SUPPRESSION OF PYROLYTIC DEGRADATION OF N-ALKANES IN JET FUELS BY HYDROGEN-DONORS

John M. Andrésen, James J. Strohm, Michael M. Coleman and Chunshan Song*
Applied Catalysis in Energy Laboratory, The Energy Institute
The Pennsylvania State University, University Park, PA 16802.

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ABSTRACT

The pyrolytic degradation of alkanes in jet fuels can be extensively reduced by adding suitable hydrogen donors, that suppress the formation of free radicals. Accordingly, this paper characterizes the chemical interactions between n-tetradecane and the hydrogen donors benzyl alcohol and 1,2,3,4-tetrahydro-1-naphthol. The hydrogen donors produced the expected overall enhancement on the liquid yields and reduced cracking of the n-tetradecane. The observed suppression of pyrolytic degradation was strongly related to a reduction in the alkane products adding benzyl alcohol, but the 1,2,3,4-tetrahydro-1-naphthol indicated an initial decrease in the alkenes.

INTRODUCTION

The use of hydrogen donors to suppress pyrolytic degradation of jet fuels (1-3), is a potential route to reach the JP-900 thermal stability requirement set up by the US Air Force (4). Since the fuel also functions as the main coolant for the different electronic and system components of the aircraft, the fuel temperatures may increase up to 480°C (900°F) and thermal stability to obtain reduced solid deposition is a key element in this research (5). The pyrolytic conversion of alkanes, typically found in petroleum derived jet fuels, is generally considered to involve the formation of free radicals (6). The propagation of these reactive intermediates results in a broad distribution of smaller alkane and alkene units, and triggers the aromatization of the liquid, which leads to undesirable solid depositions. As a solution, the free radicals can be halted right after the initiation step by the use of hydrogen donors (1-3). However, the chemistry involved in inhibiting free radical reactants during thermal degradation of fuels is not fully understood. This is addressed in this study, where the suppression of reactive intermediates between the n-alkane, n-tetradecane, and the hydrogen donors benzyl alcohol and 1,2,3,4-tetrahydro-1-naphthol, has been characterized.

EXPERIMENTAL

The compounds used were n-tetradecane (TD, Aldrich 99%), benzyl alcohol (BA, Aldrich 99.8%) and 1,2,3,4-tetrahydro-1-naphthol (THNol, Acros 97%). Stressing of TD alone or in different mixtures with BA or THNol were performed for 30 minutes in a fludized sandbath at 425, 450 and 475°C. A detailed description of the experimental setup and analytical determination of the product distribution using GC and GC/MS, has been reported elsewhere (1, 5).

RESULTS AND DISCUSSION

The liquid yields for the n-tetradecane (TD) stressed alone at 425, 450 and 475°C and its mixture with 0.5, 1, 3 and 5 mole% benzyl alcohol (BA) and 1,2,3,4-tetrahydro-1-naphthol, are plotted in Figure 1. The amount of gaseous products is scarce at 425°C, yielding only around 2 wt%. However, adding 0.5 mole% of either BA or THNol resulted in a marked increase in the liquids (Figure 1). At 450°C, the liquid yields are still high and the same initial rise in remaining liquid is observed with the addition of only 0.5 to 1 mole% of hydrogen donors. Rising the temperature to 475°C resulted in a significant decrease in the liquid yields. Still, the more dramatic enhancement in the liquid yields was observed after the

addition of 1 mole% of the hydrogen donors. When comparing the increase in liquid yields at the three temperatures for TD alone and with 1 mole% addition of BA or THNol, there is a significantly rise from around 1-2% at 425°C to 4-6% at 475°C, as an effect of hydrogen donors. Scheme 1 presents in a simplified manner the role of the hydrogen donors in the thermal stabilization of the fuel. The n-tetradecane is cracked due to the influence of heat into two primary radicals. The additive can cap a radical at this stage, preventing the propagation of the reaction and leaving a n-alkane product. However, if the radical is not stopped, it will abstract a hydrogen from another TD molecule. This may leave a primary radical on the TD, which yield a n-tetradecane upon stabilization. More likely, a secondary radical will be formed. Through β-scission, the secondary radical will yield a 1-alkene and a primary radical product. The extent of this cyclic process can be monitored through the concentration of 1-alkenes (in bold). The primary radical capture has been reported in the literature to be the main target for benzyl alcohol (3). However, the ability of hydrogen donors to aim specially at secondary radicals has not been described.

The ability of the hydrogen donor to capture any of the radicals will hinder the propagation reaction, resulting in an increased ratio of remaining TD in the liquid product, when compared to that initially used. Figure 2 compares this relationship for n-tetradecane at the three temperatures 425, 450 and 475°C with the addition of 0.5 to 5 mole% of THNol. Clearly, as the temperature is increased, the TD remaining over that initially is decreasing for the TD stressed alone, from about 85 mole% at 425°C to around 30 mole% at 475°C. At the three different temperatures, there is a sharp initial rise in the TD remaining content with the addition of only 0.5 to 1 mole% of THNol, similar to that found for the liquid yields. However, as the temperature becomes more elevated, a further slow increase is also observed for the addition of THNol up to 5 mole%. For BA, a similar temperature and concentration dependence was found, in accordance with that previous reported for BA at 450°C (3).

The n-alkane and 1-alkene product distributions for the series of THNol addition at 450°C are shown in Figures 3 and 4, respectively. With the addition of 0.5 mole% THNol, there is a decrease in both the alkane and alkene gaseous products (C1 to C3) in accordance with the observed increase in liquid yield (Figure 1). However, for C4 and higher there is a marked decrease in the 1-alkene products (Figure 4), when adding only 0.5 mole% THNol. The n-alkanes from C4 and higher for the TD alone and with 0.5 mole% THNol show a similar product distribution. Referring back to Scheme 1, the THNol seems to target the secondary radicals at this low concentration. Increasing the THNol concentration appears to enhance the ability of the THNol to target primary radicals as well, resulting in a steady decrease of n-alkane products (Figure 3), as the 1-alkene concentration is decreasing at a lower rate. The selective targeting of secondary radicals has also been indicated from the GC analysis of the liquid products from TD/THNol mixtures at 475°C. Figure 5 shows the ratio of the 1-alkene peak area over that of the corresponding n-alkane for TD alone and with 0.5 mole% THNol and BA addition. There is a clear reduction in the alkene/alkane ratio for the THNol mixture, supporting the finding that THNol is targeting secondary radicals at low concentrations. In addition, Figure 5 shows that BA is mainly targeting the primary radicals at 475°C, as illustrated by the relative decrease in the n-alkane peaks in comparison to that of the 1-alkenes. The different reaction mechanisms for the different hydrogen donors may result in synergistic effects from mixing small amount of both stabilizers, where each has the task of capping different radicals.

CONCLUSIONS

The most significant effect of benzyl alcohol (BA) and 1,2,3,4-tetrahydro-1-naphthol (THNol) on the stabilization of n-tetradecane takes place with the addition of 1 mole%. THNol appears to target secondary radicals to a greater extent than BA at low concentrations of the hydrogen donors.

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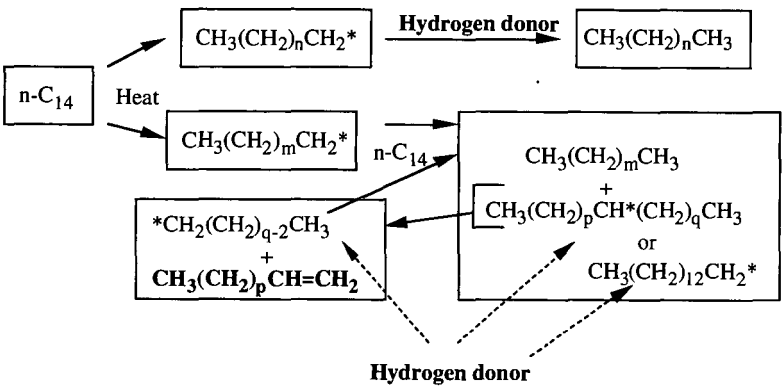

Scheme 1. General concept of the role of the hydrogen donors in stabilizing the n-alkanes leading to suppression of pyrolytic degradation.

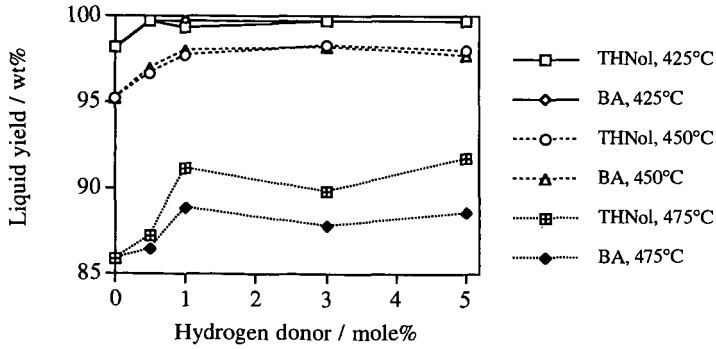

Figure 1. The changes in liquid yields with addition of the hydrogen donors benzyl alcohol and 1,2,3,4-tetrahydro-1-naphthol in the range of 0.5 to 5 mole% at 425, 450 and 475°C.

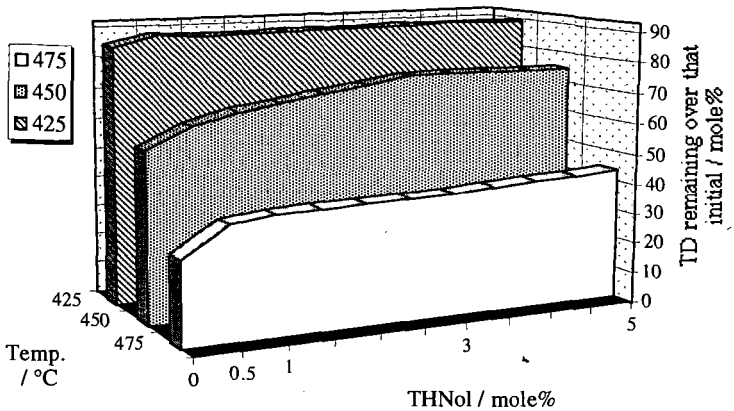

Figure 2. Comparison of remaining n-tetradecane content over its initial concentration for different mixtures with 1,2,3,4-tetrahydro-1-naphthol, stressed at 425, 450 and 475°C for 30 minutes.

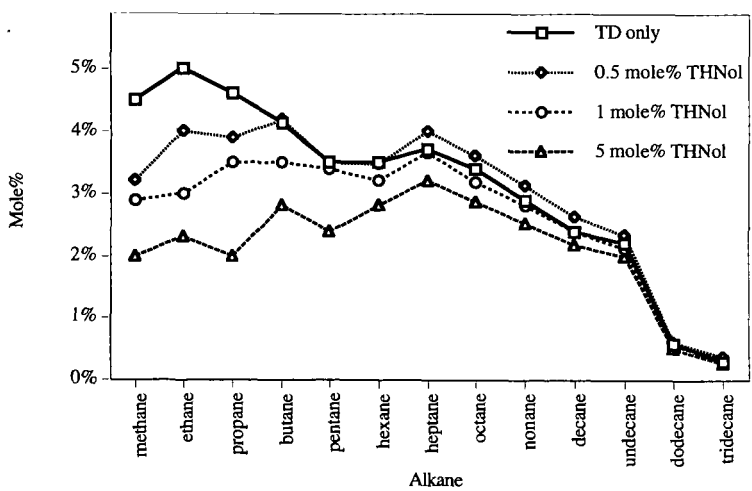

Figure 3. Variation in the n-alkane distribution for pure n-tetradecane and its 0.5, 1 and 5 mole% mixture with 1,2,3,4-tetrahydro-1-naphthol stressed at 450°C for 30 minutes.

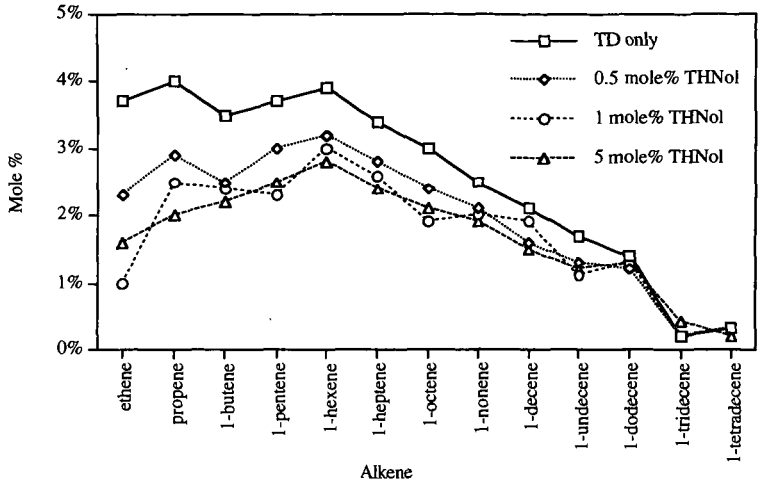

Figure 4. Variation in the 1-alkene distribution for pure n-tetradecane and its 0.5, 1 and 5 mole% mixture with 1,2,3,4-tetrahydro-1-naphthol stressed at 450°C for 30 minutes.

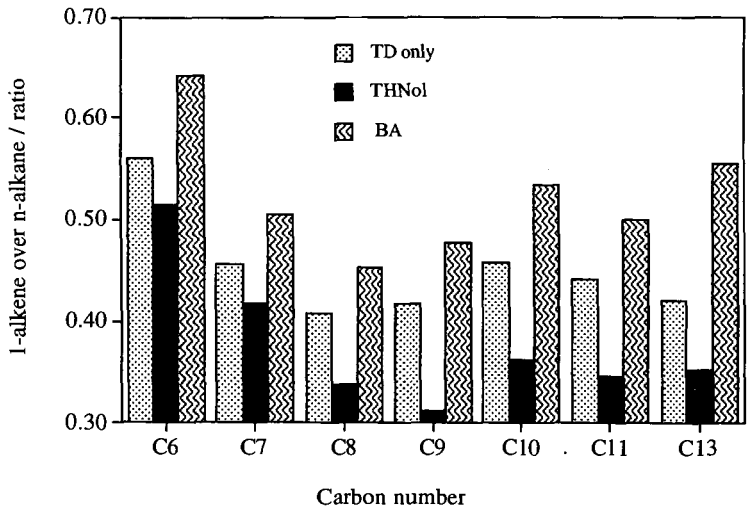

Figure 5. Ratio of the 1-alkene peak area over that of the corresponding alkane for TD alone and with 0.5 mole% THNol and BA addition at 475°C stressed for 30 minutes.