

EFFECTS OF CARBON SURFACES 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 (Heneghan et al., 1996; Eser, 1996). In our previous studies we showed that the presence of high surface area activated carbon PX-21 prevented solid deposition on reactor walls and reduced the extent of decomposition of *n*-alkanes (Eser et al., 1992; Gergova et al., 1994; Gergova et al., 1996). We have suggested that the active sites of PX-21 carbon act to stabilize the pyrolysis products and enhance the H-transfer reactions. There are other reports on the activity of solid carbons in catalyzing the reactions of hydrocarbons (Szymanski and Rychlicki, 1993; Grunewald and Drago, 1990).

In this study, we compare the effects of activated carbon and other carbon additions on thermal decomposition of *n*-dodecane, cyclohexane, and ethylbenzene, as three different types of hydrocarbons present in jet fuels, and investigate the influence of oxygen complexes present on the carbon surface on thermal decomposition of cyclohexane and ethylbenzene.

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 (Gergova et al., 1996). The high surface area activated carbon (PX-21), the carbon black (FW200), and another activated carbon (Asbury 5562) were obtained from Amoco Oil company, Degussa company in Germany, and Asbury company, respectively. Approximately 200mg of each carbon was added to model compounds prior to thermal stressing. The N_2 -BET surface areas of the three carbons are given below.

	PX-21	FW200	Asbury5562
Surface area(m ² /g)	3000	500	1200

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.

Boehm titrations (Boehm,) were performed with the three carbons to determine the concentrations of surface functional groups. For titrations, two- or three-gram samples of carbons were added in 200ml of various acidic and basic solutions prepared previously; all the solutions were 0.1M except Na₂CO₃ which was 0.05M. The solutions with added carbons were agitated for 48 hours, and filtered prior to titration. A 10 ml sample of filtered solutions was titrated with either 0.1M HCl or 0.1M NaOH solution depending on whether the acidic or basic functional groups are determined. Phenolphthalein or methylorange was used as an indicator in titrations.

The Asbury 5562 AC was bathed in strong nitric solution to oxidize its surface. A 20 g of activated carbon was bathed with 4M nitric acidic solution at 75°C for 2 hours. After bathing with acidic solution, the activated carbon was rinsed with distilled water until the washing water is neutral. The washed sample was dried in a vacuum oven. Boehm titrations were carried out on the oxidized carbon also to determine the acidic and basic functional groups on the surface.

RESULTS AND DISCUSSION

Thermal Decomposition of *n*-Dodecane. Despite the large differences in their BET surface areas the activated carbon PX-21 and the carbon black FW200 showed the same effect on thermal decomposition of hydrocarbons. Therefore, no results will be presented on the behavior of FW200 in thermal stressing experiments. 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. 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 (Gergova et al., 1996) 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 β -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 (Gergova et al., 1996).

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. Similar to the results obtained with n-dodecane, the analysis of gaseous products showed 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. These results suggest 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.

Surface Characterization of Carbons using Boehm Titration. Based on the Boehm titration results, the equivalent numbers of each basic and acidic solution neutralization were calculated. As shown in Table 1, small concentrations of basic groups are present on the surface of PX21 and 5562AC, but no basic groups are detected on the FW200. There are large concentrations of acidic groups present on both PX21 and FW200 surfaces, but relatively small concentrations of acidic groups are detected on 5562AC surface. If the acidic groups are divided into four individual groups, large concentrations of carboxyl and lactone groups are found on the surface of both PX-21 and FW200, but none is present on 5562AC. Compared to carboxyl and lactone groups, phenolic and carbonyl groups are less abundant on PX21 and FW200 surfaces than those on 5562AC.

It appears that PX21 and FW200 with high concentrations of surface acid groups, especially carboxyl and lactone groups, are very active during thermal decomposition of hydrocarbons. In contrast, 5562AC with low concentrations of acidic groups, but relatively high concentrations of phenolic and carbonyl groups did not show much activity during thermal stressing of hydrocarbons. These results suggest that oxygen functional groups are important for the activity of carbon surfaces during thermal decomposition of hydrocarbons.

Effects of Oxidation of 5562 Asbury Activated Carbon on Thermal Degradation of Ethylbenzene and Cyclohexane. Upon oxidation of 5562 Asbury activated carbon with nitric acid solution, all basic groups are decreased from 0.48 meq/g to 0.3 meq/g, and all acidic groups are increased from 0.65 meq/g to 2.1 meq/g (see Table 1). The oxidation treatment increased the concentrations of all major acidic groups except the phenolic group.

Untreated and oxidized Asbury 5562 activated carbon were used in thermal stressing experiments with ethylbenzene and cyclohexane. The thermal stressing of ethylbenzene and cyclohexane (10ml) was done with 300mg of as-received and oxidized 5562AC. Liquid product analysis shows that oxidized 5562AC shows the same effect during ethylbenzene pyrolysis as that observed with PX-21 and FW200, that is, more extensive cracking of alkyl side-chain was obtained with oxidized 5562AC than that observed with as-received 5562AC present. The addition of oxidized 5562AC promotes cracking reactions and increases the amount of carbonaceous deposit on the reactor wall. The liquid products obtained with the oxidized 5562AC was much darker in color. Figure 4 shows that the addition of the oxidized carbon gave much higher concentrations of benzene, methylbenzene, dimethylbenzene, styrene and methylethylbenzene compared to those obtained with the untreated 5562AC. The major product was dimethylbenzene. The amount of ethylbenzene remaining was drastically reduced when the oxidized 5562AC was added during pyrolysis experiments (see Fig. 5). These results are the same as those obtained from the pyrolysis of ethylbenzene with PX21 or FW200.

In contrast to ethylbenzene pyrolysis, the addition of oxidized 5562AC inhibited the thermal cracking of cyclohexane and gave much higher concentrations of benzene in the liquid products

(see Fig. 6,7). The data shown in Figure 3 clearly demonstrates the dehydrogenation activity of oxidized 5562AC indicated by the increase in benzene concentration, however the isomerization activity (i.e., cyclohexane to methylcyclopentane) was reduced with the oxidized 5562AC. These results suggest that oxidized 5562AC behaves like PX-21 and FW200 in promoting hydrogen transfer reactions.

It is important to note that even a very inactive carbon like Asbury 5562AC became active upon simple oxidation with nitric acid. These results confirm that oxygen functional groups, in particular acidic groups, on carbon surfaces play an important role during pyrolysis of hydrocarbons in the presence of added carbons. Some important reactions which appear to be catalyzed by active carbon surfaces include dehydrogenation of hydrocarbons, stabilization of free radicals at early stage of pyrolysis, and cracking of side chains on alkylaromatics.

CONCLUSIONS

Thermal decomposition behavior of hydrocarbons is strongly influenced by the presence of an activated carbon PX-21 and a carbon black FW200. The addition of PX-21 and FW200 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 hydrogen deficiency of the aromatic compound compared to the two alkanes.

Boehm titrations showed the most active carbons such as PX-21 and FW200 contain large concentrations of acidic, but low concentrations of basic surface groups. Especially carboxyl and lactone type groups are present in high concentrations on the surfaces of PX-21 and FW200, whereas no carboxyl and lactone groups are found on the surface of Asbury 5562AC. The nitric acid oxidation process effectively produced oxygen functional groups on Asbury 5562AC and increased its activity during thermal stressing of hydrocarbons. Oxygen functional groups appear to play a key role in determining the activity of carbon surfaces during thermal stressing of hydrocarbons.

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Table 1. Surface functional groups of different carbons.

	PX21, meq/g	FW200, meq/g	5562AC, meq/g	Acid treated 5562AC, meq/g
All Basic Groups	0.40	0	0.48	0.3
All Acidic Groups	3.3	3.3	0.65	2.1
Carboxyl	1.1	1.3	0	0.52
Lactone	1.9	1.6	0	0.86
Phenolic	0.1	0.1	0.2	0.12
Carbonyl	0.2	0.3	0.45	0.60

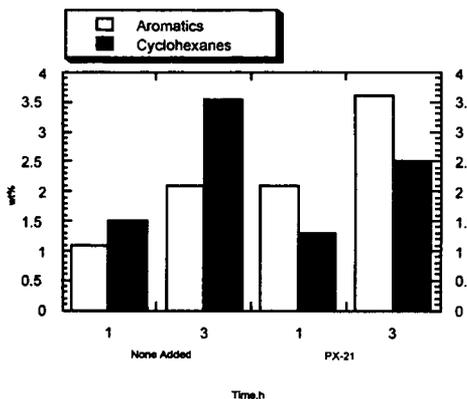


Figure 1. The concentrations of aromatics and cycloalkanes in the liquid products from the thermal decomposition of n-dodecane with/without PX-21.

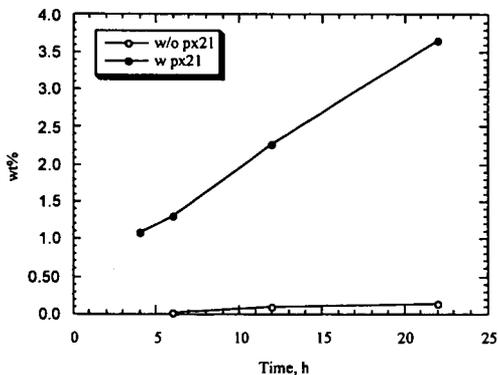


Figure 2. Benzene concentration in the liquid products from the thermal decomposition on cyclohexane with/without PX-21.

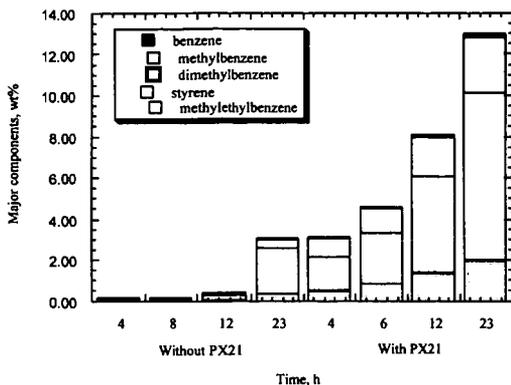


Figure 3. Concentrations of major components in the liquid products from the thermal decomposition of ethylbenzene with/without PX-21.

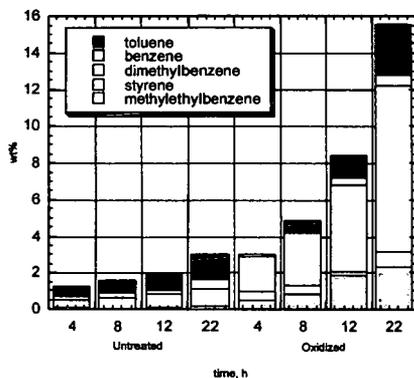


Figure 4. Major components from ethylbenzene pyrolysis with untreated/oxidized 5562AC.

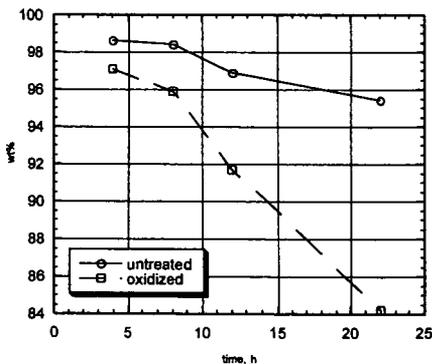


Figure 5. Ethylbenzene concentration from ethylbenzene pyrolysis with untreated/oxidized 5562AC.

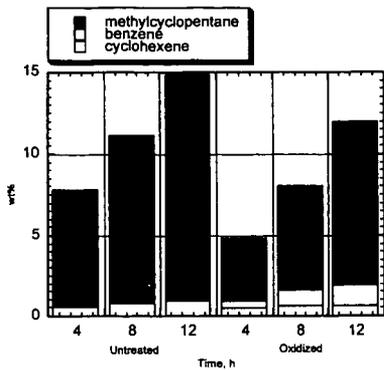


Figure 6. Major components from cyclohexane pyrolysis with untreated/oxidized 5562AC

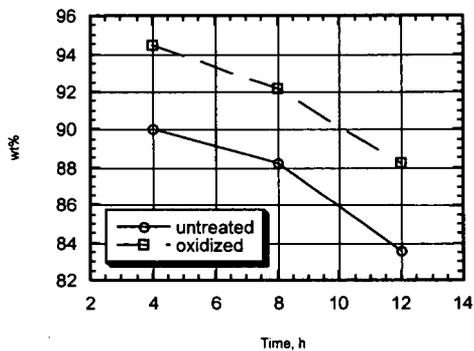


Figure 7. Ethylbenzene concentration from ethylbenzene pyrolysis with untreated/oxidized 5562AC.