

COMPARISON OF THE THERMAL STABILITY OF COAL-DERIVED JET FUELS IN THE AUTOXIDATIVE AND PYROLYTIC REGIMES UNDER BATCH AND FLOW CONDITIONS

John M. Andrésen, James J. Strohm 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 thermal stability of coal- and petroleum-derived jet fuels and the associated model compounds decahydronaphthalene and n-tetradecane, as they go through the autoxidative and pyrolytic regime both under batch and flow conditions, was studied. Under batch reactor conditions, the decahydronaphthalene showed excellent thermal stability up to 500°C, whereas the n-tetradecane started its cracking process at around 450°C. Flow reactor studies mirrored the thermal decomposition of the model compounds, although the cracking appeared at higher bulk fuel temperatures. The thermal behavior of the experimental jet fuels also confirmed that the paraffinic proportion of the fuels is the main reason for thermal fuel degradation.

INTRODUCTION

Cycloalkane-rich liquids, such as those derived from coal, have great potential as precursors for advanced jet fuels that meet the more stringent thermal stability requirements for the future high-Mach jet aircraft [1]. Currently, commercial planes are utilizing conventional paraffinic based jet fuels that may be exposed to temperatures up to 300°C [2]. However, as the flight speed will be increased to high Mach numbers, the fuel is expected to experience temperatures as high as 482°C (900°F) or above, since the jet fuel also functions as the main coolant for the different electronic and mechanical parts of the aircraft. Even though the residence time at such elevated temperatures is expected to be fairly short (matter of minutes or less), the jet fuels presently used have been shown to form solid deposit that can lead to catastrophic malfunction of the jet aircraft. The current jet fuels are petroleum-derived and consequently rich in linear alkanes, which are highly susceptible to pyrolytic cracking, resulting in coking [3]. The thermal stability of a jet fuel in the pyrolytic regime can be greatly enhanced by utilizing liquids rich in cycloalkanes [4]. This is the case for hydrotreated coal-derived liquids, where the aromatic structures have been transformed over to their corresponding cyclo-alkanes [5]. An additional problem with jet fuels is the presence of dissolved oxygen from air, which reacts with the fuel during the autoxidative regime (150-250°C) before the fuel and its oxygenated reaction products enter the pyrolytic regime (400-500°C) [6]. Accordingly, the present study compares the thermal stability of coal- and petroleum-derived jet fuels and associated model compounds, as they go through the autoxidative and pyrolytic regime, both under batch and flow conditions. Differences in chemical reactivity between linear- and cyclo-alkane model compounds are related to the superior thermal stability of the coal-derived jet-fuels.

EXPERIMENTAL

The samples investigated were the two model compounds tetradecane (TD, Aldrich 99%) and decahydronaphthalene (DHN, Aldrich 98%, a mixture of cis- and trans-decahydronaphthalene), a hydro-treated light cycle oil (DA/HT LCO) and a coal-derived jet fuel named JP8C.

For the batch study, a volume of 5 ml was charged into a microautoclave with a total volume of 25 ml [7]. The system was pressurized with 100 psi of air and heated in a fluidized sandbath. The heating-rate used was approximately 5°C min⁻¹ from room temperature and the microautoclaves were removed upon reaching 250, 350, 450 and 500°C. After reaction, the microautoclaves were rinsed of sand and quenched. When the microautoclaves were cooled to ambient temperature, the gas phase and liquid fraction were removed for analysis. The tube and the stem of the microautoclave were washed in pentane until a clear color was obtained and then dried. The amount of solid deposition was determined from the increase in weight of the tube and stem.

The GC-MS analysis of the liquid products was performed on a Shimadzu GC-174 coupled with a Shimadzu QP-5000 MS detector. The column used was a Restek XT15 column with a coating phase of 5% diphenyl / 95% dimethyl polysiloxane and it was heated from 40 to 290°C with a heating rate of 6°C min⁻¹.

The flow reactor is outlined in Figure 1. The fuel tank was degassed with high-purity N₂ (99.9%) to ensure the absence of oxygen for the pyrolytic study. In addition, the jet fuel was purged with air to compare our autoxidative studies in batch reactors with those of the flow reactor. An HPLC pump was used to pressurize the jet fuel up to 700 psi with a flow rate of 6 ml/min. Within the furnace, a 0.040" (1.02 mm) ID silcoteel tubing was used. This ensured a liquid hourly space velocity (LHSV) of 450. The temperature profile was established by welding thermocouples to the tubing in addition to inserting thermocouples within the tubing and at the

exit of the furnace (the last thermocouple is indicated in Figure 1, where also a silcosteel union tee was used to minimize catalytic jet fuel degradation). The temperature profile is shown in Figure 2 and is somewhat different to that reported in the literature for other flow reactor systems [8]. The GC/MS traces are reported according to the exit temperature of the actual fuel. Immediately after exiting the furnace, the jet fuel is cooled by refrigerated ethylene glycol. The tubing used is also silcosteel to avoid secondary reactions during cooling of the stressed jet fuel. The cooled jet fuel is then filtered to accumulate any solids formed using a 0.8 μm filter. Further, a back pressure valve is used to control the furnace pressure. The cooled jet fuel is then allowed to enter a storage vessel, where the liquid products are separated from the gaseous products.

RESULTS AND DISCUSSION

Batch reactor studies The content of the liquid remaining for n-tetradecane (TD), decahydronaphthalene (DHN) and the coal-derived jet fuel JP8C stressed under the influence of air in the temperature range 250 to 500°C is compared in Figure 3. At low temperatures (250 - 350°C), the formation of gas and solid products is very small. However, as the temperature is increased to 450°C and indeed for the one stressed at 500°C, the content of liquid remaining is reduced. Especially the linear alkane, TD, has a drastic lowering of the liquid phase, reaching a level below 80%. The coal-derived jet-fuel, JP8C, shows an improved thermal stability compared to TD, where above 90% of the liquid remains, while the cycloalkane, DHN, shows the highest ability to resist thermal cracking. The reduction in the liquid produces gas and solids, and although not shown here the linear alkane forms about 0.2 wt% solid residue already at 250°C. The solid deposition is not significantly increased at 350°C, but rises sharply when stressed further to 500°C, following a similar trend to the solid deposition found using flow-reactor studies [8, 9]. The vast difference in liquid yields between liquids rich in linear alkane and those mainly containing cyclo-alkane (including the JP8C and LCO HT/DA) as showed in Figure 2, can be explained further by studying the ability of the different hydrocarbons to resist thermal cracking. Figure 4 shows the variation in the remaining concentration of TD and DHN in the liquid products with temperature, taking into account the formation of gas and solids. In the autoxidative zone the reduction in the concentration of the two compounds is small. However, as the temperature reaches the pyrolytic regime, a great difference in thermal stability of the two compounds is shown. At 500°C only around 35% TD is remaining, while 85% of the DHN has not reacted.

The above differences in thermal stability can be related to the differences in the oxidation chemistry in the autoxidative zone and the thermal stability of the oxygenated compounds from linear- and cyclo-alkanes to remain in the liquid. Figure 5 shows the GC/MS trace of the reaction products from stressing of TD in air up to 250°C. A range of linear alkane products is present as the tallest peaks in the different peak clusters. A row of compounds with oxygen functional groups is associated with each linear alkane, such as acids, aldehydes and ketones. The compounds present at 250°C do not alter when stressed up to 350°C, but a drastic change in the product distribution appears as the temperature is increased to 450°C. At this temperature the concentration of n-alkanes are greatly increased and also 1-alkenes are produced as a result of thermal cracking [10]. Although, some oxygenated compounds still remain in solution, the reactivity of these species clearly adds to the thermal degradation of the linear alkane, TD. The cyclo-alkane, DHN, also experiences some oxidation in the autoxidative zone, as shown in Figure 6. The mixture of trans- and cis-decahydronaphthalene used here (retention time of 14 and 15 minutes, respectively), gave oxygenated products which appear in a narrow retention time range of 18 to 21 minutes. Particularly ketones and alcohols dominate, where compounds such as 2-butyl cyclohexanone and decahydronaphthol are abundant. The presence of alcohols in the products from DHN indicates that oxygenated cyclo-alkane compounds are more stable than their linear equivalents. As the temperature is increased to 450°C only small changes in the product distribution occur, which again confirm the higher stability of cyclo-alkanes derived compounds, where oxygen is captured. By further increasing the stressing up to 500°C, non-oxygenated single ring compounds, such as 1-methyl cyclohexene, appear at lower retention times, but still the oxygenated compounds are present. The development of the hydrogen-donor tetrahydronaphthalene may also further enhance the thermal stability of the liquid.

The changes in the product distribution from the coal derived jet fuel, JP8C, stressed under air at 250 and 500°C are shown by the GC/MS traces in Figure 7. At 250°C, JP8C is rich in one and two ring cyclo-alkanes, and at longer retention times a series of long-chain linear alkanes in the range of C12 to C18 is present. When stressed up to 500°C, only small changes in the cyclo-alkane distribution occur, while the concentration of the linear alkanes has decreased drastically. Based on the study of stressing TD in both the autoxidative zone and further in the pyrolytic regime, the reduction in the linear alkane concentration can be due to the following two reasons. Firstly, the tendency of linear alkanes to react with oxygen and form less stable compounds, and secondly, the lower thermal stability of the linear alkanes themselves in comparison to cyclo-alkanes.

Flow reactor studies The findings from the batch reactor studies were further correlated with stressing of model compounds under flow conditions both in the absence and presence of oxygen. Silcosteel tubing was used in this work to minimize any metal surface-catalyzed fuel decomposition. Figure 8 shows the concentration of DHN remaining as a function of the exit temperature of the liquid. With a LHSV of 450, DHN presents a similar behavior when stressed under both N₂ and air, where the thermal cracking of the liquid takes place at temperatures above 620°C. Indeed, nearly identical evaluation of the DHN both under N₂ and air supports the findings from the batch reactor studies that the air uptake by DHN is reduced in comparison to linear alkanes such as TD. Flow reactor studies using TD were also carried out. However, the TD generated extensive coke formation resulting in blockage of the 1/16" tubing through the furnace. This was observed under both N₂ and air, where the dotted vertical line in Figure 8 shows the temperature at which the TD under oxidative conditions started coking, while the solid line indicates the same temperature for TD under inert atmosphere. The fact that TD actually cokes at temperatures where DHN is essential unconverted again supports the previous findings from the batch reactor studies. The difference in the thermal stability of cyclo-alkanes and linear alkanes is also illustrated in Figure 9, showing the GC/MS traces of the LCO derived jet fuel, DA/HT LCO, stressed alone with fuel outlet temperatures of 520 and 620°C. With a LHSV of 450 very little jet fuel degradation takes place when the maximum fuel outlet temperature was 520°C, and the GC/MS trace is virtually identical to those reported on the initial DA/HT LCO fuel [3, 5]. Increasing the temperature to 570 and 590°C (not shown here) there is some pyrolytic cracking of the jet fuel, but it is not before 620°C that the appearance of aromatic compounds starts becoming significant. This scenario is somewhat different to that of the batch reactor studies, where similar changes were observed at a lower temperature for the coal derived jet fuel JP8C (Figure 7). On the other hand, during the batch reactor studies the jet fuel had residence times substantial longer than that of the present flow reactor experiments. However, again there are only slight changes in the cyclo-alkane compounds, and as expected the thermal exposure at 620°C has cracked virtually all the long chain alkanes into lighter compounds and aromatic compounds, opening the possibility for detrimental solid deposition.

CONCLUSIONS

The changes in product distribution for a linear alkane, n-tetradecane (TD), and a bicyclic alkane, decahydronaphthalene (DHN) were related to a cycloalkane-rich coal-derived jet fuel, JP8C, in batch reactors and a light cycle oil-derived jet fuel, DA/HT LCO, under flow conditions. Under batch conditions, the linear TD showed less thermal stability than that of JP8C, and particularly lower than that of DHN when stressed under air. This was associated with the formation of a range of oxygenated compounds from TD such as acids, aldehydes and ketones, which showed lower thermal stability than those oxygenated compounds derived from DHN. The flow reactor studies confirmed the findings under batch conditions, but the temperatures at which cracking occurs were shifted to considerably higher temperatures.

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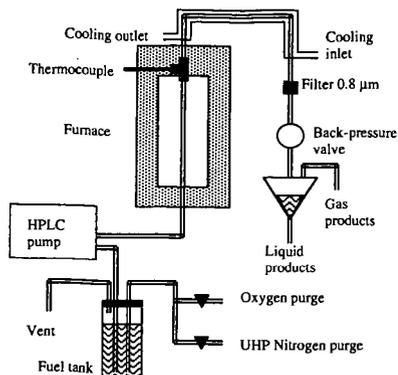


Figure 1. Outline of flow reactor.

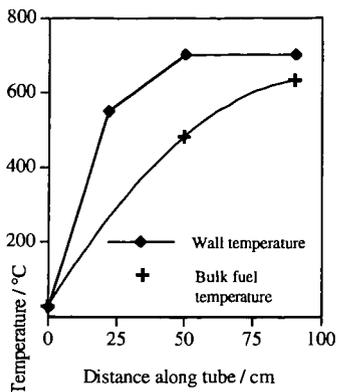


Figure 2. Temperature profile of the flow reactor system, showing correlation between wall and actual bulk fuel temperatures.

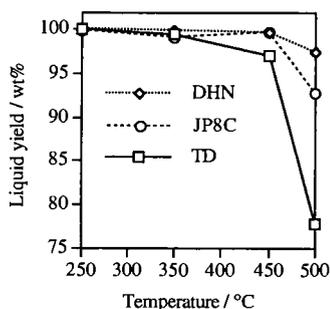


Figure 3. Comparison of liquid remaining for TD, DHN and the coal-derived jet fuel JP8C stressed in batch reactor under the influence of air in the temperature range 250 to 500°C.

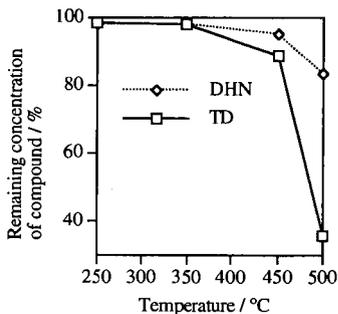


Figure 4. Variation in the remaining concentration of tetradecane and decahydronaphthalene with temperature stressed under 100 psi air in batch reactor.

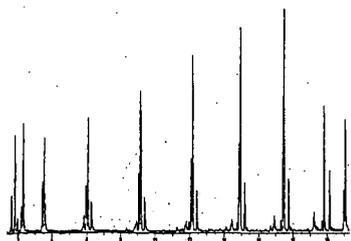


Figure 5. GC/MS trace of the reaction products from stressing TD in batch reactor under 100 psi air up to 250°C.

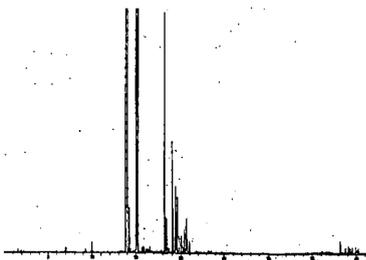


Figure 6. GC/MS trace of the reaction products from stressing DHN in batch reactor under 100 psi air up to 250°C.

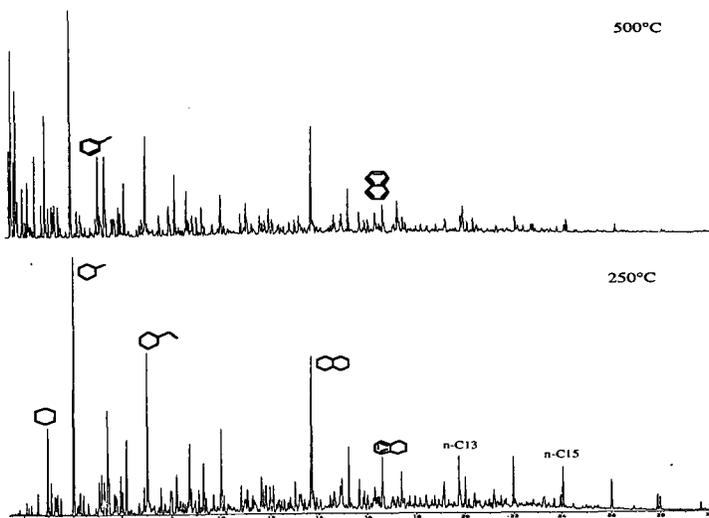


Figure 7. GC/MS traces of the coal derived jet fuel, JP8C, stressed under 100 psi air in batch reactors from room temperature to 250°C (bottom) and 500°C (top).

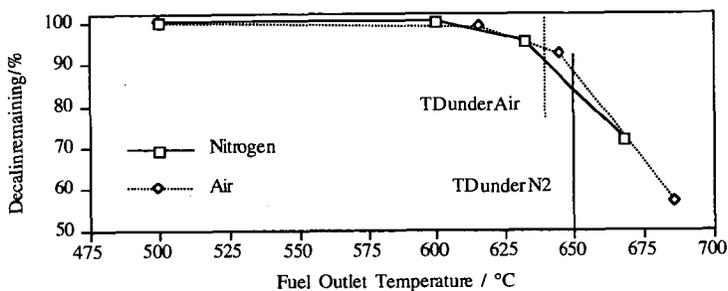


Figure 8. Remaining concentration of DHN with temperature under flow conditions.

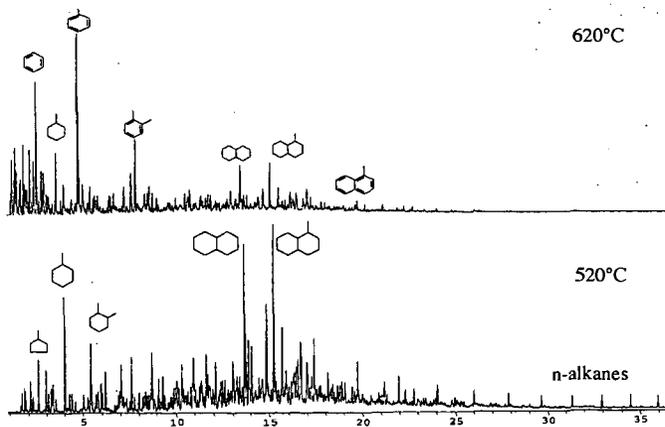


Figure 9. GC/MS traces of the DA/HT LCO jet fuel under flow conditions at fuel outlet temperatures of 520 and 620°C.