In this investigation, we will use the molecular modeling suite, Gaussian 03, to investigate a series of hydrocarbons, some of which are important fuels. We will calculate the molecular structure (geometry), a theoretical value for the heat of formation, and heat of combustion for these compounds. The values we calculate are far from exact values. Within any computational software, we are using a very approximate model to describe the interactions between positively charged nuclei and electrons that make up the molecule. Each level of approximation is called a model chemistry and comparisons can be made between the structures and energies of molecules all calculated with a specific model chemistry. It is of interest to compare these theoretical values to experimental values when they are available. This comparison can validate the use of a particular model chemistry for a class of related molecular systems for which there may be no experimental values or to calculate properties not easily measured by experiment. Some model chemistries provide us with data that are easily related to tabulated experimental data. Molecular geometries given from calculations can be compared with X-ray or NMR determined structures when they are available.

Another property that semi-empirical model chemistries can provide is the theoretical heat of formation. This value can readily be compared with tabulated values in the CRC handbook and online at the NIST Webbase (http://webbook.nist.gov). Values determined from the AM1 semi-empirical model chemistry have been found to differ on average by 5-10 kcal/mole from experimental values.¹ Heats of formation can be used to determine heats of combustion. These are particularly useful when examining fuels such as ethanol and octanol.

Pre-lab:

Read the section on thermochemistry in the text in preparation (Atkins, 7th ed, Section 2.7-2.8).

Write out the equation for a hydrocarbon combustion reaction and indicate the quantities we will have to compute to determine the heat of combustion for each compound listed below.

In addition to the compounds listed below, come up with 3 additional compounds that you will study with our model chemistry.

Prep work to be done prior to your lab section:

For these calculations we will also compare the results from two different semi-empirical model chemistries: the AM1 method and the PM3 method. In preparation for this investigation you will need to set up your laboratory notebook with a title, a short description of what we are trying to accomplish in the investigation, as well as the equation for combustion. Tabulate the data you look up for each of your compounds. As well, you will need to look up the heat of formation for each of the compounds below and tabulate them so that we have a reference point for our calculations.
### Compounds

<table>
<thead>
<tr>
<th>Ethylene</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Methanol</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Butanol</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Toluene</td>
</tr>
<tr>
<td>Kerosene (C_{11}H_{24})</td>
<td>Octane (n-C_{8}H_{18})</td>
</tr>
</tbody>
</table>


Notes: Hyperchem

**Steps**

Get comfortable with WebMO. Login in at [http://bert.chem.gac.edu/](http://bert.chem.gac.edu/) and follow Computational tools to WebMO login. You will be given a username and password for the class. To get started with WebMO there are brief instructions on Bert at [WebMO help](http://webmo.net/). You can also visit the WebMO software page at: [http://webmo.net/](http://webmo.net/)

Use WebMO to draw and optimize water, CO2, and O2 with the AM1 semi-empirical method. We will use Gaussian 03 (see: [http://www.gaussian.com/](http://www.gaussian.com/)) on the first available computational server. Tabulate the bond angles and bond lengths. Do they correspond with your expectations? Now carry out a vibrational frequency calculation on each and view the three water vibrational modes by clicking view in the job display window. What are the three frequencies? Describe them qualitatively and proved the quantitative data. How do these match with experimental data (see NIST Webbase)? You will need to carry out an optimization and frequency calculation for each molecule studied in order to get the Enthalpy values that are calculated by Gaussian 03 using statistical mechanics.

From these calculations record the energy and enthalpy for each compound. Note that these are not the heats of formation, but you are using differences so they are equally valid in the thermochemical calculations. You will compare these with those tabulated in your Excel spreadsheet to verify its operation.

Draw your remaining compounds and carry out calculations on each, including the three you gave in your pre-lab assignment.

Download the Excel spreadsheet by selecting the appropriate computational jobs clicking on spreadsheet.

The initial calculation is single-point with no geometry optimization. Repeat the above calculations with geometry optimization. (do-optimization)

Using Excel or SigmaPlot, graph the heat of formation calculated for each molecule using both methods versus the experimental values you looked up (NIST Webbase). Add columns in your Excel spreadsheet to calculate the heat of combustion for your compounds as well as the heat of combustion/gram.
Which compound is the most efficient fuel?

Discuss the advantages/disadvantages of ethanol, 85% ethanol, and 10% ethanol as fuels.

Discuss the accuracy of your calculations and compare the results.

Complete your discussion and tabulate your results in your notebook to be turned in by the next laboratory period. Note any trends you observed.

Submit the values for the compound(s) you chose to http://bert.chem.gac.edu/pchemsubmita.html using the appropriate entry fields. Post these results as soon as possible. You will need to discuss and tabulate the other data posted (See: http://bert.chem.gac.edu/cgi-bin/datasaved.pl?file=Hydrocarbons) here by others in your own laboratory report.*

*This site does not seem to be working as of 9/6/05.

**I will inform you during your lab section whether you will need to complete this step or not.