EFFECTS OF ACTIVATED CARBON SURFACE ON THERMAL DECOMPOSITION OF HYDROCARBONS

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Introduction

Deposition of carbonaceous solids on metal surfaces in the fuel system has been a major concern for the development of advanced aircraft with high thermal loads. [1,2]. We have shown that adding activated carbon to n-dodecane suppresses the thermal decomposition of n-alkanes at high temperatures and prevents solid deposition on metal surfaces [3-5]. There are other reports on the activity of solid carbons in catalyzing the reactions of hydrocarbons [6-8].

In this study, we compare the effects of activated carbon addition on thermal decomposition of n-dodecane, cyclohexane, and ethylbenzene, as three different types of hydrocarbons present in jet fuels.

Experimental

Thermal stressing experiments were carried out on 10 ml n-dodecane, cyclohexane and ethylbenzene in 316 stainless steel batch reactors at 450°C for 1 to 23 hours in a nitrogen atmosphere [5]. The high surface area activated carbon, PX-21 was obtained from Amoco oil company. Approximately 200mg of an activated carbon PX-21, obtained from Amoco Oil Company, was added to model compounds prior to thermal stressing [5].

Gas chromatography (GC) of liquid samples was conducted using a Perkin-Elmer 8500 GC with fused silica capillary column. Gas products were also analyzed by Perkin-Elmer Auto System GC. Compounds in the liquid products were identified by capillary Gas Chromatography-Mass Spectrometry (GC-MS) using a Hewlett-Packard 5090 II GC coupled with 5971A mass selective detector.

Results and Discussion

Thermal Decomposition of n-Dodecane

Figure 1 shows the total concentrations of cycloalkanes and aromatics in the products obtained from stressing of n-dodecane at 450°C for 1 and 3 h with and without added PX-21. The results indicate when PX-21 is added, higher concentrations of aromatic compounds are obtained in the products, indicating that the carbon surface promotes dehydrogenation reactions, possibly through hydrogen shuttling activity, as proposed before [5] and discussed below.

In gaseous products, hydrogen and ethane concentrations were higher, whereas ethylene concentration was lower with PX-21 compared to those obtained without PX-21. Higher ethane and lower ethylene concentrations with PX-21 can be attributed to the stabilization of ethyl radicals (formed by ß-scission reactions) on the carbon surface. Combined with the data on the concentrations of cycloalkanes and aromatics in the liquid products, the gas analysis suggests that the carbon surface shuttles hydrogen from cycloalkanes to stabilize the free radicals produced by thermolysis of n-dodecane. In other words, the carbon surface appears to be active in both dehydrogenation (e.g., of cycloalkanes) and hydrogenation (e.g., of ethyl radicals) reactions. One possible mechanism for the proposed hydrogen shuttling activity is the sequential hydrogenation and dehydrogenation of aromatic ring systems on the carbon surface. The stabilization of free radicals on carbon surface can explain why thermal decomposition of n-dodecane is suppressed with inhibition of solid deposition on metal surfaces [5].

Thermal Decomposition of Cyclohexane

Thermal stressing of cyclohexane with/without PX-21 gave similar results to those obtained from stressing n-dodecane. The addition of PX-21 inhibited the thermal cracking of cyclohexane and gave much higher concentrations of benzene in the liquid products. The data shown in Figure 2 clearly demonstrates the dehydrogenation activity of PX-21 which produced, in long duration experiments, almost 30 times higher benzene concentrations compared to that obtained without PX-21.

The analysis of gaseous products showed, similar to the results obtained with n-dodecane, that the presence of PX-21 gave higher concentrations of hydrogen and ethane, and lower concentrations of ethylene compared to those obtained without PX-21.

Thermal Decomposition of Ethylbenzene

In contrast to the results obtained from stressing n-dodecane and cyclohexane, the additions of PX-21 promoted cracking reactions and increased the amount of carbonaceous deposit on the reactor wall. The liquid products obtained with PX-21 was much darker. Figure 3 shows that much higher concentrations of benzene, methylbenzene, dimethylbenzene, styrene and methylethylbenzene were obtained when PX-21 was added to ethylbenzene. The major product was dimethylbenzene.

The gas analyses showed the same trends as those observed with n-dodecane and cyclohexane, that is, higher concentrations of hydrogen, ethane (and methane), and lower concentrations of ethylene were obtained when PX-

21 was present. There was almost no ethylene present in the gases obtained with PX-21. It appears that the carbon surface still acts as a hydrogen shuttler to methyl and ethyl radicals, but compared to n-dodecane and cyclohexane reactions, there is much less amount of hydrogen to shuttle. It appears that demethylation of the ethyl group (producing a resonance stabilized benzyl radical) and methylation of subsequently formed methylbenzene (to produce dimethylbenzene) are the major reactions. The higher extents of cracking observed with PX-21 can be attributed to the abstraction of hydrogen by the carbon surface which, in this case, appears to destabilize the pyrolysis system.

Conclusions

Thermal decomposition behavior of hydrocarbons is strongly influenced by the presence of an activated carbon, PX-21. The addition of PX-21 inhibits thermal decomposition of n-dodecane and cyclohexane and solid formation on reactor walls, but promotes the decomposition of, and solid formation from, ethylbenzene. The increased stability of n-dodecane and cyclohexane systems is explained by effective hydrogen shuttling on the carbon surface. Increased extents of cracking and solid formation from ethylbenzene can be attributed to the relative hydrogen deficiency of this aromatic compound compared to the two alkanes.

Acknowledgments

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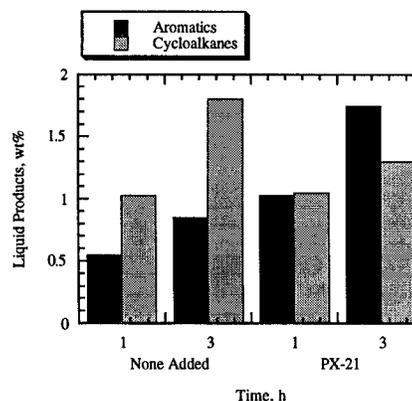
Figure 1. The concentration of aromatics and cycloalkanes in the liquid products from the thermal decomposition of n-dodecane with/without PX-21.
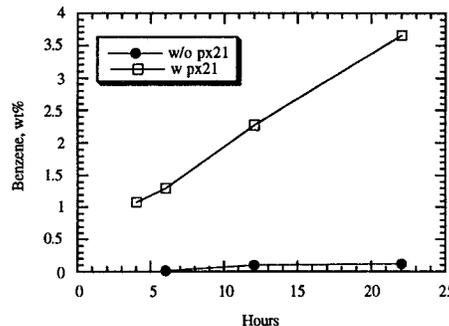

Figure 2. Benzene concentration in the liquid products from the thermal decomposition of cyclohexane with/without PX-21.
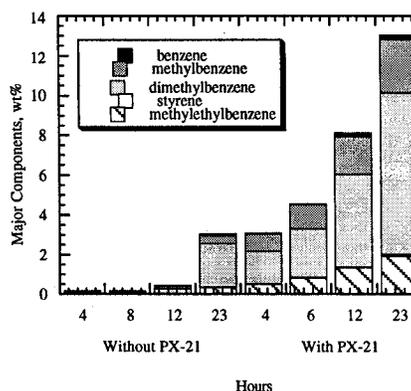

Figure 3. Concentrations of major components in the liquid products from the thermal decomposition of ethylbenzene with/without PX-21.

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