

# ALKYLATED INTERMEDIATE OF CYCLO-ALKANES FOR STABILIZATION OF PARAFFINIC JET FUELS UNDER PYROLYTIC CONDITIONS

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## ABSTRACT

The thermal stability of linear alkanes, such as tetradecane, in the pyrolytic regime is enhanced by the addition of cyclo-alkanes, in particular decalin. Based on the product distribution from the thermal stressing of their mixtures, decalin was found to target primary radicals, particularly by a sharp reduction in the n-alkane products in relation to that of the 1-alkene. This thermal interaction has been further examined by GC/MS analysis, which revealed the formation of alkylated intermediates of decalin that stabilizes the paraffinic species in the pyrolytic regime.

## I. INTRODUCTION

Jet fuels for high Mach applications are required to operate under severe thermal stressing, where exposures up to 900°F are expected<sup>1</sup>. Liquids rich in cyclo-alkanes have been found to have superior stability at high temperatures compared to those high in paraffinic content<sup>2</sup>. This has been associated with two factors. Firstly, cyclo-alkanes themselves have higher thermal stability than linear alkanes<sup>3</sup>. At 450°C after 1 hour, most of a linear alkane such as tetradecane has been pyrolyzed into different products, while trans-decalin mostly remains unconverted. This has been linked to the ability of the trans-decalin to form tertiary radicals after hydrogen abstraction. Further, hydrogen abstraction will transform the decalin into tetralin, which will act as a hydrogen donor<sup>4</sup> and will strongly enhance the thermal stability of trans-decalin even at low concentrations. On the other hand, as tetradecane experiences hydrogen abstraction forming primary and secondary radicals, this leads to rapid decomposition due to propagation reactions. Secondly, previous studies have shown that decalin improves the thermal stability of tetradecane<sup>5</sup>. Again, this can be based on the buildup of tetralin from the pyrolytic H-abstraction from decalin, where the tetralin will strongly affect the propagation reaction in the mixtures. However, the thermal enhancement effect of decalin has been found at temperatures and concentrations, where the formation of tetralin from decalin can be neglected<sup>5</sup>. Therefore, there must exist additional routes in which the decalin quench the propagation reaction generated from the pyrolytic degradation of tetradecane. Accordingly, this work has studied the reactive intermediates involved during pyrolysis of mixtures with decalin and tetradecane at 450°C, stressed from 12 to 120 minutes. There was a clear thermal stability enhancement with the addition of decalin at all times. The reduction in the thermal cracking of tetradecane was found to derive from the capture of radicals by the decalin, forming alkylated derivatives. By increased thermal stressing, these were further dehydrogenated to form tetralins, which again act as a hydrogen source for stabilization.

## II. EXPERIMENTAL

The compounds used were tetradecane (TD, Aldrich 99%) and decalin (DHN, Aldrich 98%, a mixture of 46 mole% cis- and 54 mole% trans-decalin). Stressing of TD alone or in 5 or 30 mole% mixtures with DHN were performed for 12, 30, 60 and 120 minutes in a fluidized sandbath at 450°C as reported elsewhere<sup>2</sup>. The GC-MS was performed on a Hewlett-Packard 5890 Series II GC coupled with a HP 5971A MS detector and a J&W DB-17 column, which was heated from 40 to 290°C with a heating rate of 6°C min<sup>-1</sup>.

## III. RESULTS AND DISCUSSION

Figure 1 shows the remaining TD content over its initial concentration for TD alone and 5 and 30 mole% mixtures with DHN, stressed at 450°C for 30, 60 and 120 minutes. As the TD is stressed, its thermal stability can be expressed on the basis of the amount of TD remaining in the liquid over the amount in the original mixture weighted against the liquid yield of the experiment. This ratio is therefore normalized, and any enhancement in this ratio when DHN is added compared to that

of the TD alone indicates that the DHN is indeed improving the thermal stability of the linear alkane. With increasing stressing time, there is a dramatic decrease in the TD remaining content with no DHN added, from around 56 mole% at 30 minutes to 11 mole% at 120 minutes. When DHN is added there is a significant increase at all stressing times in the TD remaining content. A rapid increase in the thermal stability is achieved with only 5 mole% DHN addition, followed by a slower rise up to 30 mole% DHN mixture. The ratio of the TD remaining content for the 30 mole% DHN mixture over that of TD stressed alone gives an indication of the extent of interaction between the DHN and the TD. The effect of adding 30 mole% DHN is clearly dependent on the stressing time, where the extent of interaction is rising from 17% after 30 min stressing, to 24% at 60 min and is significantly increased to nearly 140 % at 120 min. Clearly, several reaction mechanisms are involved as discussed below.

Figure 2 compares the changes in the C4 to C10 product range from the thermal decomposition of TD with 30 mole% DHN addition at 450°C stressed for 12, 30, 60 and 120 minutes. The n-alkane and 1-alkene peaks appear in pairs, where the n-alkane has a slightly lower retention time than the 1-alkene. After 12 minutes stressing, the concentration of the cracking products is very low (5%), and the amount of 1-alkenes is slightly higher than that of the n-alkanes. At 30 minutes reaction time, the concentration of cracking products has increased to over 30%, and the relative distribution of the 1-alkene is now slightly lower than the n-alkane. As the stressing time is further risen to 60 minutes, the 1-alkene concentration is decreasing due to hydrogenation, alkylation or cyclization reactions<sup>6</sup>. The 1-alkenes are ultimately disappearing after 120 min exposure at 450°C. Compared with the stressing of TD alone at 450°C<sup>6</sup>, the relative concentration of 1-alkenes is higher at all times in the DHN mixture. The 1-alkene/n-alkane relative distributions found after 1 hour for the 30 mole% DHN mixture are comparable to those after only 30 minutes stressing for TD only. This indicates that the DHN is interacting with the thermal decomposition of the 1-alkanes by reducing their probability for hydrogen abstraction and capturing primary radicals, which promotes their alkylation. The ability of the DHN to affect the 1-alkane concentration through suppression of the n-alkanes is further illustrated in Figure 3, where the ratio of the 1-alkene peak area over that of the corresponding n-alkane for TD alone and with 30 mole% DHN addition after 30 minutes reaction time at 450°C is compared. This ratio is around 60% for TD stressed alone and there is a clear increase in the alkene/alkane ratio for the DHN mixture, giving values about 90%. This indicates that DHN indeed is targeting the primary radicals resulting in enhanced thermal stabilization of TD or other paraffinic liquids typical for jet fuels.

The route of preventing the thermal cracking of the linear alkanes by DHN is strongly connected to the ability of the cylo-alkane to become alkylated. Figure 4 compares the GC-MS trace for ethyl-DHN (166 a.m.u.) and dodecyl-DHN (306 a.m.u.) identified in the remaining liquid after stressing the 30 mole% DHN mixture at 450°C for 60 minutes. The main features are deriving from the DHN-ion, giving rise to the mass at 137 and below. The alkylated masses give rise to the parent ions, where the DHN-ion with a mass of 137 combined with either ethyl (mass of 29) or dodecyl (mass of 169) are deriving from the parent ions ethyl-DHN (166) and dodecyl-DHN (306), respectively. Other masses identified are 180, 194, 208, 222, 236, 250, 264, 278 and 292, indicating that alkyl substitution in the whole range C2 to C12 has taken place. However, no evidence of methyl, tridecyl or higher alkyl substitution was found. Neither was any DHN substituted with two alkyls identified. This strengthens the evidence that the thermal stability effect of DHN is initially associated with the capturing of primary alkyl radicals by substitution as illustrated in Scheme 1. The hydrogen abstraction of TD generally leads to a secondary radical. The secondary radical produces a 1-alkene and a primary radical through  $\beta$ -scission. If the primary radical is not captured, it will start a propagation reaction leading to further decomposition of the TD and rapid transformation of the 1-alkenes. The introduction of DHN captures primary radicals in two consecutive steps. First, the primary radical will abstract a hydrogen from the DHN, where the formation of a tertiary radical is favored. Second, the tertiary radical will recombine with a different primary radical. The above scheme will result in two overall effects. Firstly, the thermal decomposition of TD is halted and secondly, the product distribution will favor 1-alkenes. This alkylation process was further confirmed through studies on the stressing products from TD/DHN mixtures after only 30 minutes at 450°C. However, when increasing the stressing time to 120

minutes, the studies on the cracking products show that tetralin is the main product from the thermal decomposition of DHN. This confirms that dehydrogenation of decalin into tetralin is a further stabilizing factor, which becomes increasingly important at longer stressing times.

## CONCLUSIONS

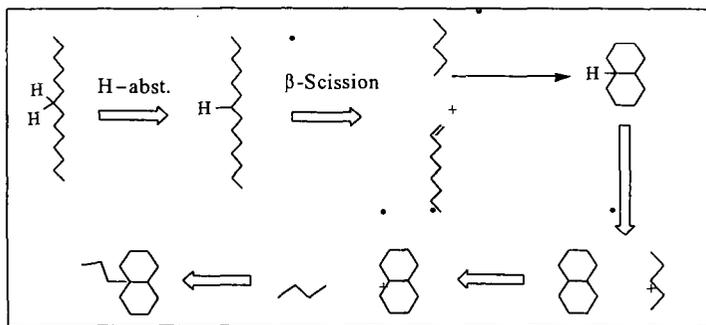
Tetradecane (TD) has been stressed alone and in mixtures with 5 and 30 mole% decalin (DHN) at 450°C, with stressing times ranging from 12 to 120 minutes. A significant increase in the amount of TD remaining was observed at all stressing times upon the addition of DHN. The improved thermal stability of the TD-DHN mixtures was mainly associated with the reduced cracking of the TD due to interactions with the DHN. Enhancements of up to 140% in the ratio of TD remaining over that initial for 30 mole% DHN addition compared to that of TD by itself, were observed. The suppression of the production of linear alkanes was found to derive from the capture of primary radicals by the DHN, forming alkylated derivatives. With increasing stressing times, these were further dehydrogenated to form tetralins, which again act as a hydrogen source for stabilization.

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Scheme 1. Simplistic view of the thermal stability effect of DHN associated with the capturing of alkyl radicals by substituting them to their structure.

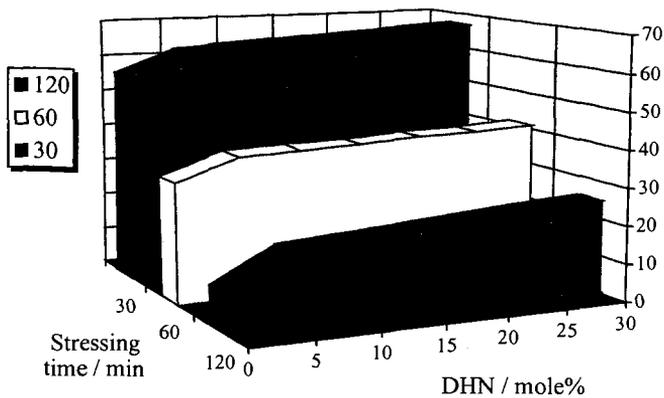


Figure 1. Comparison of remaining TD content over its initial concentration for different mixtures with DHN stressed at 450°C for 30, 60 and 120 minutes.

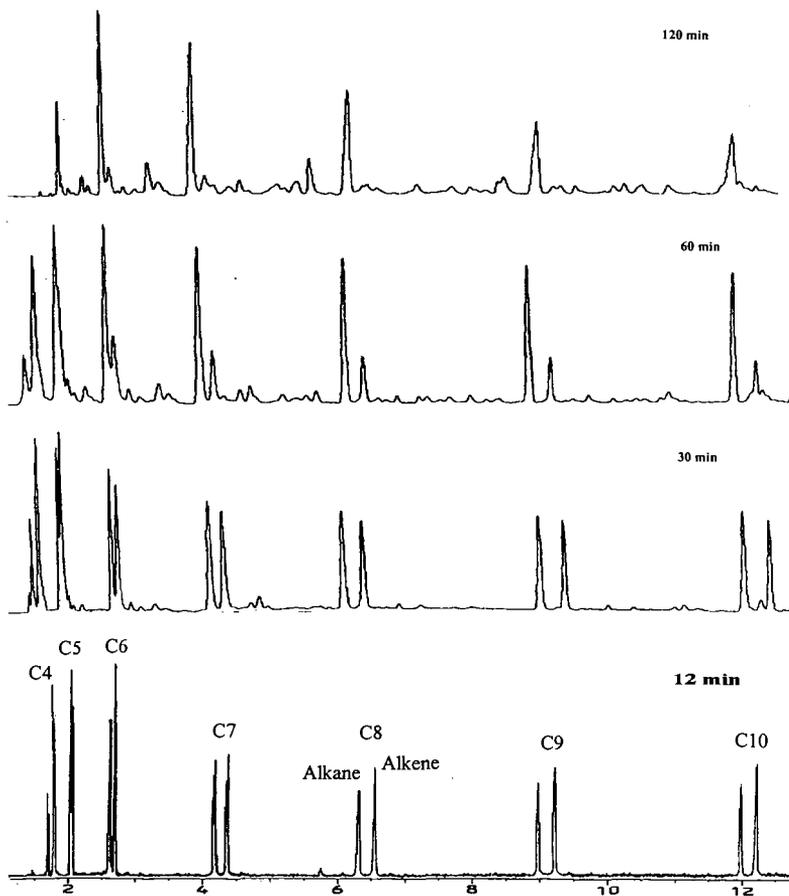


Figure 2. Changes in the TD pyrolysis products C4 to C10 after stressing the mixture of 70 mole% TD with 30 mole% DHN for 12, 30, 60 and 120 minutes at 450°C.

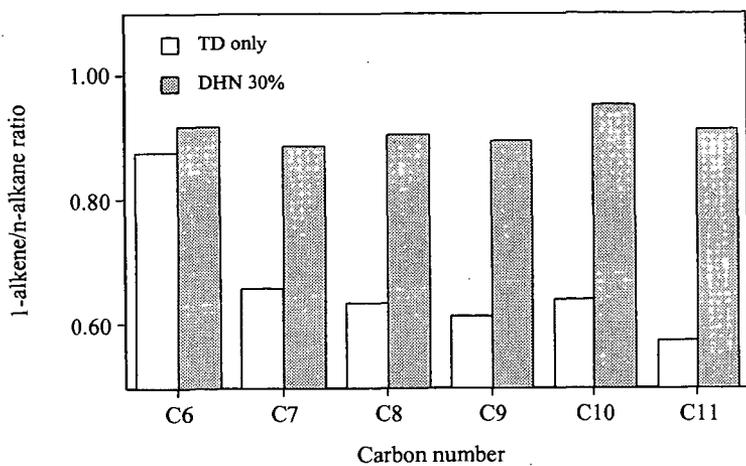


Figure 3. Ratio of the 1-alkene peak area over that of the corresponding alkane for TD alone and with 30 mole% DHN addition at 450°C stressed for 30 minutes.

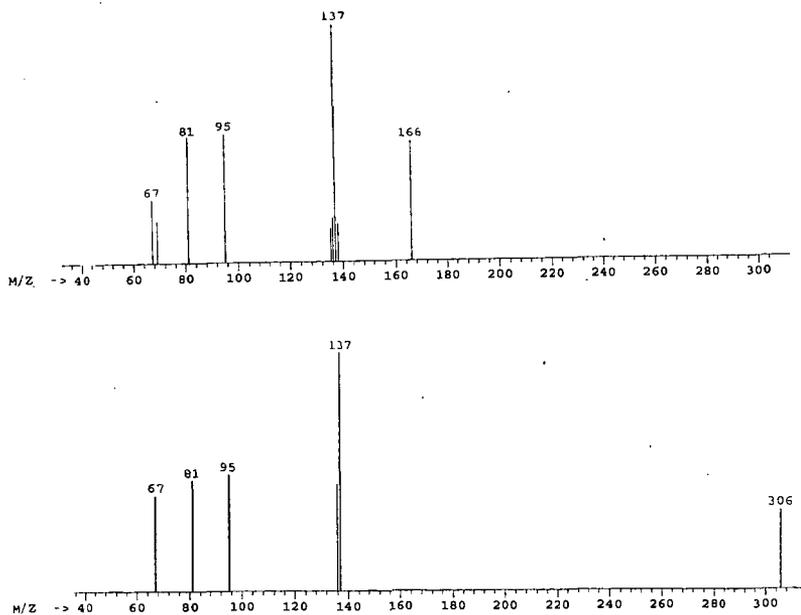


Figure 4. GC-MS traces for ethyl-DHN with parent mass 162 a.m.u. (top) and dodecyl-DHN (306 a.m.u., bottom).