl- and pentyl-benzene at 8.3 wt%, 4.1 wt% and 2.2 wt%, respectively. Derivatives of indane and tetralin may also be present at 4.3 wt%. Naphthenes, distributed from C9 to C13, are composed of monocyclic and bicyclic molecules at 22% and 7 wt%, respectively.

1.3.2. Synthetic Paraffinic Kerosene – Hydroprocessed Esters and Fatty Acids (HEFA-SPK)

Three additive-free HEFA-SPK (HEFA-50, HEFA-30 and HEFA-20) were studied. They are composed mainly of linear and branched alkanes (>99.5 wt%). HEFA-20 and HEFA-30 have around 90 wt% of branched paraffins and HEFA-50 has a sensibly higher fraction (93 wt%). Fig. 2 illustrates their composition according to carbon number. The distribution of branched alkanes has a bimodal shape centered on C12 and C16–C17. The distribution of linear alkanes presents a bimodal curve centered on C10–C11 and C17 for HEFA-20 and HEFA-30 and a C11-centered unimodal distribution for HEFA-50.

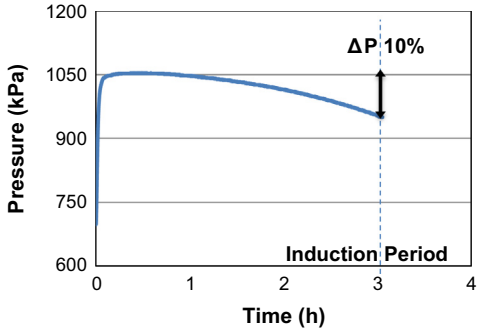

Fig. 1. Illustration of pressure variation during the oxidation of n-decane at 140 °C, induction period (IP) equals 3.05 h.