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Towards an optimal formulation of alternative jet fuels: Enhanced Oxidation and Thermal Stability by the addition of cyclic molecules

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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 120-160°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.

Keywords

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 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, alkynaphthalenes 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 120-160°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 (5ml) 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 Figure 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: \( \tau_{IP} = 0.014 \times IP + 1.229 \), indicating a relative error of about 2%. This value is in agreement with the level indicated in PetroOxy standard for middle distillate fuels (ASTM D7545) 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.
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 JetA-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.

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-C13, are composed of monocyclic and bicyclic molecules at 22% and 7%wt, respectively.
Table 1: Chemical composition of Jet A-1 and HEFA-SPK

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>JET-A1</th>
<th>HEFA-20</th>
<th>HEFA-30</th>
<th>HEFA-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content</td>
<td>%m/m</td>
<td>86.43</td>
<td>84.77</td>
<td>84.76</td>
<td>84.71</td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>%m/m</td>
<td>13.57</td>
<td>15.23</td>
<td>15.24</td>
<td>15.29</td>
</tr>
<tr>
<td>Molar weight</td>
<td>g/mol</td>
<td>140.8</td>
<td>201.69</td>
<td>198.53</td>
<td>188.41</td>
</tr>
<tr>
<td>N-paraffins</td>
<td>%m/m</td>
<td>17.03</td>
<td>8.93</td>
<td>9.52</td>
<td>6.73</td>
</tr>
<tr>
<td>I-paraffins</td>
<td>%m/m</td>
<td>27.25</td>
<td>90.65</td>
<td>90.41</td>
<td>93.25</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>%m/m</td>
<td>29.39</td>
<td>0.02</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Mono-aromatics</td>
<td>%m/m</td>
<td>25.65</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Di-aromatics</td>
<td>%m/m</td>
<td>0.69</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Unknowns</td>
<td>%m/m</td>
<td>0</td>
<td>0.41</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>%m/m</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**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). Figure 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.
Pure reagents: To evaluate the impact of molecule structure on stability, several pure molecules were evaluated. Five alkylaromatics presenting different branching configurations and number of benzene cycles, namely, toluene, xylene, n-propylbenzene (n-PB) and 1,2,4-trimethylbenzene (TMB) and 1-methylnaphtalene (1-MN). Tetralin, n-propylcyclohexane and decalin are tested to evaluate the impact of the partial or total hydrogenation of aromatics. Purity of the chemical products is above 96% for all reagents. N-decane and n-dodecane are commonly used as model surrogates for middle-distillate transport fuels[11][12]. In this work, we selected n-decane as more representative of the kerosene cut. The list of reagents purity and additional information are summarized in Table 2.

Table 2: List of the pure reagents tested

<table>
<thead>
<tr>
<th>Chemical family</th>
<th>Molecule designation</th>
<th>Abbreviation</th>
<th>Purity</th>
<th>Molecular weight</th>
<th>Molecular Formula</th>
<th>Skeletal formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkane</td>
<td>n-decane</td>
<td>n-C10</td>
<td>99</td>
<td>212.4</td>
<td>C10H22</td>
<td></td>
</tr>
<tr>
<td>Cyclic alkane</td>
<td>n-propylcyclohexane</td>
<td>n-PCH</td>
<td>99</td>
<td>126.2</td>
<td>C9H18</td>
<td></td>
</tr>
<tr>
<td>Cyclic alkane</td>
<td>decalin</td>
<td>decalin</td>
<td>98</td>
<td>138.3</td>
<td>C10H20</td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>toluene</td>
<td>toluene</td>
<td>97</td>
<td>92.1</td>
<td>C7H8</td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>xylene</td>
<td>xylene</td>
<td>97</td>
<td>106.2</td>
<td>C8H10</td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>1,2,4 trimethylbenzene</td>
<td>TMB</td>
<td>98</td>
<td>120.2</td>
<td>C9H12</td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>n-propyl-benzene</td>
<td>n-PB</td>
<td>98</td>
<td>120.2</td>
<td>C9H12</td>
<td><img src="image" alt="n-propyl-benzene" /></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------</td>
<td>------</td>
<td>-----</td>
<td>-------</td>
<td>-------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Aromatic</td>
<td>tetratin</td>
<td>tetratin</td>
<td>99</td>
<td>132.2</td>
<td>C10H12</td>
<td><img src="image" alt="tetratin" /></td>
</tr>
<tr>
<td>Aromatic</td>
<td>α-methyl-naphthalene</td>
<td>1-MN</td>
<td>96</td>
<td>142.2</td>
<td>C11H10</td>
<td><img src="image" alt="α-methyl-naphthalene" /></td>
</tr>
</tbody>
</table>

**Blends:** Mixtures of the abovementioned pure reagents with HEFA were carried out at three blending rates: 5, 10 and 25%vol. The first two are situated on both sides of the current specification for minimum aromatics content for alternative jet fuels (8%wt), whereas, the last value corresponds to the aromatic content of the conventional Jet A-1 used in the present study. Only HEFA-SPK-30 was used for the mixtures as the three HEFA-SPK presented very similar oxidation behaviors (section 3.1.1). Mixtures of reagents with n-decane were also studied at 5, 10, 25 and 50%vol.

## 2 RESULTS AND DISCUSSION

### 2.1 Evaluation of the oxidation stability of HEFA-SPK, Jet A-1 and their blends

Figure 3.a presents the induction period (IP) as a function of the inverse of temperature (1000/T). The logarithm of IP is a linear function of the inverse of temperature indicating a typical Arrhenius trend of the global reactivity. The IPs of the three HEFA were similar in the temperature range investigated. This may result from either similar reactivity of the paraffins composing HEFA (although there are small changes in the fraction of normal and branched alkanes and chain length distribution), or compensating variances. The IP of HEFA is 2-3 times lower than that of jet fuel. This may be explained by the difference in chemical composition, mainly; cyclic compounds (aromatics/naphthenes) present at 55%wt in Jet A-1 that have different reactivity compared to paraffins. Besides, Jet A-1 contains antioxidant additives and, possibly, other naturally occurring antioxidants, heteroatoms or contaminants that can influence its reactivity as well [13][14]. Figure 3.b illustrates the effect of adding Jet A-1 on HEFA oxidation stability. We observe a non-linear and non-monotonous variation of the IP due to the addition of Jet A-1. First, IP increases to reach a maximum at intermediate concentration (25-75%vol). We note that the oxidation stability of HEFA/Jet A-1 mixtures is higher than that of Jet A-1 for an added fraction above 25%vol of Jet A-1.

In the next part of the study, we focus on the impact of cyclic molecules on OTS of HEFA, in an attempt to assess the non-linear, oxidation-inhibiting behavior observed with HEFA/Jet A-1 blends.
2.2 Evaluation of the oxidation stability of cyclic molecules

The oxidation stability of several cyclic pure compounds was evaluated from 120 to 160°C. Figure 4 illustrates the induction period as a function of the inverse of temperature (1000/T) and Figure 5 illustrates the influence of molecule structure on IP at 140°C.

2.2.1 Oxidation stability of alkylaromatics

1-MN has almost twice as high induction period as toluene (Figure 5.a) in spite of the weaker α C-H Bond Dissociation Energy (BDE) of alkynaphthalenes compared to structurally-related alkylbenzenes (2-3 kcal/mol)[15]. This trend can be associated to two phenomena:

1. **an autoretarding effect**: among 1-MN oxidation products, some have an oxidation inhibiting effect [16]. For example, methynaphthoquinones were identified by Igarashi et al.[15] as the most likely autoxidation retarders formed during methynaphthalene oxidation, which can trap alkyl radicals R° more effectively than peroxy radicals ROO°.

2. **a self-inhibiting effect**: the decomposition methynaphthoxyl radical can be responsible of first order chain termination. This radical is produced mainly by the decomposition of an intermediate radical formed by the addition of 1-MN peroxide to the naphthalene ring. This trend is amplified at higher temperature [15].

The IP of n-propylbenzene (n-PB) is 50% lower than that of toluene (Figure 5.c). It is mostly accepted that increasing the normal chain-length reduces the oxidation stability of alkylaromatics; the global reactivity of n-PB was found to be 3 times higher compared to that of toluene at 60°C[17]. Similarly, IP of alkylbenzenes having C5 to C18 side chain-length measured by Zuidema[4] presented a quasi linear dependency of IP with the side chain-length. This can be associated partly with the higher ratio of secondary-to-primary carbon atoms, the former having a lower C-H BDE favoring H-abstraction.
reactions. Similar behavior is known for linear alkanes with increased reactivity along with the chain length. The rate of consumption measured by Gernigon[18] increased with chain length for C10 to C14 n-alkanes.

IP data of toluene, xylene and TMB (Figure 4.a) indicate a small influence of the number of methyl groups on the benzene ring. IP of xylene and toluene are sensibly close from 120-160°C. IP of TMB was 40% different from that of toluene from 120-160°C. Figure 5.b compares the three reagents along with benzene measured elsewhere[19] at 140°C showing a small influence on IP of the number of methyl groups. Note however that Opeida[20] observed an increase of the global reactivity with the number of methyl groups on the benzene ring at a lower temperature range (60°C).

Figure 4: Induction period of pure reagents, HEFA-SPK and n-decane function of inverse temperature from 120-160°C. a) alkylaromatics, b) napthenes and tetralin. Symbols: full diamonds †: 1-MN, full circles •: xylene, star *: toluene (almost identical to xylene), blank diamonds ○: n-PB, full squares ■: tetralin, full triangles ▲: decalin, cross +: n-PC, bold solid line: n-decane and bold broken line: HEFA-SPK-30.
2.2.2 Oxidation stability of cyclic alkanes and tetralin

Figure 4.b presents the IP of cyclic alkanes, namely, decalin and n-propylcyclohexane (n-PC) as well as tetralin from 120-160°C. In comparison with n-PB, n-PC presents a lower IP especially at high temperature (4 times at 140°C). The IP of decalin was roughly similar to n-PC except at low temperature. Previous works comparing aromatics versus their hydrogenated derivatives, e.g. cyclohexane / benzene [19], decalin or tetralin/naphthalene [4] noted a higher stability of aromatics.

2.2.3 Summary

The oxidation stability of the tested cyclic compounds showed a significant influence of the molecular structure. They can be ranked as follows according to induction period (IP) criterion, alkylaromatics >> n-decane > cyclic alkanes > HEFA-SPK > tetralin at 140°C. However, temperature can have a strong influence on oxidation stability for paraffins, cyclic alkanes and tetralin in comparison with alkylaromatics. For example, n-decane has an oxidation stability close to several alkylaromatics, namely, toluene, xylene and n-PB at low temperature (120°C), however it decreases significantly with temperature.

2.3 Study of the Cooxidation of HEFA-SPK with cyclic compounds

In this section, the oxidation stability of binary mixtures of HEFA-SPK with cyclic compounds is evaluated. A parallel is drawn with mixtures of n-decane with the same cyclic compounds tested at 140°C. Results are presented in Figure 6.

2.3.1 Cooxidation of HEFA-SPK with alkylaromatics

A non-linear logarithmic trend was observed with the addition of 1-MN. For example, the addition of 10%vol to HEFA-SPK significantly increased the induction period (27 times) approaching the IP of 1-MN itself, in agreement with previous measurements [5][21]. This trend is particularly interesting given that the addition of low fraction (5-10%vol) of 1-MN allows to improve significantly the oxidation stability of HEFA-SPK. A comprehensive investigation by Igarashi et al. [22] on the influence of added 8-22%vol...
A fraction of naphthalene, 1-MN and 2-MN to n-hexadecane at 160°C demonstrated a retarding effect of similar amplitude for the three components. This allowed to favor the chemistry of naphthalene nucleus instead of that of methyl group chemistry [21]. The oxidation retarding effect was associated to an increase of the termination rate constant ($k_t$) through two competing pathways:

1. **a second-order termination**: through the addition of two peroxyl radicals (Reactions 3-4). This pathway is increasingly important with (methyl) naphthalene concentration.

2. **a first order chain termination**: through (methyl)naphthoxyl radical formation (Reactions 2-5).

Scheme 1 illustrates both pathways for 1-MN. At advanced oxidation progress methylnaphthalene can additionally produce oxidation inhibitors as abovementioned.

![Scheme 1: Termination major pathways in 1-methylnaphthalene / n-alkane cooxidation][22], $R$ designates all the peroxyl radicals present, n-decane (poly)peroxide, 1-MN peroxide and hydrogen peroxide.

In the case of alkylbenzenes, namely, xylene, n-PB, TMB and toluene, the induction period increased almost linearly with their volume fraction in HEFA-SPK (Figure 6.a) which suggests a different oxidation mechanism from that involved in 1-MN/paraffins mixture. The IP with 10%vol. of alkylbenzenes is about twice as high as HEFA-SPK.
2.3.2 Cooxidation of HEFA-SPK with decalin and tetralin

The IP of decalin/HEFA-SPK blends goes through a peak (twice as high as HEFA-SPK) at around 10%vol. of decalin (Figure 6.a). This result suggests an interesting inhibiting effect of decalin on the oxidation of paraffins at low concentration[23][24]. In a similar manner, the addition of tetralin to HEFA-SPK presents a pronounced retarding effect for a concentration below 10%vol. Although the intrinsic IP of tetralin is roughly equal to that of HEFA-SPK, the IP of their mixture at 10%vol is 4.6 folds higher than HEFA-SPK. The antioxidant activity of tetralin at low concentration was previously evidenced in mixtures with cumene[25]; the addition of 3% mol of tetralin reducing cumene reactivity by two third. This trend was associated to the difference in propagation and cross termination rate constants. Besides, tetralin comprises four benzylic hydrogen atoms allowing to inhibit the cooxidation reactions involving peroxy radicals in antioxidation regime[26]. In addition, tetralin oxidation can lead to the formation of several oxygen-substituted hydrogen donors, including α-tetralone and α-tetralol (phenolic compounds), that contribute to refrain oxidation progress as well[27]. Compared to decalin, tetralin is known to be a better hydrogen donor, which may explain higher oxidation retardation observed here. However, at higher concentration, the oxidation kinetics of tetralin becomes leading so the IP of Tetralin/HEFA mixture tends to that of tetralin. Previous work of Gernigon [18] support this hypothesis; the consumption rate of reactants during the oxidation of a blend of 40%wt tetralin with alkanes and aromatics showed a higher rate for tetralin consumption compared with the other constituents of the blend.

![Figure 6: Impact of the addition of cyclic compounds on the oxidation stability of: a) Cyclic compounds in HEFA-SPK at 140°C, b) Cyclic compounds in n-decane at 140°C. Symbols: full diamonds •: 1-methylnaphthalene, full circles ●: xylene, star *: toluene, blank squares☐: 1,2,4, trimethylbenzene, blank diamonds△: n-PB, full squares ■: tetralin, full triangles ▲: decalin.](image-url)
2.3.3 Comparison of the influence of cyclic molecule on HEFA-SPK and model n-decane

Figure 6.b illustrates IP results using n-decane instead of HEFA-SPK in mixtures with cyclic compounds. Results present very similar trends to those observed for HEFA-SPK. First, we observe an oxidation inhibiting effect with the addition of all alkylaromatics. IP increases almost linearly with added alkylbenzenes, namely, xylene, n-PB and toluene, and with a logarithmic trendline with the addition of 1-MN. The IPs of mixtures of n-decane/decalin and n-decane/tetralin go through maximums respectively 1.6 and 4.5 times higher than that of HEFA-SPK. Similar trends observed in HEFA-SPK and n-decane suggest similar driving cooxidation kinetics of some paraffins with the cyclic molecules evaluated here. This initial finding broadens the application of the present study results, and would require deeper investigation.

2.3.4 Summary

The addition of cyclic molecules influences the oxidation stability of HEFA-SPK differently function of their structure. Alkylaromatics, namely, 1-MN, toluene, xylene and TMB improve the oxidation stability of HEFA-SPK. Tetralin and decalin improve HEFA stability at concentration below 25%vol. only.

2.4 Impact of molecule structures on deposit formation

Thermal stability measurements were carried out at 325°C using the test procedure described in section 1.2. Deposit rating of the tubes and the variation of filter pressure gradient (dP filter) are illustrated in Figure 7.a and b, respectively. JFTOT results indicate a very good thermal stability of HEFA-SPK. Tube rating and dP filter indicate 1 and 0, respectively. These levels are far below the specification of HEFA-SPK (3 and 25mm Hg, respectively).
2.4.1 Deposit formation from alkylaromatics/HEFA-SPK blends

The addition of 5% vol. toluene or xylene induced low tube rating and filter dPs indicative of low deposition tendency. Increasing the volume fraction to 15% vol. had no influence for toluene while it increased the quantity of tube deposit for xylene. Using 25% vol. resulted in significant amounts of deposits with tube rating that exceeded the accepted level (Figure 7.a) for both reagents. In the studied conditions, the addition of both toluene and xylene at 5% vol. does not degrade the thermal stability of HEFA.

The addition of 5% and 25% vol. of 1-MN to HEFA-SPK produced a high amount of deposits at 325°C. Tube ratings indicate 4 and >4, respectively. A mixture of 25% vol. 1-MN and HEFA-SPK generated a large volume of insolubles inducing significant increases of filter dPs. 1-MN drastically reduces the thermal
stability of HEFA-SPK at 325°C even at low concentration, although having a significant oxidation retarding effect as described in section 2.3 (Figure 7.a).

2.4.2 Deposits formation from tetralin and decalin/HEFA-SPK blends

JFTOT test with HEFA-SPK/5%vol. tetralin indicate a better thermal stability. The tube rating level was below HEFA-SPK with no change in the filter dP as illustrated in Figure 7. Higher concentrations (15% or 25%vol.), led however to significant amounts of deposits while tube ratings indicate levels above 3.

Tube ratings of the blends of 5, 15 and 25%vol. decalin/HEFA-SPK indicate a very low deposition rate with levels as low as that of HEFA-SPK. Filter dP remain very low. In previous studies, decalin was found more thermally stable and produced fewer deposits than alkanes both at pyrolytic regime 450°C[28] and autoxidation regime from 93–162°C[5]. Song and Lai[29] have underlined the influence of steric confirmation with higher thermal stability of trans-decalin compared with cis-decalin at 450°C. This aspect was not considered in the present work as a commercial decalin (purity >98%) composed of a mixture of cis and trans isomers was used. Decalin, as a hydrogen donor effective in a wide temperature range, allows to stabilize the radicals generated from HEFA-SPK molecules cracking.

2.4.3 Summary

These results lead to an original finding regarding the influence of cyclic molecules on deposits formation. In fact, previous works examined the influence of mixtures of aromatics on thermal stability[30][31] and evidenced in general a higher deposition tendency exacerbated by the presence of diaromatics. In a complementary perspective, the use of pure molecules in the present work allowed to emphasize molecular structure impact. The addition of specific cyclic molecules to HEFA-SPK, namely, xylene, toluene, tetralin (up to 5%) and decalin (up to 25%) allowed to improve or conserve a good thermal stability of HEFA-SPK. Considering the oxidation stability result presented in section 2.3, these molecules acted as oxidation inhibitors as well. Thus, representing good candidates to improve simultaneously oxidation and thermal stability.

3 SUMMARY AND CONCLUSIONS

In this study, the oxidation and thermal stability of three HEFA-SPK were measured with PetroOxy and JFTOT tests. HEFA-SPK was 2-3 times less stable than conventional Jet A-1. This was associated with the differences in chemical composition partly, the presence of cyclic compounds in jet A-1. Thus, we evaluated the influence of pure cyclic molecules on OTS of HEFA-SPK. The addition of cyclic molecules to HEFA-SPK induces different behaviors. Alkylbenzenes increased almost linearly the induction period of HEFA-SPK. 1-MN, induced a non-linear logarithmic increase of IP. Tetralin and decalin acted as oxidation inhibitors at low concentration although having inherently a low stability. This study led to an original finding regarding the influence of the molecule structure of several cyclic molecules on deposits formation. Besides improving the oxidation stability, the addition of low fraction of tetralin and decalin and several methylbenzenes such as xylene and toluene to HEFA-SPK allowed to improve or maintain good thermal stability according to JFTOT results. These molecules, naturally present in conventional
fuels may represent good candidates to improve oxidation and thermal stability of HEFA-SPK. By acting on the formulation itself, they bring a complementary perspective to additive packages widely used for aviation fuels. These results encourage further developments towards fit-for-purpose formulations of future alternative jet fuels. Further investigations would allow to evaluate their potential on different jet fuel feedstocks and operating conditions.

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**4 REFERENCES**


**GLOSSARY**

- Fossil jet fuel or conventional jet fuel: jet fuel produced from fossil source and conventional petroleum refining process.
- Alternative fuel: biofuel that can be used in mixture with fossil jet fuel.
- Alternative jet fuel or biojet: a blend of fossil jet fuel and an alternative fuel
- Jet fuel: includes all jet fuels: fossil jet fuel and alternative jet fuel
- HEFA-SPK or HEFA: Synthetic Paraffinic Kerosene- Hydroprocessed Esters and Fatty Acids. It is an alternative fuel
- IP: Induction Period
- 1-MN: 1-methylnaphthalene
- n-PB: n-propylbenzene
- TMB: 1,2,4-trimethylbenzene
- n-PC: n-propylcyclohexane