

SUPERCritical-PHASE THERMAL DECOMPOSITION OF JET FUEL COMPONENTS: MIXTURE STUDIES

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INTRODUCTION

Jet fuels consist of hundreds of compounds, including long-chain alkanes, alkylbenzenes, and alkylcyclohexanes (Lai and Song, 1995). Coal-derived fuels also contain significant amounts of decalins and tetralins. In a previous paper (Yu and Eser, 1998), we have presented the results from the thermal decomposition of some typical jet fuel model compounds, including C₁₀-C₁₄ n-alkanes, n-butylbenzene (BBZ), n-butylcyclohexane (BCH), decalin, and tetralin, under supercritical conditions. The studies on pure model compounds have provided valuable information on jet fuel thermal decomposition. However, these studies can not answer the question on how individual compounds interact with each other during the thermal reactions of jet fuels.

In this work, the thermal decomposition of some binary mixtures of jet fuel model compounds was studied under supercritical conditions. Five binary mixtures were used in this study, including n-C₁₂/n-C₁₀, n-C₁₂/n-C₁₄, n-C₁₂/BBZ, n-C₁₂/BCH, and BBZ/BCH. Every mixture consists roughly of 50 wt% of each component.

EXPERIMENTAL

The n-C₁₀, n-C₁₂, and n-C₁₄ were obtained from Aldrich while BBZ and BCH were obtained from TCI America. All model compounds have 99+% purity and were used as received. Thermal reaction experiments were carried out in a Pyrex glass tube reactor with a strain point of 520 °C. In a typical experiment, the reactor was loaded, sealed, and then plunged into a fluidized sand bath preheated to the desired temperature. After a given reaction time, the reactor was removed from the bath and then was cooled down using pressurized air.

A Perkin Elmer 8500 gas chromatograph (GC) equipped with a DB-17 column and a flame ionization detector (FID) was used for the quantitative analysis of liquid products. The compounds in liquid products were identified by gas chromatography-mass spectrometry (GC-MS) using a Hewlett Packard (HP) 5890 II GC connected with an HP 5971A mass selective detector. The identifications of major compounds were also made by running standard mixtures. The gaseous products were not analyzed because of the extremely low yields.

RESULTS AND DISCUSSION

Reaction Rates. The changes in conversions of individual model compounds with reaction time were obtained from the thermal decomposition of the mixture at 425 °C for 15-60 min with a loading ratio of 0.36. The loading ratio was defined as the ratio of the initial sample volume at room temperature to the reactor volume. Figure 1 shows the conversion of n-C₁₂ as a function of reaction time for the thermal decomposition of the pure compound, in n-C₁₂/n-C₁₀ mixture, and in n-C₁₂/n-C₁₄ mixture. One can see that the conversion of n-C₁₂ is affected by the presence of the second compound. While the conversions for the decomposition of n-C₁₂ in n-C₁₂/n-C₁₄ mixture are higher than those for the decomposition of pure n-C₁₂, the conversions of n-C₁₂ in n-C₁₂/n-C₁₀ mixture are slightly lower than those for the decomposition of pure n-C₁₂. These results suggest that the lighter alkane inhibits the decomposition of the heavier one while the heavier alkane accelerates the decomposition of the lighter one.

Figure 2 shows the conversion of n-C₁₂ as a function of reaction time for the thermal decomposition of the pure compound, in n-C₁₂/BBZ mixture, and in n-C₁₂/BCH mixture. It can be seen that the presence of BBZ accelerates the decomposition of n-C₁₂ and the presence of BCH inhibits the decomposition of n-C₁₂. The increased decomposition rate of n-C₁₂ in the presence of BBZ can be explained by the increased radical concentration, resulting from the much faster initiation reaction of BBZ. The increase in radical concentration leads to an increase in the rates of hydrogen abstraction from n-C₁₂ and thus an increase in n-C₁₂ decomposition rates. On the other hand, the addition of BCH to n-C₁₂ reduces the radical concentration for the

decomposition of n-C₁₂ because some of the radicals produced from n-C₁₂ decomposition abstract hydrogen atoms from BCH instead of n-C₁₂.

Figure 3 shows a comparison of BBZ conversions from the thermal decomposition of pure BBZ, in BBZ/n-C₁₂ mixture, and in BBZ/BCH mixture, under similar conditions. It seems that n-C₁₂ and BCH exhibit very similar inhibiting effect on the decomposition of BBZ. This is probably due to very comparable hydrogen abstraction rates from C₁₂ and BCH by free radicals. The decomposition of BBZ is inhibited by the addition of n-C₁₂ or BCH because some of the radicals, which would abstract hydrogen atoms from BBZ in the absence of n-C₁₂ or BCH, abstract hydrogen atoms from n-C₁₂ or BCH. Since the rates of hydrogen abstraction from n-C₁₂ and BCH are comparable, both compounds exhibit similar inhibiting effect on the decomposition of BBZ.

Product Distributions. The major components in liquid products from supercritical-phase thermal decomposition of n-C₁₂/BBZ mixture were identified. Figure 4 shows the GC chromatogram of the liquid products from n-C₁₂/BBZ mixture at 425 °C for 60 min with an initial reduced pressure ($P_r = P/P_c$) of 2.04. The initial reduced pressure was calculated at the given temperature and loading ratio using the Soave-Redlich-Kwong equation of state (Soave, 1972). The products produced from the thermal decomposition of the binary mixture include those found in the decomposition of the pure compounds and those found only in the mixture reactions. The products formed from the decomposition of n-C₁₂ component include series of n-alkanes and 1-alkenes lighter than n-C₁₂ and some heavy normal and branched alkanes. The products produced from the decomposition of BBZ component include toluene, styrene, ethylbenzene, benzene, allylbenzene, tetralin, and some secondary products, including n-propylbenzene, isopropylbenzene, sec-butylbenzene, isobutylbenzene, n-pentylbenzene, 1-propylbutylbenzene, 1,3-diphenylpropane, 1,4-diphenylbutane, and four C₆-diphenyls. Some products unique to the reaction of the mixture are also formed, including six C₁₄-benzenes, a series of high n-alkylbenzenes up to n-dodecylbenzene, a series of 1-propylalkylbenzenes up to 1-propylundecylbenzene, and some other alkylbenzenes with branched side chains.

Figure 5 shows a comparison in product distributions between supercritical and sub-critical conditions. The reactions were carried out at 425 °C for 60 min. Two loading ratios were used: 0.36 (supercritical, $P_r = 2.04$) and 0.08 (sub-critical, $P_r = 0.77$). It can be seen that supercritical conditions favor the formation of n-alkanes, toluene, and high-molecular-weight compounds, and suppress the formation of 1-alkenes and styrene.

CONCLUSIONS

Individual compounds interact with each other in the thermal reactions of binary mixtures. The compound with low reactivity inhibits the decomposition of the compound with high reactivity while the latter accelerates the decomposition of the former. Supercritical-phase thermal decomposition of n-C₁₂/BBZ mixture produces not only the products found in the decomposition of pure compounds but also the products unique to the reaction of the mixture. High-pressure supercritical conditions result in the formation of significant amounts of high-molecular-weight compounds.

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REFERENCES

1. Lai, W.-C.; Song, C. *Fuel*, **1995**, *74*, 1436.
2. Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
3. Yu, J.; Eser, S. This symposium.

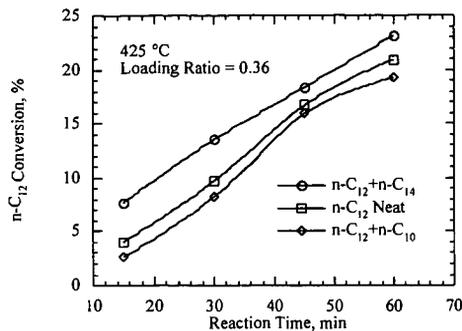


Figure 1. Conversion of n-C₁₂ versus reaction time from thermal decomposition of pure compound, in n-C₁₂/n-C₁₀ mixture, and in n-C₁₂/n-C₁₄ mixture.

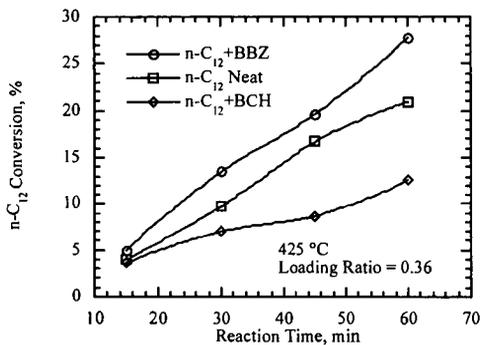


Figure 2. Conversion of n-C₁₂ versus reaction time from thermal decomposition of pure compound, in n-C₁₂/BBZ mixture, and in n-C₁₂/BCH mixture.

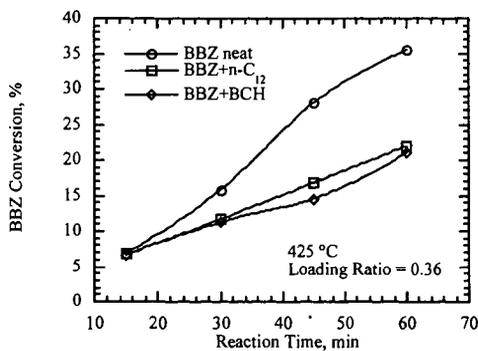


Figure 3. Conversion of BBZ versus reaction time from thermal decomposition of pure compound, in BBZ/n-C₁₂ mixture, and in BBZ/BCH mixture.

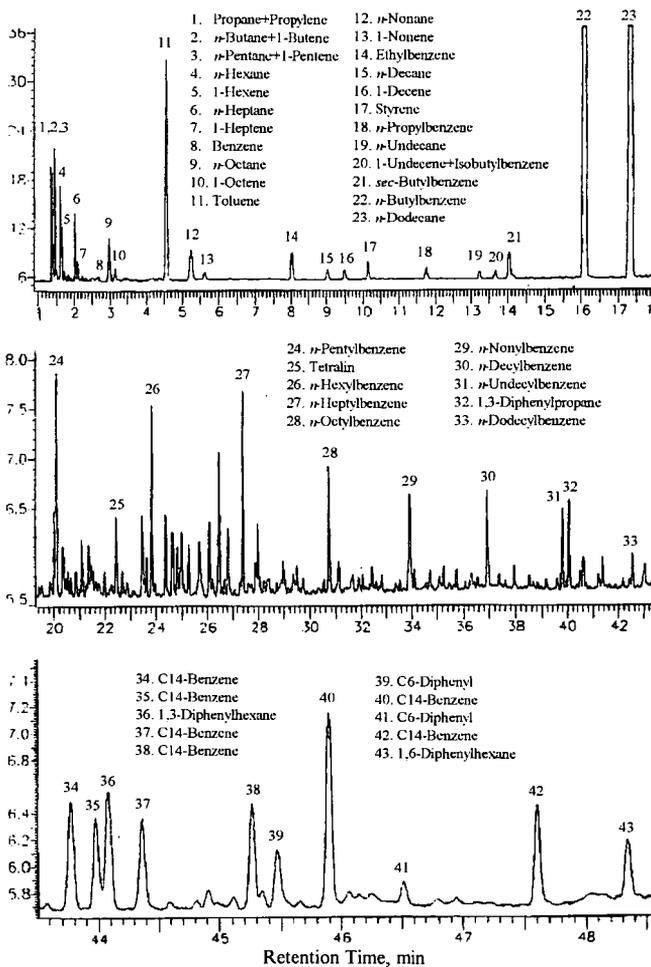


Figure 4. GC chromatogram of liquid products from thermal decomposition of *n*-C₁₂/BBZ mixture at 425 °C for 60 min with a loading ratio of 0.36.

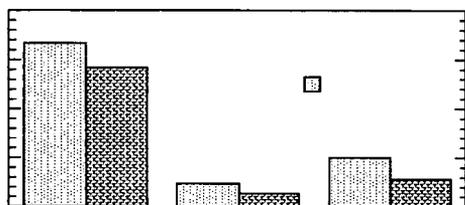
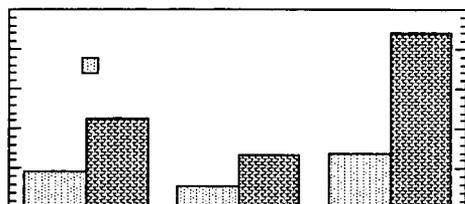
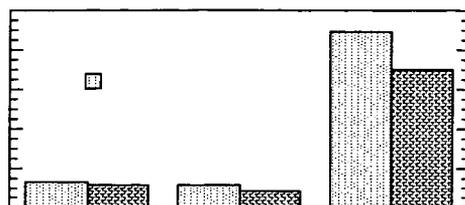


Figure 5. Comparison of product distributions between supercritical and sub-critical conditions.