STUDY OF INCIPIENT CARBON DEPOSITION FROM TETRADECANE IN THE PRESENCE OF ADDITIVES

Prashant C. Sanghani and André L. Boehman
Fuel Science Program, Department of Material Science and Engineering
The Pennsylvania State University, University Park PA 16802

Introduction

Carbon formation from jet fuels under pyrolytic conditions is an issue of great concern. Carbon formation from hydrocarbons in jet fuel occurs through liquid phase as well as vapor phase processes[1]. Thermal stability of a hydrocarbon is defined as its resistance to chemical decomposition and carbon deposit formation at elevated temperatures. Thermal stability requirements for future jet fuels have been set at 908°F (482°C).

Jet fuel stability is increased by introducing additives. A number of high temperature thermal stabilizers have been reported [2]. By far THQ (tetrahydroquinoline) has been found to be the best. Although THQ is best in preventing carbon (deposit) formation, it is not the cheapest. Therefore, from a practical standpoint it may not be possible to have 10-20 weight % THQ in jet fuels as the additive. The question addressed here is whether blending THQ with other practical thermal stabilizers (additives) can achieve the same thermal stability as that achieved using only THQ.

Finally future jet fuels very likely will be made by blending various hydrocarbon streams in petroleum refineries. These hydrocarbon streams have a wide range of stability. It is necessary to know the quantity of stable mixture that should be added to an unstable mixtures to prevent incipient carbon deposition. Understanding the kinetics of these processes is a prerequisite for predicting the fuel behaviour. Kinetic study is a next step for this work.

Mixtures of tetradecane and three additives (tetralin, tetrahydroquinoline, and t-decalin) are used in this study. Tetradecane was used because it represents one of the major component of petroleum-based fuels.

Experimental

Various mixtures of tetradecane, tetralin, decalin, and tetrahydroquinoline (THQ) were stressed at 450 and 478°C under a nitrogen environment. All mixtures were fixed at 5.46 g of $C_{14}H_{30}$. Additives were used at 4, 10 and 20 mole% concentrations. About 600-700 milligram of -16µm stainless steel (SS316) powder was charged into a microautoclave reactor for each test. Deposits form preferentially on the steel powder because of its high surface area. Incipient carbon deposition is examined by measuring the amount of deposit formed on the SS316 powder using TGA.

Results and Discussion

Tables 1 and 2 show the amount of carbon formed from mixtures at 450 and 478°C for a time duration of 2 hours. The minimum amount of measurable weight change is 2 mg.

From Table 1 we can see that THQ and mixtures of 3 additives at 4 mole% work well in preventing incipient deposition at 450°C. Although tetralin is a well known hydrogen donor, 4 mole% tetralin did not prevent deposits. It may be because hydrogen donation from tetralin is slower than the degradation of tetradecane. Also, the amount of carbon reported here is fairly low, merely 10 mg.

Table 2 shows incipient carbon deposition at 478°C. We can see that the additives do not work as well at higher temperature. Carbon formation from neat $C_{14}H_{30}$ was not measured at 478°C because neat $C_{14}H_{30}$ produces significant deposits (>300mg) and no longer represents incipient deposition. Mixtures with 10 mole% additive do not show improvement in preventing incipient deposition from $C_{14}H_{30}$ over the 4 mole% case. This is also an indication of a decrease in effectiveness of the additives with an increase in temperature. Twenty mole% THQ and tetralin reduced carbon deposition from $C_{14}H_{30}$ by a factor of 2. Ten mole% THQ and tetralin were better than three additives at 10 mole%, which is also an indication of the poorer stabilizing capacity of decalin.

Table 1. Carbon Deposition, 2 hours at 450°C

	Deposit mass, mg
Neat $C_{14}H_{30}$	9.52
$C_{14}H_{30}$+TET(4%)	9.52
$C_{14}H_{30}$+THQ(4%)	0
$C_{14}H_{30}$+3additives(4%)	0

Table 2. Carbon Deposition, 2 hours at 478°C

	Deposit mass, mg
$C_{14}H_{30}$+THQ(4%)	236.45
$C_{14}H_{30}$+3additives(4%)	255.98
$C_{14}H_{30}$+THQ(10%)+TET(10%)	155.94
$C_{14}H_{30}$+3additives(10%)	263.91
$C_{14}H_{30}$+THQ(20%)+TET(20%)	114.9

Mixtures of tetradecane and 3 additives at 10 mole% level were pyrolyzed for time periods of 12 to 90 minutes. Figure 1 shows the amount of carbon produced vesus time. We see that very little carbon appears before 50 minutes. After 60 minutes, carbon deposition increases rapidly. Therefore as soon as the system starts building carbon, it is very difficult to control the process further.

Gas chromatography (GC) and gas chromatography mass spectrometry (GC/MS) was performed on liquid products obtained after pyrolysis. Figure 2 shows that the concentration of tetradecane drops to a very low level in 50 minutes. Figure 3 shows concentrations of tetralin, t-decalin, and THQ. We see that THQ dissapperance is faster than tetralin and t-decalin. In about 60 minutes both THQ and tetralin concentrations reduced significantly. After 60 minutes very little THQ or tetralin remains available. During the same period, we observed the rapid rise in deposit mass.

Conclusions

The ability of additives to stabilize fuel is a strong function of temperature. Additives that work at 450°C may not at all work at 500°C. Sufficient amounts of additive must be present at all times to stop carbon deposition. On blending tetralin and decalin with THQ, it is still possible to achieve stabilizing effect at 450°C.

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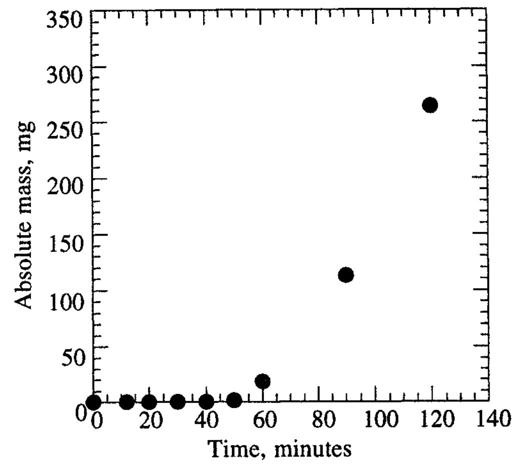

Figure 1. Deposit mass versus reaction time.

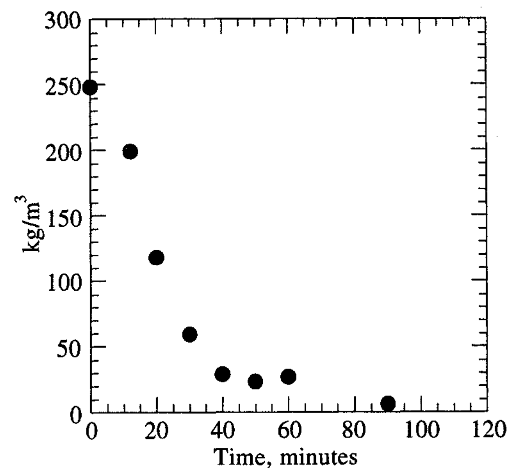

Figure 2. Concentration of $C_{14}H_{30}$ vs time.

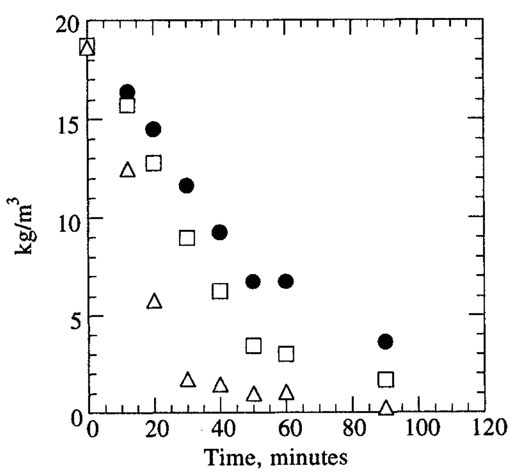

Figure 3. Concentration, THQ (Δ), Tetralin (□), t-decalin (●) vs Time.