

U.S. DEPARTMENT OF ENERGY  
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

**NUCLEAR WASTE TECHNICAL REVIEW BOARD  
EBS PANEL MEETING**

**SUBJECT: EXPERIMENTAL INVESTIGATION  
OF HYDROUS PYROLYSIS OF  
DIESEL FUEL**

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**PLEASANTON, CALIFORNIA  
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# Experimental Investigation of Hydrous Pyrolysis of Diesel Fuel

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## Hydrous Pyrolysis:

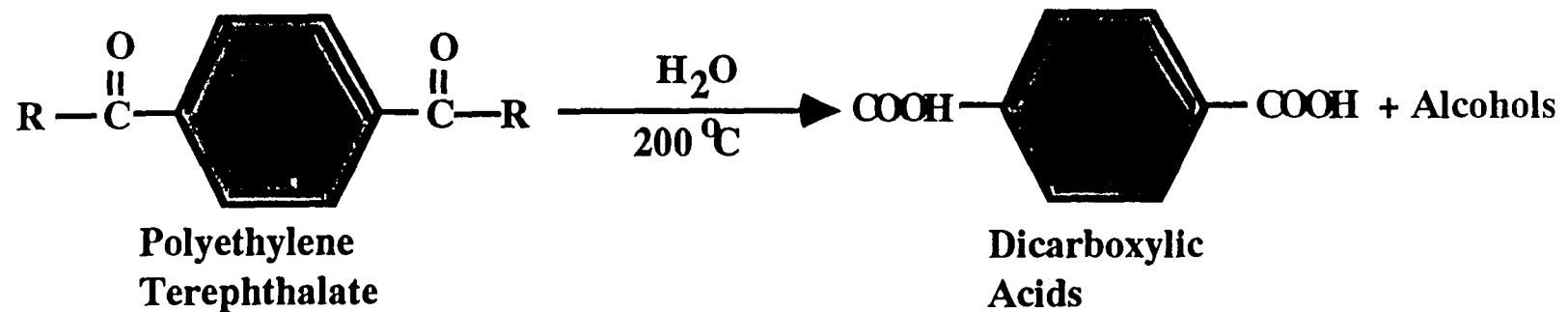
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- Diesel fuel and other hydrocarbon phases may be among materials that remain inside a nuclear waste repository.
- Temperature will rise during some period of time following the emplacement of waste.
- Some water will be present and available to react with organic materials in the repository system.
- Under these conditions, some organic compounds may undergo hydrous pyrolysis reactions that generate geochemically important products.
- It is not yet possible to predict the chemical consequences of hydrous pyrolysis reactions.



## Some Organic Compounds Undergo Hydrous Pyrolysis Reactions at High T:

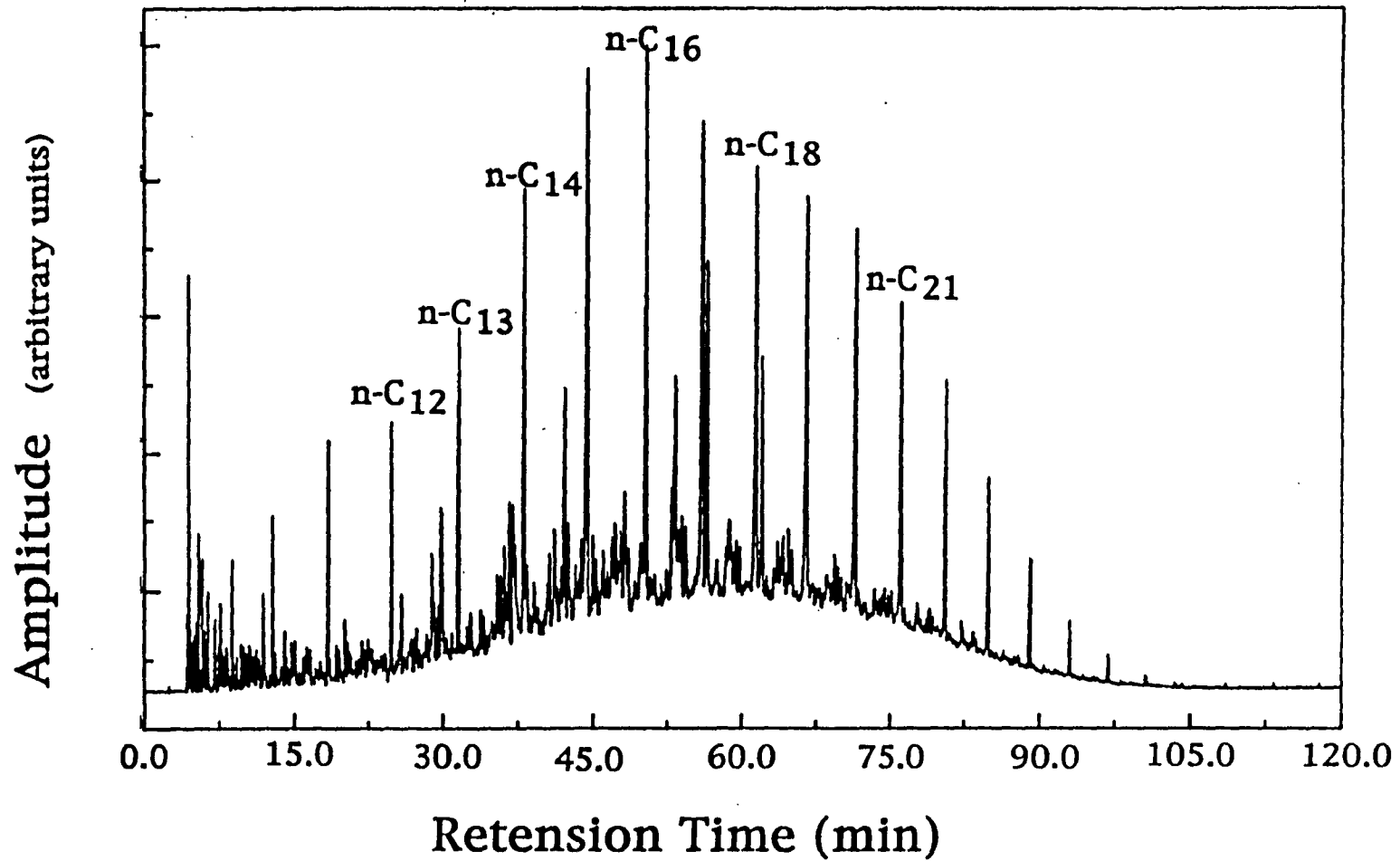
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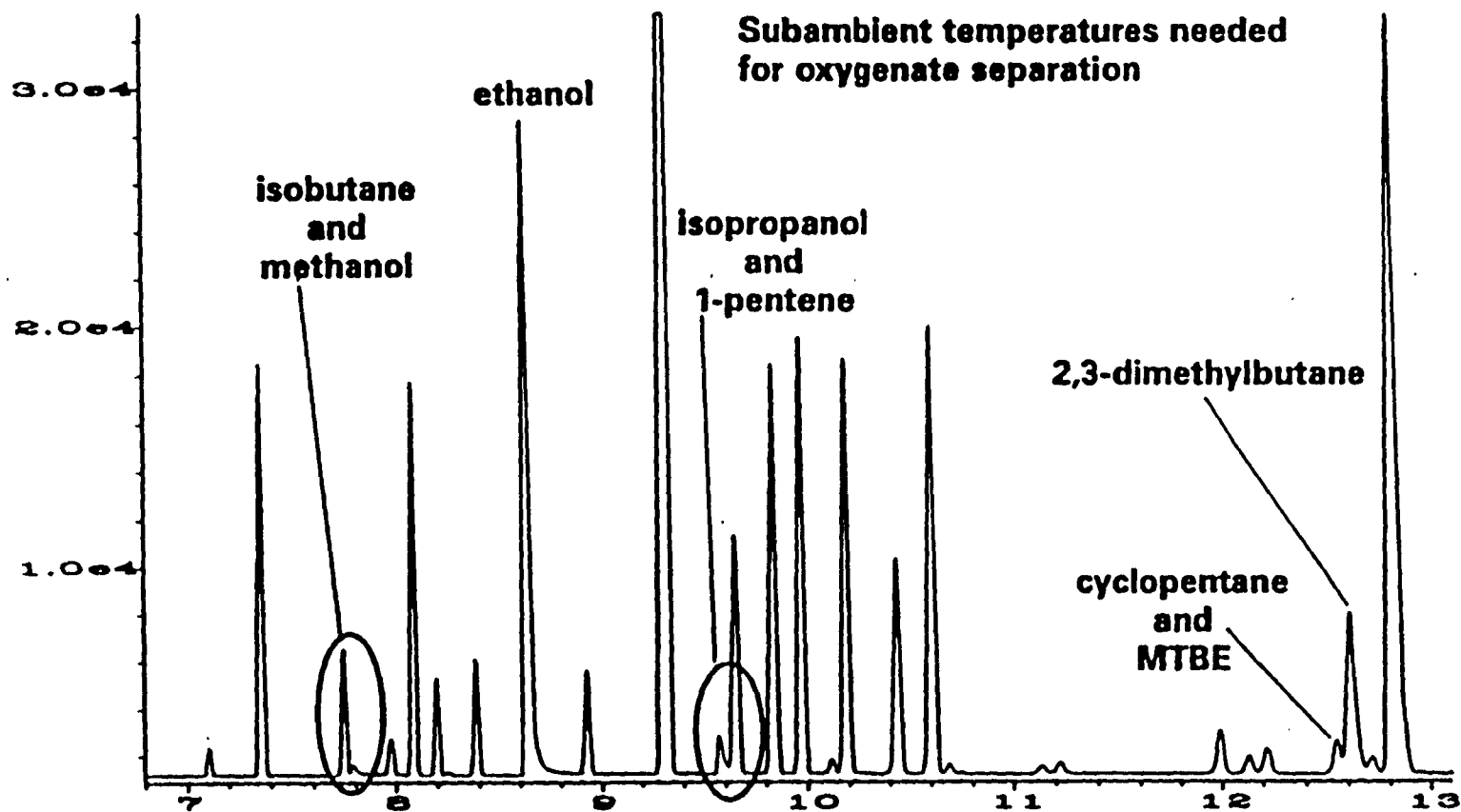
From Siskin and Katritzky (1991)



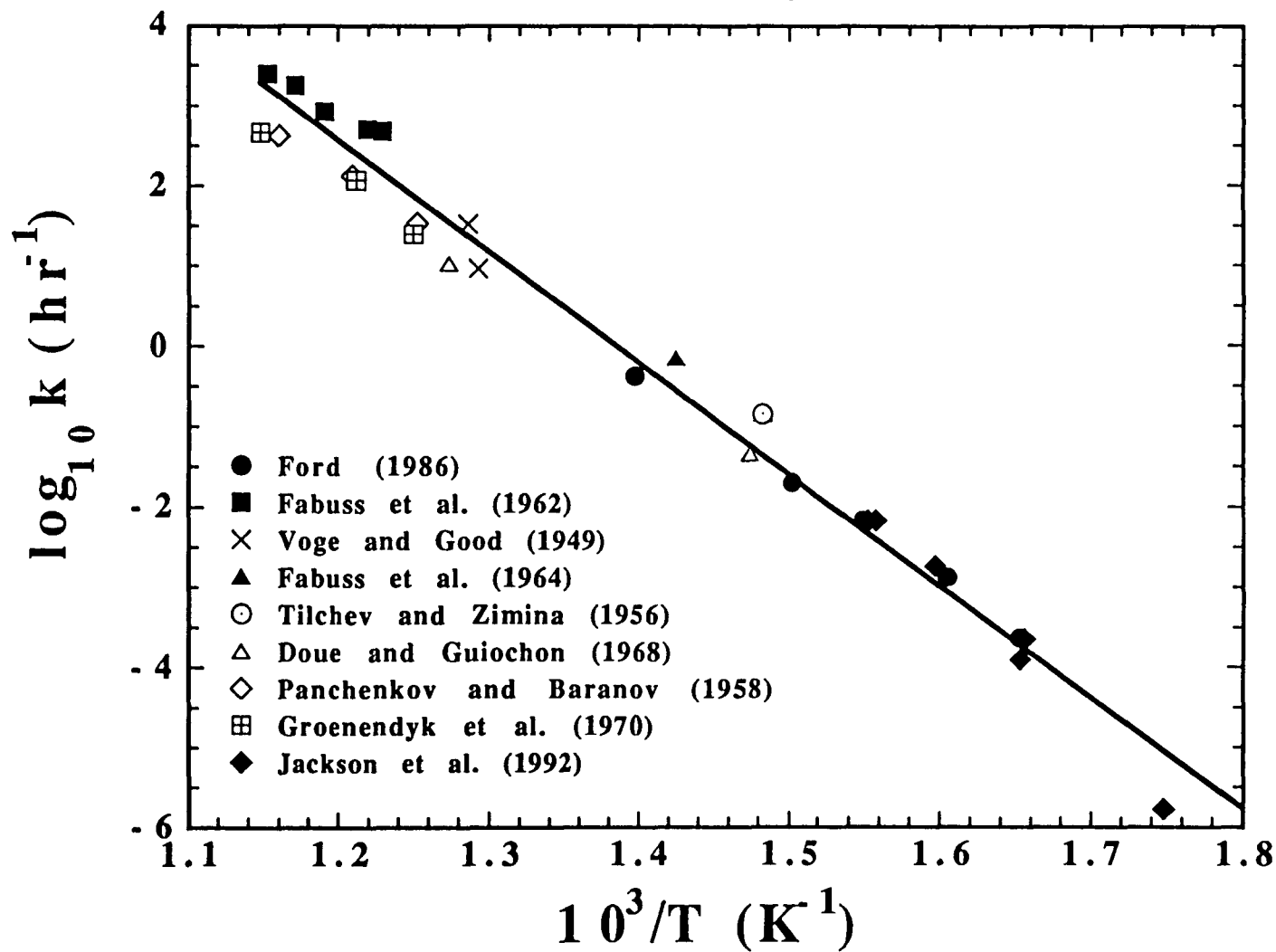
# Sample Gas Chromatograph of Diesel Fuel Fraction:

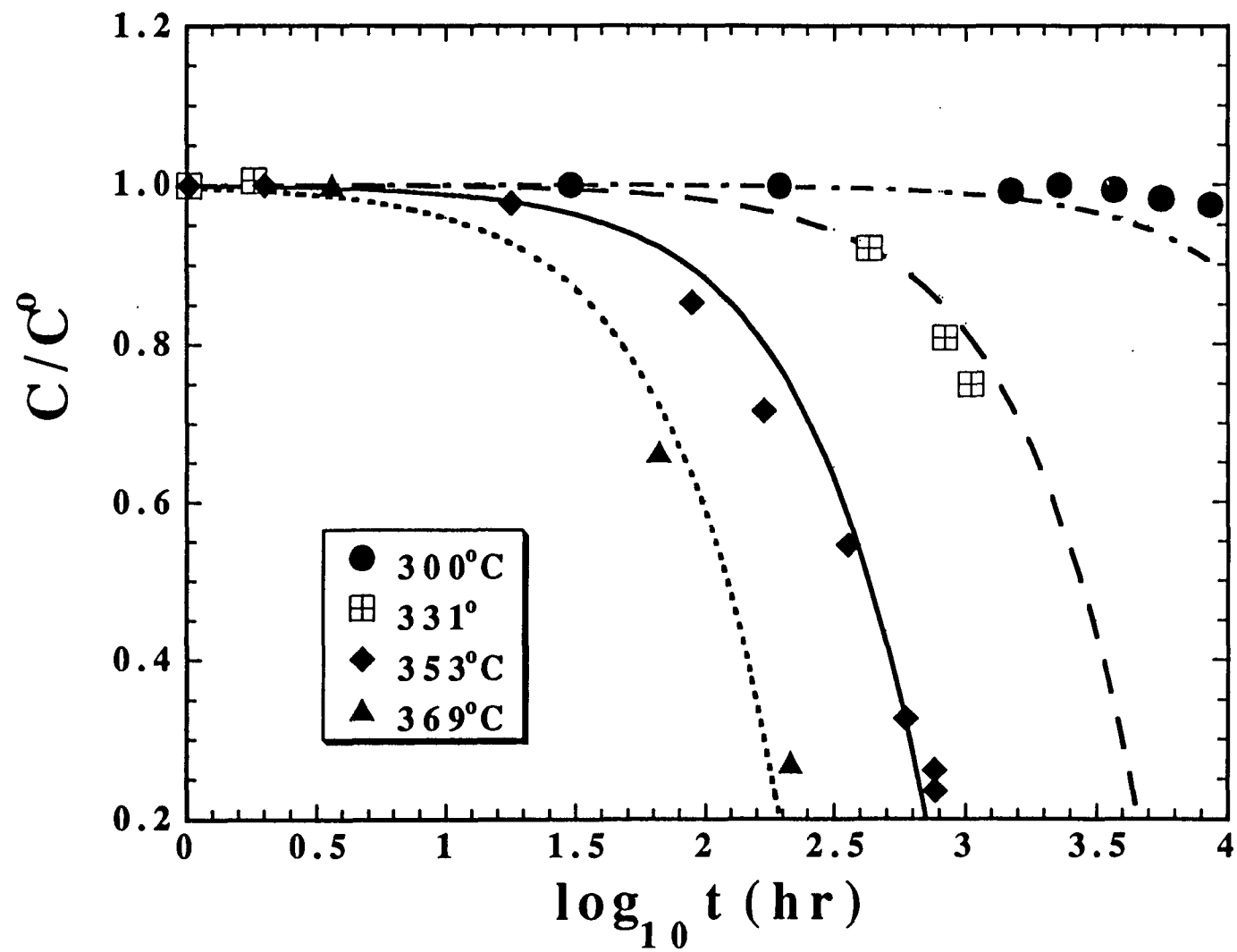


# Detailed Hydrocarbon Analysis of Gasoline (C<sub>1</sub>-C<sub>5</sub> Separation at 35° C Starting Temperature)



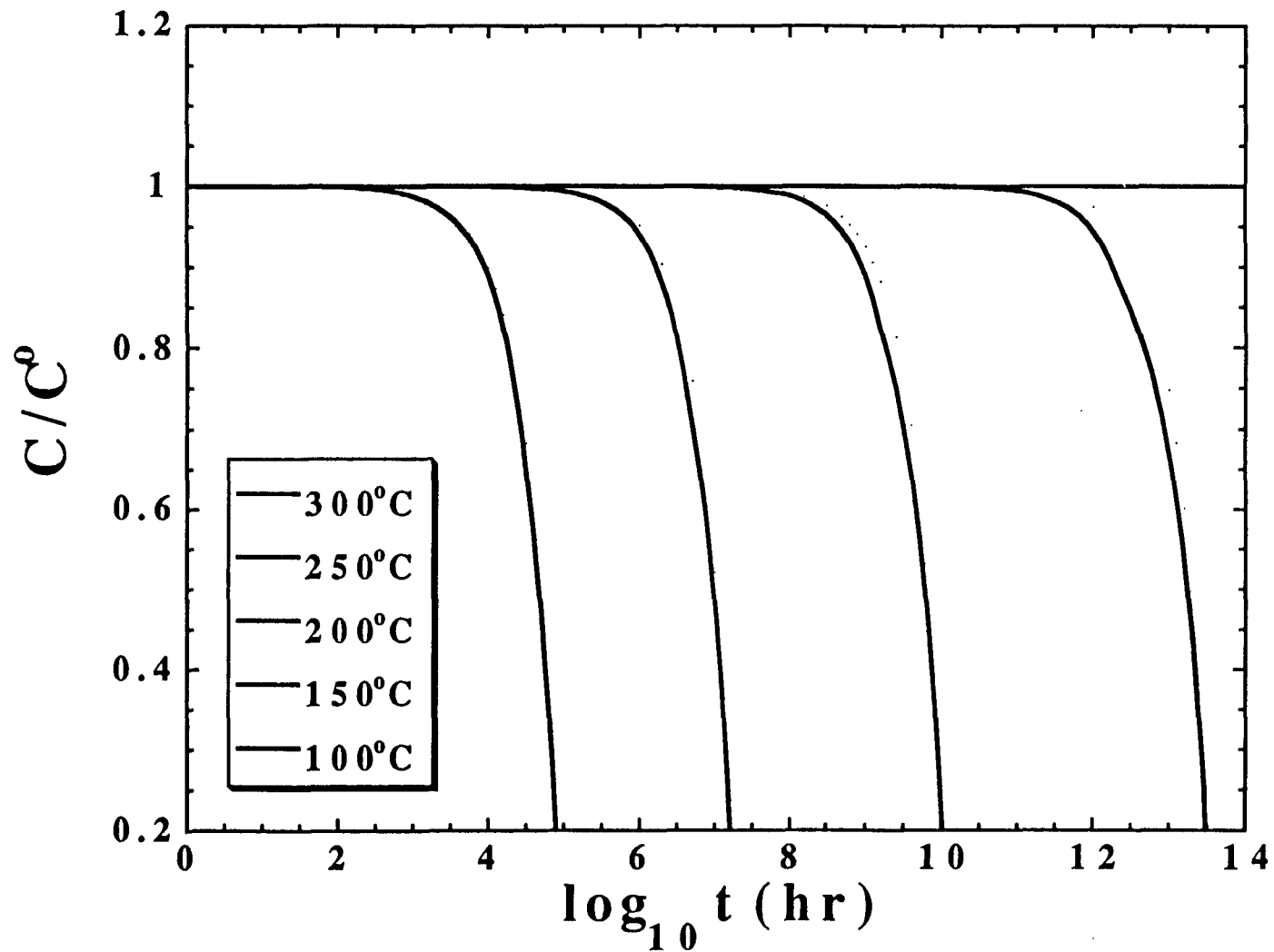
# Arrhenius Plot for n-C<sub>16</sub> Cracking Rates



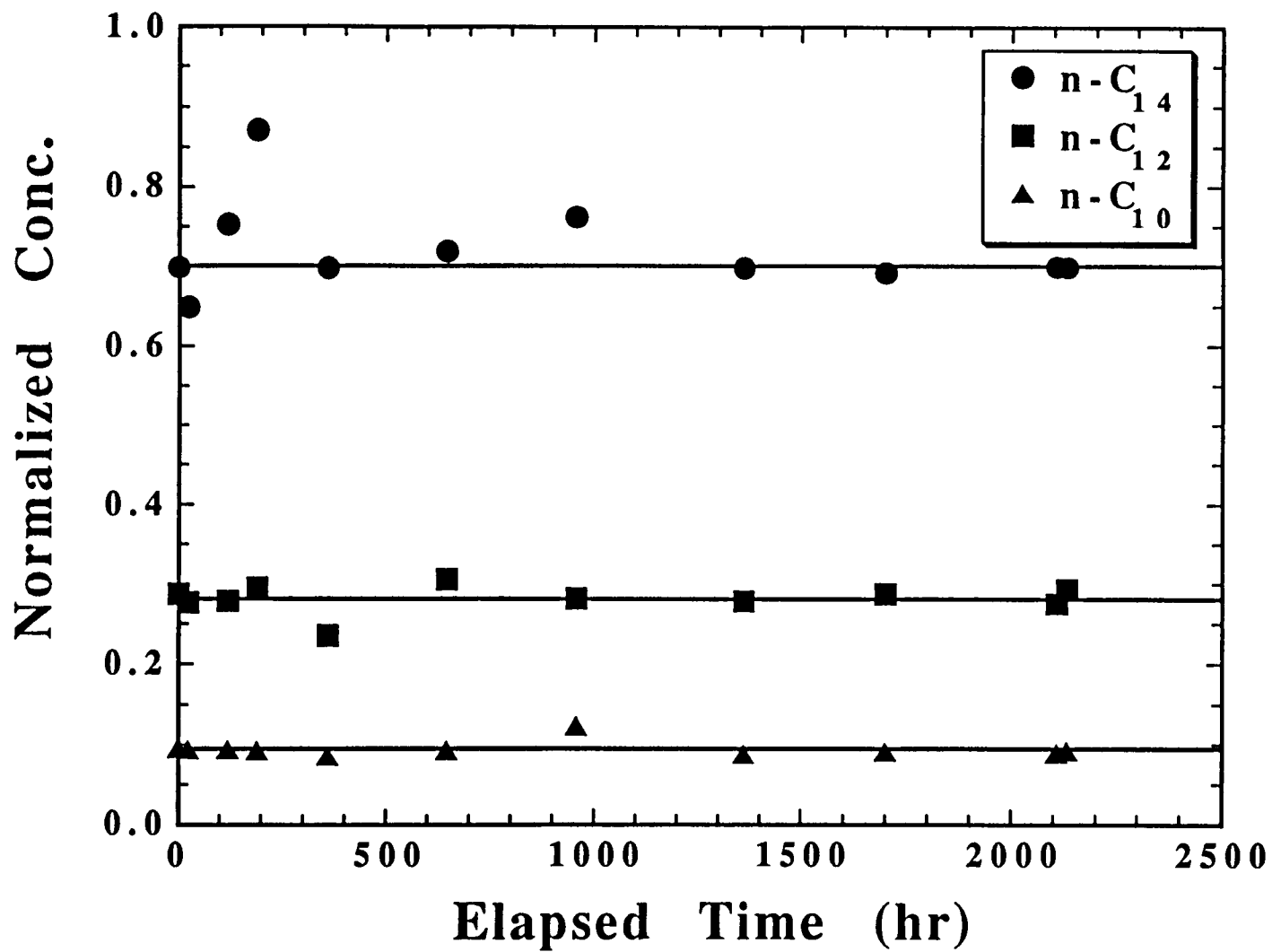


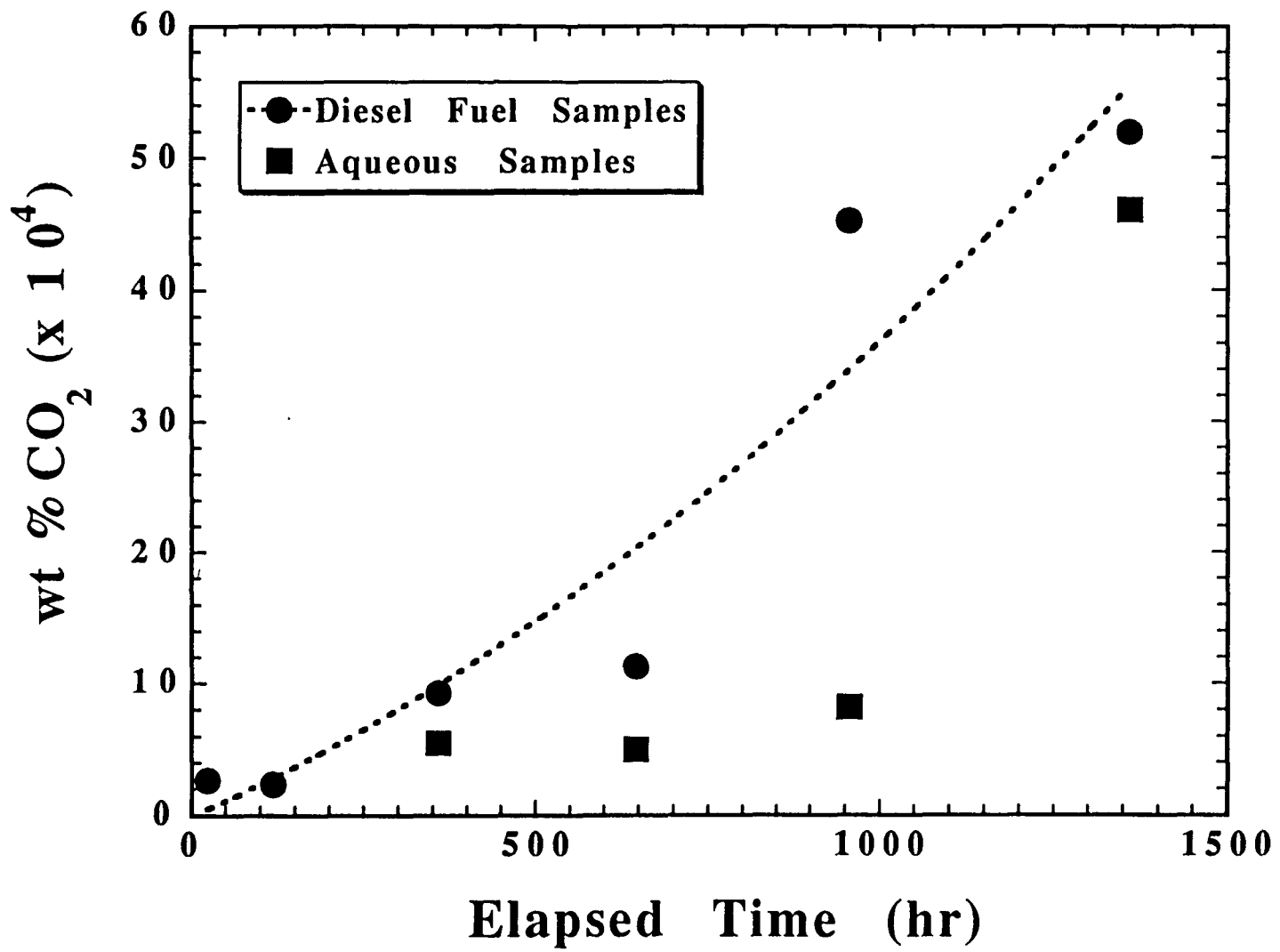


# Extrapolated n-Hydrocarbon Stability Curves

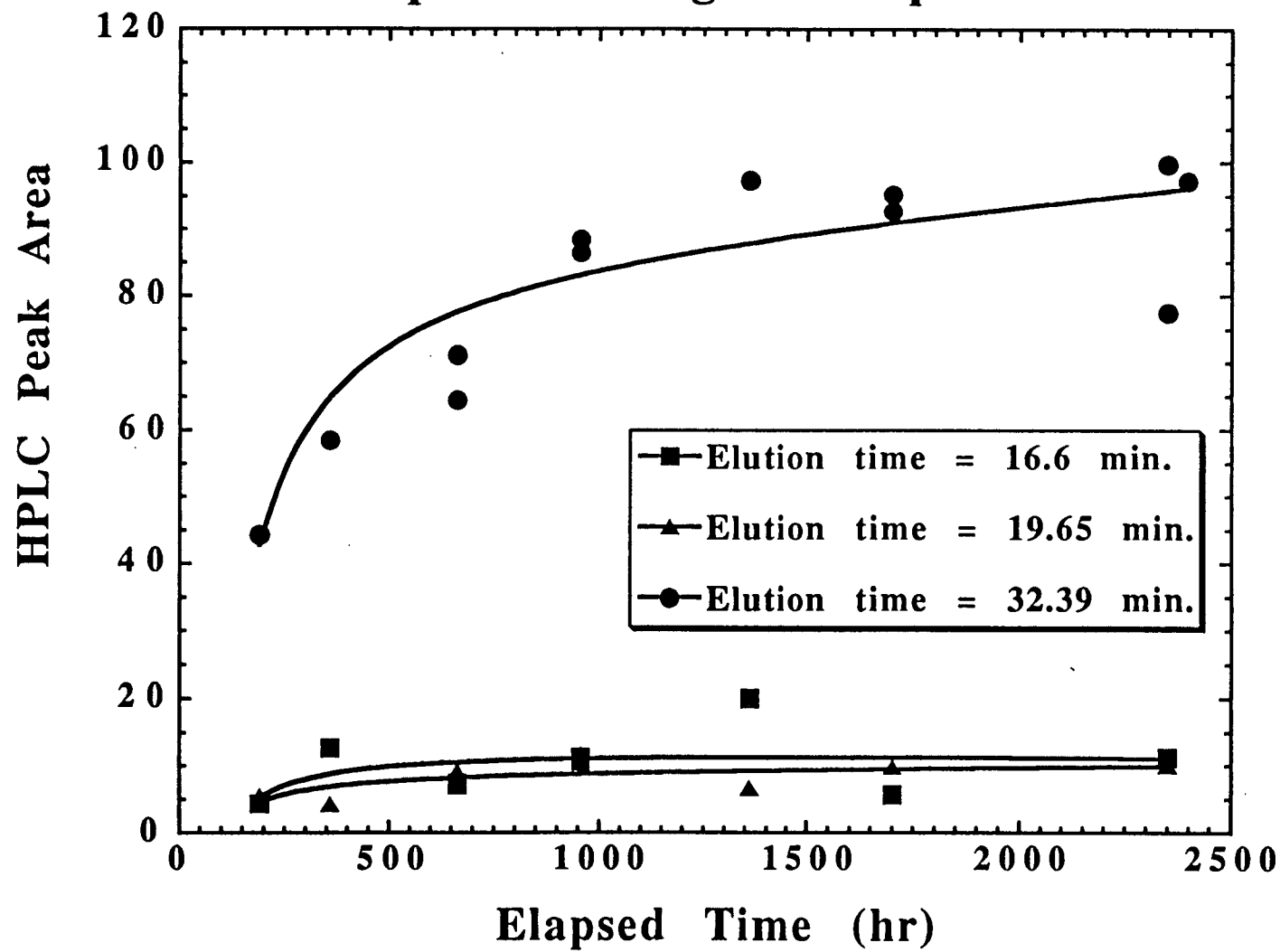


# Concentrations Relative to $n-C_{16}$

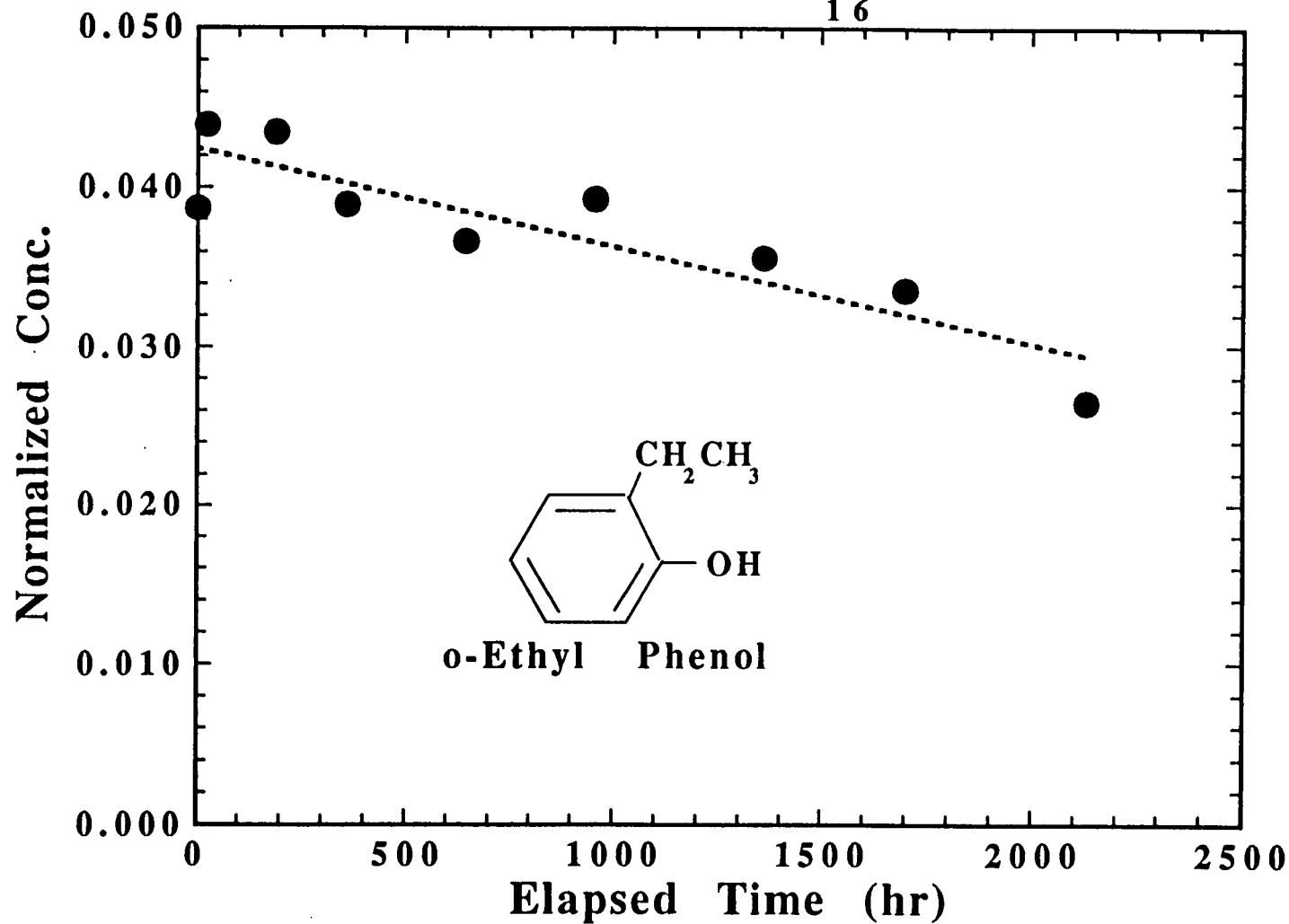




# Aqueous Organic Species



Decreasing Concentration of Minor  
Oxygen-Bearing Compounds  
Relative to n-C<sub>16</sub>





## Conclusions:

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- Most of the major hydrocarbon phases in diesel fuel will probably persist under expected repository conditions.
- Hydrous pyrolysis reactions involving some diesel components can be expected to occur.
- Pyrolysis products could influence aqueous chemistry by changing pH or contributing complexing ligands (e.g., sulfate or carboxylic acid anions).
- Organic reactions may also influence local redox chemistry by consuming available oxygen (e.g., CO<sub>2</sub> formation reactions).
- Catalysis or microbiological metabolism may significantly enhance rates for the destruction of many hydrocarbon phases.