

Research question

How does the chain length of straight chain primary alcohols affect its enthalpy of combustion?

Background information

One major problem currently facing the world is that it is running out of fossil fuels. One proposed alternative source to fossil fuels in internal combustion engines are alcohols. This is due to their high octane numbers as well as fairly widespread availability and affordability (Abdullah et al). As a biofuel, they are considered to be a renewable energy source and thus better for the environment than non-renewable fossil fuels. They also produce lower greenhouse gas emissions (Ashkok & Nanthagopal), but their effectiveness is limited to how well they can adapt to current fossil fuel-based infrastructure. Methanol and ethanol are the alcohols that are typically considered to be the most promising alternatives, given their low molecular weight, which improves efficiency by improving combustion pressure, as well as being of significantly lower cost (Kasibhatta). In internal combustion engines, an important value for engine performance is the enthalpy of combustion. This investigation will be focused on determining the enthalpies of combustion of primary straight chain alcohols through computational chemistry.

Primary alcohols are organic compounds with a hydroxyl group attached to a primary terminal carbon. The only exception to this is methanol, which while it is not technically considered a primary carbon, it shares similar properties to the rest of the primary alcohols and is considered to be a primary alcohol. Alcohols have relatively higher boiling points than their organic counterparts, due to the high prevalence of hydrogen bonding in the hydroxyl group. Alcohols react with oxygen to combust and create heat energy, expanding air which is then harnessed to propel engines.

To measure the enthalpies of combustion, computational chemistry will be used rather than experimental chemistry. Computational chemistry has emerged as an indispensable tool, employing theoretical models and computational algorithms to investigate chemical properties and phenomena. Its foundation lies in the application of quantum mechanical principles, notably the Schrödinger equation, to determine molecular properties.

There are two main computational chemistry methods: *ab initio* and semi-empirical methods. These differ in their accuracy, with *ab initio* methods being more accurate, at the cost of requiring greater computing power and time. Semi-empirical methods streamline calculations by adding simplifications and experimental parameters. Given that *ab initio* methods were available, and that the molecules studied were not too complex (complex molecules can increase computing power requirements to an unreasonable level, a significant drawback to *ab initio* methods), it was decided to use that method. Semi empirical methods do produce results with regards to enthalpy of formation significantly easier and to an extent more accurately; however given that many of these models were trained on the experimental data that was going to be used to compare the results of the investigation with, it is pretty much pointless to run this investigation with semi empirical methods, as that would be quite simple. Some results from the semi empirical methods (semi empirical meaning part experimental) would be directly from databases, rendering this investigation useless.

The Hartree-Fock (HF) method is an *ab initio* method that provides an approximate solution to the time-independent Schrödinger equation for multi-electron systems. Since solving the Schrödinger

equation is evidently infeasible for the molecules relevant to this investigation, HF introduces simplifications to make computing values possible within a reasonable timeframe. The core principle of the HF method lies in the one-electron approximation. Each electron is assumed to move within an "average field" generated by the combined influence of all other electrons and the nuclei. This average field accounts for the repulsive electrostatic interactions between electrons. Another important aspect of the HF method is how it guesses molecular orbitals. The initial orbitals are used to calculate the average field experienced by each electron, which is then used to refine the original guess for the molecular orbitals. This cycle continues until the wavefunction and energy converge to a self-consistent solution. This is why it is important to have a somewhat reasonable starting geometry, in order to reduce computing time.

While the HF method offers a valuable foundation for more advanced computational approaches, it has limitations. Notably, it neglects electron correlation, which refers to the instantaneous influence that the position of one electron has on the positions of other electrons. This omission can lead to inaccuracies in situations where electron-electron interactions play a significant role, such as in radical systems or molecules with strong bonds between atoms of similar electronegativity. In this case though, with fairly regular organic molecules these should be reduced to a minimum.

Gaussian is a fairly well known and widely used computational chemistry package. It can be used for both *ab initio* and semi empirical methods, but for the purposes of this investigation only the *ab initio* methods will be used. It draws upon the principles of quantum mechanics to model molecular systems. To start, molecules to be investigated with Gaussian should be geometrically optimized using the built in "Geometry optimization" function, which finds the molecule's most energetically favorable geometry by guessing based off it's current geometry, which is required for subsequent calculations. Gaussian also provides tools to calculate vibrational frequencies, dipole moments, and numerous other molecular properties relevant to chemical research.

WebMO was used to aid the investigation. It is a computational chemistry interface that is designed to be connected to computational chemistry software. To be clear, Gaussian (or any other computational chemistry package) is useable without WebMO, but WebMO makes calculations significantly easier. It allows for the creation of molecules using it's built-in molecule builder. It does provide some computation, where it can "clean up" the molecule on request. This is a rough guess, using bond strengths and VSEPR theory to get the molecule to something more reasonable for Gaussian to work with. This does save time and computational power for the geometry optimization, giving it a solid starting point.

Variables

Variable	Type	Explanation
Chain length of alkane branch	Independent	This is the chain length of the alkane branch.
Enthalpy of formation	Dependent	This is dependent as it is the value measured through the computation.
Basis Set	Controlled	The same basis set was used each time, 6-31G(d), keeping the level of accuracy consistent. Choosing different basis sets <i>will</i> result in significantly different values.
Pressure	Controlled	The measured pressure was 1 atm.
Temperature	Controlled	The measured enthalpy was measured at room temperature, or 298.15 K.

Table 1 List of variables

Methodology

1. The required software was downloaded; if that is an impediment to the replicability of the investigation then WebMO does offer a demo server, which is free to use and requires no download. The investigation *is* replicable on the demo server.
2. On WebMO, the molecule was created by adding carbon atoms in a straight chain by dragging and clicking, to create a single bond. One terminal carbon is single bonded to an oxygen molecule. To select the oxygen molecule, the element selector was selected. It is unnecessary to add hydrogen atoms.
3. “Cleanup – Mechanics” was selected. Before proceeding to “job options”, if a “molecule not symmetric” prompt popped up, it was ignored.
4. Under job options, the calculation was set to “Optimize + Vib Freq”. If there are computing power concerns/limits, the jobs can be run separately under the jobs “Geometry optimization” and “Vibrational frequency”, obviously in that order. The theory and basis set were set to Hartree-Fock and 6-31G(d), with all other parameters left unchanged from the default.
5. This process was repeated for the other molecules in the homologous series up to 1-pentanol.
6. The results were exported as a spreadsheet, using WebMO’s export function.

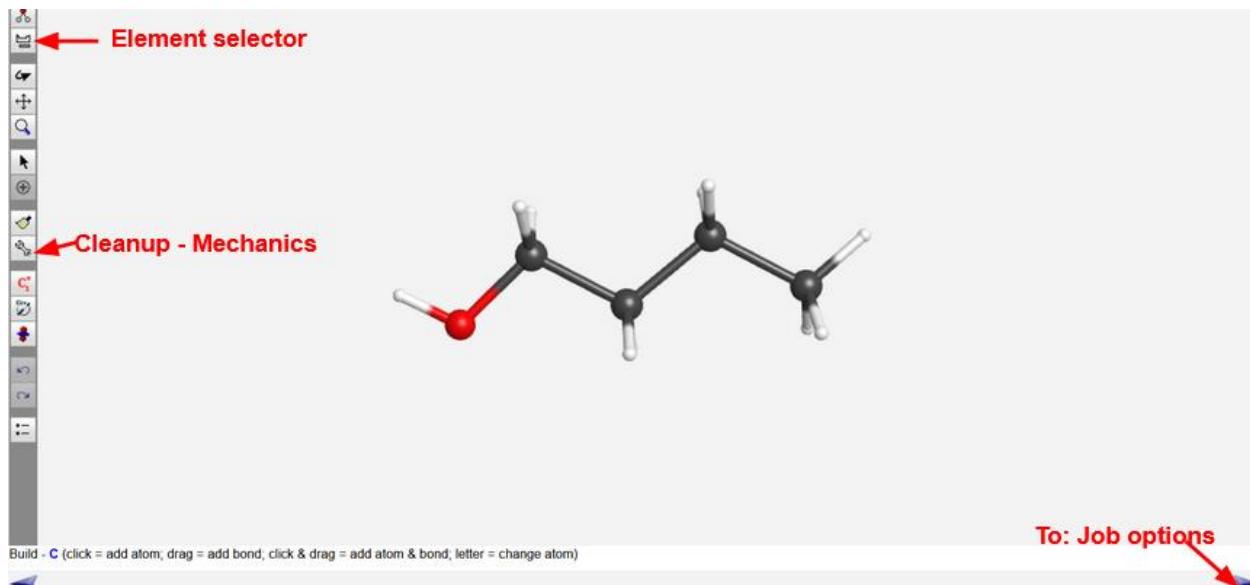


Figure 1 Screenshot from WebMO molecule building page (own annotations)

Safety, ethics, and environment

As this is a computation-based experiment, there are no ethical or safety considerations that need to be considered. However, the environmental factor that may have seemed trivial in the past has been increasingly under the global spotlight (Belton, 2021). Running CPU-intensive computations does contribute to global warming and not wasting energy intensive CPU resources is key. Of course, the computations are still less wasteful than traditional lab-based experiments and an important tool in green chemistry, as it can act as a guide or starting point for experiments.

Quantitative data

Molecule	ZPE (Hartree)	Internal Energy (Hartree)	Cv (cal/mol-K)	Entropy (cal/mol-K)
Methanol	0.069273	-114.233	6.478	53.281
Ethanol	0.086017	-153.986	12.654	63.815
1-propanol	0.116653	-192.989	17.224	71.154
1-butanol	0.147187	-231.991	21.731	78.484
1-pentanol	0.177698	-270.994	26.27	85.742

Figure 2 Quantitative data table (direct export from WebMO data)

Evidently, no qualitative data was observed.

Other required data:

Atom	Electronic energy (Hartree)
Hydrogen	-0.49681
Carbon	-37.5886
Oxygen	-74.6566

Figure 3 Quantitative data table (direct export from WebMO data)

Enthalpy of formation of carbon dioxide (kJ/mol)	Enthalpy of formation of water (kJ/mol)
-393.52	-285.83

Figure 4 Enthalpies of formation (NIST WebBook)

Enthalpy of formation at 0k (kJ/mol)	Correction value (kJ/mol)
216.0199	4.22584
711.1963	1.046
246.8142	4.35136

Figure 5 Ochterski Data (will be used later)

Data processing

Molecule	ZPE + RHF energy (Hartree)
Methanol	-114.164
Ethanol	-153.900
1-propanol	-192.872
1-butanol	-231.844
1-pentanol	-270.817

Figure 6 Finding the actual electronic energy

The actual electronic energy is the sum of the ZPE and RHF which was performed on excel.

To find the enthalpy of formation, an equation is used similar to Hess' law. The electronic energy of the constituent atoms are subtracted from the total electronic energy of the alcohol, giving the difference as a placeholder for the enthalpy of formation.

Sample calculation (Methanol):

$$\begin{aligned} \text{Electronic energy}_{\text{Carbon}} + 4 * \text{Electronic energy}_{\text{Hydrogen}} + \text{Electronic energy}_{\text{Oxygen}} \\ = \text{Electronic energy}_{\text{Methanol}} + \text{"Enthalpy of formation"} \end{aligned}$$

$$(-37.5886) + 4 * (-0.49681) + (-74.6566) = -114.164 + \text{"Enthalpy of formation"}$$

$$-0.06844 \text{ Hartree} = \text{"Enthalpy of formation"}$$

Molecule	“Enthalpy of formation” (Hartree)	“Enthalpy of formation” (kJ/mol)
Methanol	-0.068	-179.689
Ethanol	1.085	2849.560
1-propanol	1.475	3872.927
1-butanol	1.864	4896.294
1-pentanol	2.255	5922.287

Figure 7 Worked data

Following the steps taken by Ochterski, using the aforementioned “Ochterski data”, the same sort of equation was applied, where the “enthalpy of formation” was subtracted from the sum of the enthalpies of formation at 0k ($0k \Delta H_f$), which were then corrected to room temperature using the correction value.

Worked example (Methanol):

$$(-\text{“Enthalpy of formation”}_{\text{Methanol}}) + 0k \Delta H_f(\text{carbon}) - \text{Correction value}_{\text{Carbon}} + 0k \Delta H_f(\text{oxygen}) - \text{Correction value}_{\text{oxygen}} + 4 * 0k \Delta H_f(\text{hydrogen}) - 4 * \text{Correction value}_{\text{hydrogen}} = \Delta H_f$$

$$(179.68922) + 711.19632 - 1.046 + 246.81416 - 4.35136 + 4 * 216.01992 - 4 * 4.22584 = \Delta H_f$$

$$1979.47866 \text{ kJ/mol} = \Delta H_f$$

Molecule	Actual enthalpy of formation value (kJ/mol)
Methanol	1979.47
Ethanol	83.96
1-propanol	194.33
1-butanol	614.11
1-pentanol	412.45

Figure 8 Actual enthalpy of formation values

To find the enthalpy of combustion, that value is used as is the enthalpies of formation of Carbon dioxide and water (as well as diatomic oxygen, which has an enthalpy value of 0) in an *actual* application of Hess' Law.

Worked example (Methanol):

$$\Delta H_c(\text{Methanol}) = \Delta H_f(\text{CO}_2) + 2 * \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{Methanol})$$

$$\Delta H_c(\text{Methanol}) = -393.52 + 2 * -285.83 - 1979.47$$

$$\Delta H_c(\text{Methanol}) = -2944.66 \text{ kJ/mol}$$

Molecule	Enthalpy of combustion (kJ/mol)	Value to match literature convention (kJ/mol)
Methanol	-2944.66	2944.66
Ethanol	-1728.50	1728.50
1-propanol	-2518.22	2518.22
1-butanol	-3617.35	3617.35
1-pentanol	-4095.04	4095.04

Figure 9 Enthalpy of combustion table

Analysis

Here is a graph of the data:

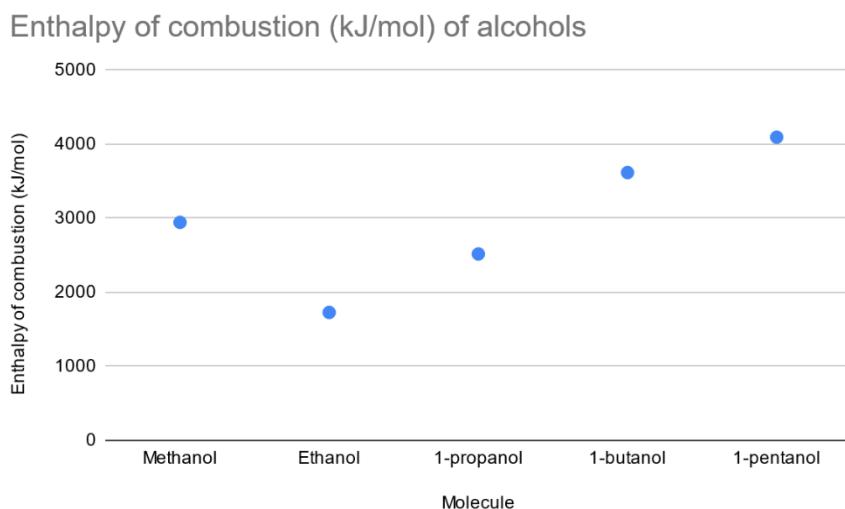


Figure 10 Graph of results

The methanol value is obviously erroneous, so if we take that as an outlier, we can see that there is a positive correlation between chain length and the enthalpy of combustion of straight chain alkanes.

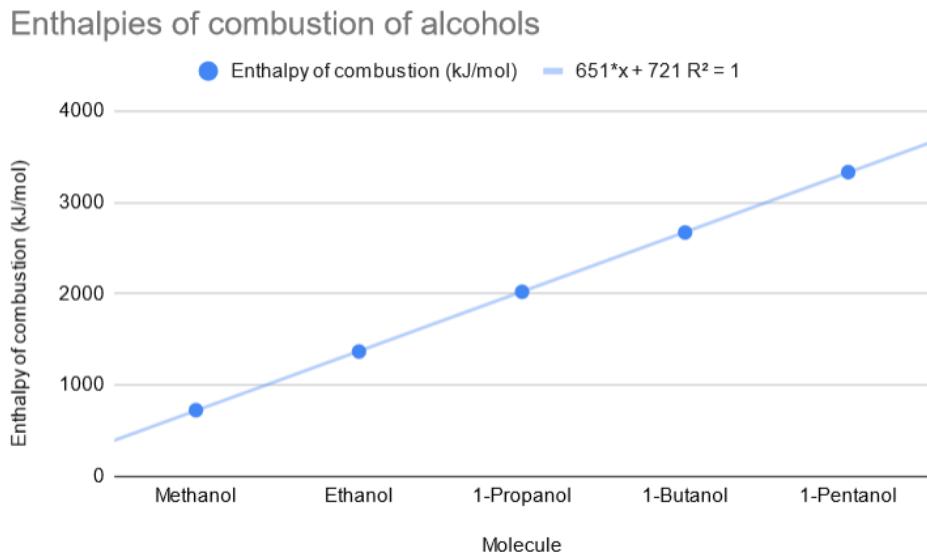


Figure 11 Literature values from NIST webbook of enthalpies of combustion (equation left for clarity, where x is the number of carbon atoms in the chain) (own work)

The above literature values were obtained from the NIST WebBook of molecule information. It can be seen here that the addition of more carbons in the straight chain alkane increases the enthalpy of combustion linearly, up to at least 1-pentanol. Methanol was obviously an outlier. This is due to the fact that the value went into the negatives in the beginning of the data processing, which messed up the rest of the operations.

Limitations

The database values, based on many highly qualified people's experimental data, are assumed to be fairly reliable. Other literature values in other databases are nearly, if not actually, identical. The databases have been around for a while, so it would be a fair assumption that if something was egregiously wrong then it would have been spotted by now. As well, given that the molecules studied are fairly common and small, the experimental data is relatively easily replicable (i.e. the data provided is not some obscure on off thing).

On the other hand, the computational software does not have a built-in uncertainty in the classic sense, like having measurement uncertainties in labware. The computations were run multiple times for confirmation purposes, which all producing the exact same results, as expected. It then becomes fairly difficult to calculate a numerical uncertainty, but due to the simulated nature of the experiment, it is pretty useless to calculate a numerical uncertainty. There would also be a level of unreliability on the uncertainty, and as chemistry is an empirical science, this value is only really useful as a guideline for further lab studying or to provide an estimate to economize lab resources and time. Computational chemistry results, especially fairly basic ones run on a personal computer should be considered in deference to high quality empirical results, making the uncertainty fairly moot. However, it is in the interest of accuracy and truthfulness that the reliability of the data is considered and how we know these results would be different from empirical results. For example, the HF method by definition always overestimates its values due to one of its core simplifications; modeling electrons within an averaged electrostatic field generated by all other electrons and the nuclei, which leads to its characteristic overestimation of molecular energies and stability. This was seen in this investigation, although interestingly enough the difference was not uniform, nor did it show any trend. Perhaps with a more accurate basis set, systematic error could be explored and quantified.

Of course, these are only the “known unknowns”, or the factors that have been taken into account by the developers of the software and basis sets. There could be other physical and chemical factors that would affect these results that the algorithms would not have considered. These factors would not be taken into account due to the nature of basic computational chemistry; it can only output what it is told to output, and cannot make “accidental discoveries” that are key in developing and progressing scientific knowledge. There really is not that much serendipity at such a basic level of computational chemistry, and considering the nature of the science, it is a severe limitation in this investigation.

Conclusion

The research question “How does the chain length of straight chain primary alcohols affect its enthalpy of combustion?” was addressed using Gaussian software run on WebMO. The data showed that as the length of the straight chain alkane increased, the enthalpy of combustion also increased. The *ab*

initio method was obviously unreliable. It has been concluded that to compute values for the enthalpy of formation of molecules, it would be better to use semi empirical methods, since that's what they were designed for. The most natural continuation of this investigation would be to perform this experiment in a real-life lab setting. The results would either support the validity of the computation software or, much more probably, poke holes in it. Either way, using computers in chemistry is helpful for analyzing trends and to support the environment.

It is important to note that the enthalpy of combustion values are not the be-all end-all in terms of evaluating a substance for engine performance. The relatively lower energy density of straight-chain primary alcohols, compared to traditional fossil fuels, does present a significant challenge to their widespread adoption as biofuels (Kasibhatta). For example, cars running on alcohol-based fuels will experience a decreased driving range compared to gasoline for the same fuel tank size. To compensate for this effect, larger fuel tanks, more frequent refueling, or specific engine modifications would be required. One potential extension to this investigation would be to investigate the viability of alcohol based fuels with this restriction in mind.

Another continuation would be to evaluate secondary alcohols and other organic molecules to form a comprehensive outlook on the topic. These organic molecules could include others in the primary alcohols series, with longer chains, although their real world utility as fuels is highly doubtful. As well, if possible, it would be interesting to run these computations on a more powerful device, with a more accurate basis set. This would obviously lead to more accurate values.

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