Chemistry Internal Assessment:

Factors affecting the enthalpy of combustion values of alcohols:

Background & Introduction:

The idea for this investigation came about when I was studying about organic chemistry in class. We learnt the relation of the enthalpy of combustion[1] values with the homologous series[2]. Various factors are taken into consideration but one of these aspects that really interested me, was to link to the position of these functional groups[3] and the number of carbon atoms and their effect on the enthalpies of combustion values. So, I decided to take up the functional group of alcohols and research about the effects that these 2 factors have on the enthalpy of combustion values and the appropriate reasons for the same.

In this research, for analysing the effects of the position of the hydroxyl group, I have chosen to investigate different types of alcohols, falling into the three categories primary, secondary and tertiary[4]. I have chosen to take the isomers of 3 compounds, them being, Propanol Isomers, Butanol Isomers and Pentanol Isomers. Additionally, I will also be evaluating how there are significant changes in the enthalpy values in primary alcohols itself. The number of carbon atoms will then be taken into consideration. Why I have chosen to take these compounds is because of the significant changes in the enthalpy values for both the factors that I will be talking about.

My aim in this investigation would be to find out how factors like an increase in carbon atoms, and changes in the position of the hydroxyl group effect the enthalpy of combustion

[1] Refer to Appendix 2 – Important definitions
[2] Refer to Appendix 2 – Important definition0073
[3] Refer to Appendix 2 – Important definitions
[4] Refer to Appendix 2 – Important definitions

values. By comparing and analysing the appropriate data of the combustion values of each of these alcohols, I will state a hypothesis according to the data that I collect and evaluate effectively in my IA.

Research Question:

How does the position of the hydroxyl group effect the enthalpy of combustion values of alcohols?

How does the number of carbon atoms effect the enthalpy of combustion values of alcohols?

Hypothesis:

I hypothesize that by changing the position of the hydroxyl group in each type of alcohol, from primary secondary and tertiary, the enthalpy of combustion will increase. This is because strong bonds require higher energies to be broken down than weak bonds so it can be said that more energy would be released during an exothermic reaction of tertiary alcohols than primary alcohols. Hence the enthalpy values will rise as we move down the homologous series.

Moreover, I also hypothesize that by increasing the number of carbon atoms, the value for enthalpy of combustion will increase. This is because, as the number of carbon atoms increases, the number of bonds that need to be broken and formed increases. For this to take place, more heat energy is required and hence the enthalpy of combustion values increase. For example, methanol has a lower enthalpy of combustion value than pentanol because methanol has fewer number of carbon atoms and hence less energy is required to break down the bonds than in pentanol, thereby having a lower enthalpy value than pentanol.

Methodology:

In this research I will be using data from various databases and with graphical representations I will analyse the data from the different sources and take a close look at the uncertainties that they contain and how the 2 factors mentioned above, the position of the hydroxyl group and the number of carbon atoms, affect the values of enthalpy of combustion.

The independent variables for this investigation are the isomers (of the compounds; propanol, butanol and pentanol) and the number of carbon atoms (from 1 carbon atom to 6 carbon atoms i.e., methanol to hexanol). The dependent variable in this research is the enthalpy of combustion of alcohol.

The control variables that I will be considering is the functional group – alcohols. The main reason why I chose to investigate specifically on alcohols is because there is a wide range of data available for its compounds and it is easier to compare between the isomers of different compounds.

I will be comparing data from 4 sources, them being:

1. NIST Webbook
2. UCSDB
3. Nvlpubs – Bureau of Standards Journal of Research
4. MIT- Research Paper

Using data from these sources I will analyse the raw data and find out uncertainties and I will analyse my findings and give justified reasoning. For comparing the values of the heat of combustion and how they are affected by changes in the position of the hydroxyl group, I will be looking at the isomers of 3 compounds[5] :

a. Propanol Isomers
b. Butanol Isomers

[5] Refer to Appendix 1

c. Pentanol Isomers

To analyse the effects of the number of carbon atoms on the enthalpy of combustion values, on top of propanol, butanol and pentanol, I will also be taking the enthalpy values of methanol and ethanol into consideration for further and effective analysis.

Justification of selected database:

1. NIST Webbook was the first preference for the source of data because it is an accredited site of the National institute of science and technology and the website is owned by the US government itself. The data present is also there for many years which makes it a much more reliable source for data.
2. The UCSDB is a good source of data. Additionally, finding all the relevant enthalpy of combustion values was also easy.
3. The nvlpubs research paper is a very detailed and old research paper from the Bureau of Standards Journal of Research which again makes it a reliable source to take data from.
4. The last source of data that I have used for this research is the research paper published by MIT – Massachusetts Institute of Technology, why I chose this research paper is because it is from one of the most well-known universities in the US, and secondly all the data available was easy to collect and analyse.

Background Information:

Alcohols are organic compounds part of the homologous series and they are hydrocarbons containing the OH group. These compounds contain only Hydrogen, Oxygen and Carbon atoms. There is a positive relationship between the number of carbon atoms and the enthalpy of combustion values. Due to the increasing number of carbon atoms the bonds get stronger as we go down through the series from methanol, to ethanol, to propanol. To break and form bonds a higher energy is required. Combustion is a reaction where energy and heat are

released, and because there is more energy in the products than there is in the reactants, the value of enthalpy is negative, suggesting that it is an exothermic reaction.

Talking about the isomers I have chosen for this research. Structural Isomers[6] as defined in the appendix, have the same chemical formula but different structural formulas. The arrangement of the position of the hydroxyl group, in this case (OH) is different. As mentioned before, the position of the hydroxyl group affects the enthalpy of combustion values.

Propanol has 2 isomers:

- 1-propanol and Iso-propanol which are both primary alcohols

Butanol has 4 isomers, them being:

- (n) butanol and Iso butanol are primary alcohols.
- Sec-butanol is a secondary alcohol
- Tert-butanol is a tertiary alcohol.

Although Pentanol has 8 isomers, I will be considering the enthalpy of heat data for only the first 7 below due to insufficient data about the 8th isomer of Pentanol (neopentanol):

- Pentan-1-ol, 2-methylbutan-1-ol and 3-methylbutan-1-ol are primary alcohols.
  Pentan-2-ol, Pentan-3-ol, 3-methylbutan-2-ol are secondary alcohols.
- 2-methylbutan-2-ol is a tertiary alcohol
- 2,2-dimethylpropan-1-ol/neopentanol, a primary alcohol (data not considered below)

Raw Data:

[6] Refer to Appendix 2 – Important definitions

All values of raw data are at 25 degrees Celsius and all compounds are in the liquid state, also units are in kJ/mol. Additionally, all values are in negative because combustion of heat is an exothermic process.

1. ***For the position of the hydroxyl group:***

			NIST Web Book		**MIT Research Paper**		**NVL Pubs – Research Paper**
Compound	Isomer of which compound	Position of Hydroxyl Group	Enthalpy values kJ/mol	Uncertainty	Enthalpy values kJ/mol	Uncertainty	Enthalpy values kJ/mol
1- propanol	Propanol	Primary	-2021.31	± 0.25	-2028.19	0.005-0.05	-2000.40
Iso-propyl	Propanol	Secondary	-2006.90	± 0.20	-2005.98	0.005-0.05	-1985.60
n-butanol	Butanol	Primary	-2670.00	± 0.20	-2673.58	0.005-0.05	-2674.40
Iso-butanol	Butanol	Primary	-2669.60	± 0.59	-	0.005-0.05	-2668.90
Sec-butanol	Butanol	Secondary	-2660.60	± 0.54	-2660.61	0.005-0.05	-
Tert-butanol	Butanol	Tertiary	-2644.00	± 0.79	-	0.005-0.05	-2631.70
Pentan-1-ol	Pentanol	Primary	-3330.91	± 0.28	-3324.61	0.005-0.05	-2393.30
Pentan-2-ol	Pentanol	Secondary	-3315.40	± 0.67	-3315.57	0.005-0.05	-
Pentan-3-ol	Pentanol	Secondary	-3312.30	± 0.46	-3312.39	0.005-0.05	-
2-methylbutan-1-ol	Pentanol	Primary	-3325.9	± 0.54	-3326.11	0.005-0.05	-
2-methylbutan-2-ol	Pentanol	Tertiary	-3303.10	± 0.46	-3303.18	0.005-0.05	-
3-methylbutan-1-ol	Pentanol	Primary	-3326.20	± 0.50	-3326.32	0.005-0.05	-
3-methylbutan-2-ol	Pentanol	Secondary	-3315.10	± 0.63	-3216.11	0.005-0.05	-

2. For the number of carbon atoms:

			UCDSB	NIST Web Book		MIT Research Paper
Compound	**The no of carbon atoms**	**Formula**	**Enthalpy of Combustion values/ Hcø kJ/mol**	**Enthalpy of Combustion values/ Hcø kJ/mol**	**Uncertainty**	**Enthalpy of Combustion values/ Hcø kJ/mol**
Methanol	1	$CH_3OH_{(l)}$	-726.0	-725.7	± 0.1	-726.13
Ethanol	2	$CH_3CH_2OH(l)$	-1367.3	-1367.6	± 0.3	-1367.54
1-Propanol	3	$CH_3CH_2CH_2OH_{(l)}$	-2021.0	-2021.31	± 0.25	-2028.19
1-Butanol	4	$CH_3(CH_2)_2CH_2OH_{(l)}$	-2675.6	-2670.0	± 0.20	-2673.58
1-Pentanol	5	$CH_3(CH_2)_3CH_2OH_{(l)}$	-3328.7	-3330.91	± 0.28	-3324.61
1-Hexanol	6	$CH_3(CH_2)_4CH_2OH_{(l)}$	-3983.8	-3984.37	± 0.44	-3982.33

Uncertainty in raw data:

The raw data values have an average uncertainty ranging from about ± 0.20 to ± 0.8, and the values are accurate to two decimal places. Wherever there were a range of values mentioned I used the values with the lowest uncertainty values. For the calculation of values from the MIT research paper, the units were in kcal/mol, to make comparison easier the values have been converted to kJ/mol using an online converting tool, thereby bringing room for a few more uncertainties in these values.

Evaluation of data sources:

The data sources used for this research are evaluated by comparing a smaller sample size of the data and eliminating the values that deviate largely from the other sources and the ones that don't fit the trend.

Table 1

			UCDSB	NIST Web Book		MIT Research Paper
Compound	**The no of carbon atoms**	**Formula**	**Enthalpy of Combustion values/ Hcø kJ/mol**	**Enthalpy of Combustion values/ Hcø kJ/mol**	**Uncertainty**	**Enthalpy of Combustion values/ Hcø kcal/mol**
Methanol	1	$CH_3OH_{(l)}$	-726.0	-725.7	± 0.1	-726.13
Ethanol	2	$CH_3CH_2OH(l)$	-1367.3	-1367.6	± 0.3	-1367.54
1-Propanol	3	$CH_3CH_2CH_2OH_{(l)}$	-2021.0	-2021.31	± 0.25	-2028.19

Table 2

			NIST Web Book		MIT Research Paper		NVL Pubs – Research Paper	
Compound	**Isomer of which compound**	**Position of Hydroxyl Group**	**Enthalpy values kJ/mol**	**Uncertainty**	**Enthalpy values/ kJ/mole**	**Uncertainty**	**Enthalpy values kJ/mol**	**Uncertainty**
1- propanol	Propanol	Primary	-2021.31	± 0.25	-2028.19	0.005-0.05	2000.40	-
Iso-propyl	Propanol	Secondary	-2006.90	± 0.20	-2005.98	0.005-0.05	1985.60	-
Tert-butanol	Butanol	Tertiary	-2644.00	± 0.79	-	0.005-0.05	2631.70	-

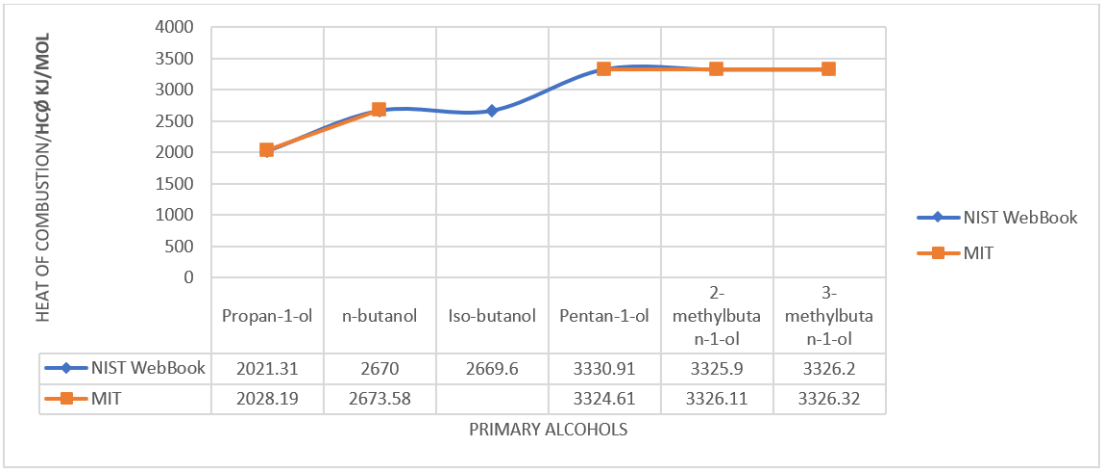
As seen in the data for the number of carbon atoms (Table 1) from the sources above, UCDSB, NIST Web Book and the Research paper, the values for a sample size of 3 alcohols(Methanol, Ethanol, and 1-propanol) are very similar and follow the same trend. In the same compound the enthalpy of combustion value between the 3 data sources is quite minuscule. These changes could be caused due to a few human errors while recording the values or they can also be caused by the usage of different methods to conduct the experiment by each source.

Moreover, looking at the data for the changes in the position of the hydroxyl group (Table 2), it can be observed that the data values from the MIT research paper and the NIST Web Book follow the trend with slight deviations of maximum 7 kJ/mol between them and this difference could be due to the use of different methods for finding the values of the enthalpy of combustion. Slight changes could also be caused by human errors. However, the values

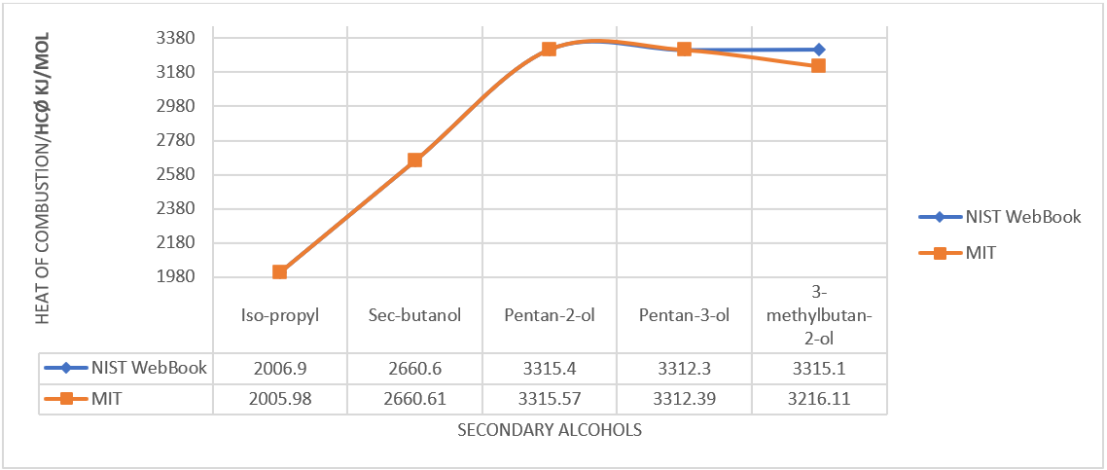
from the NVL pubs data have large variations if compared to the other 2 sources. It is approximately differing by 20 kJ/mol and due to this inconsistency in the values, I have eliminated this data source for the analysis below.

Analysis: Part (i) The effect that changes in the position of the hydroxyl group have in enthalpy of combustion values.

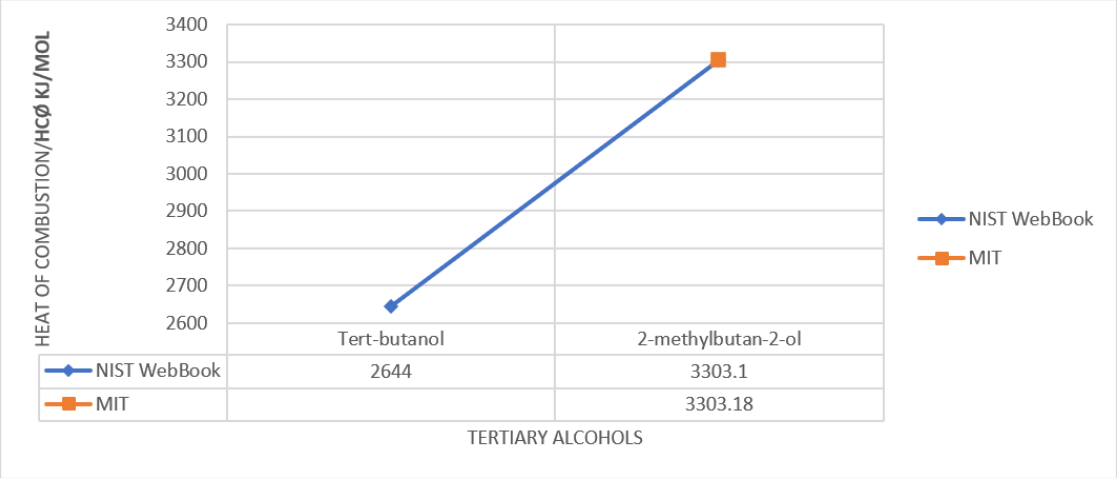
Primary Alcohols:



Secondary Alcohols:



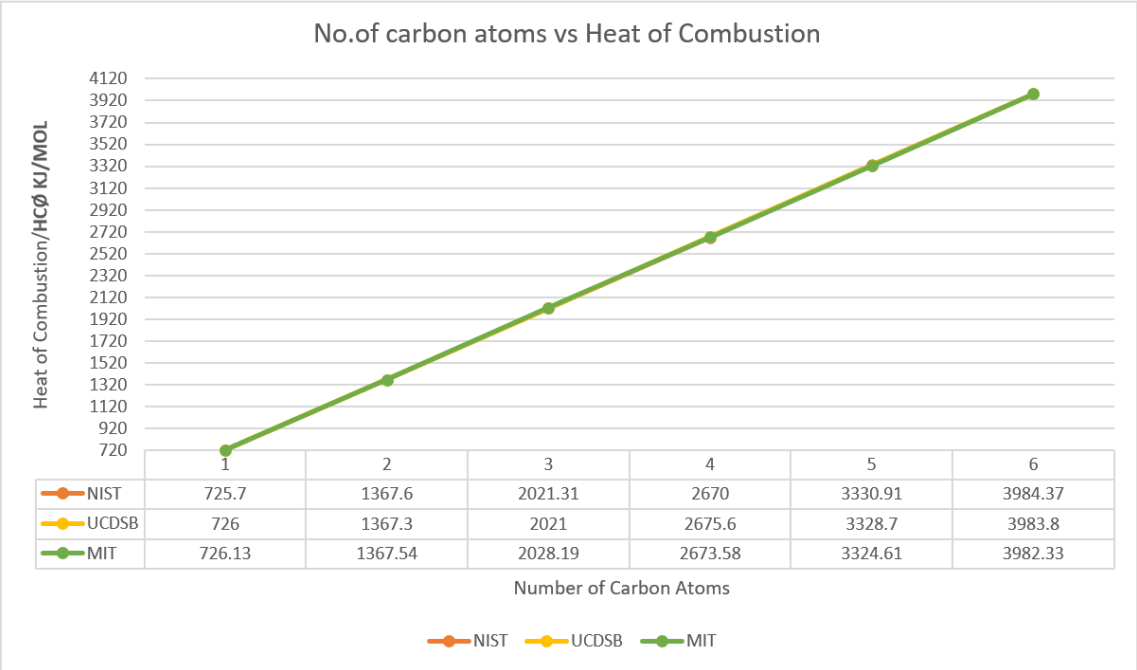
Tertiary Alcohols:



If we compare the data between the 3 charts of primary, secondary and tertiary alcohols respectively, it can be inferred that the enthalpy of combustion value increases as we move down the homologous series. Starting off at about 2000 kJ/mol for a primary alcohol, the value increases to approximately 3000 kJ/mol for a tertiary alcohol. This increase in enthalpy is due to the increased bond strength of compounds as we move down the homologous series. As we move from primary to secondary and lastly tertiary alcohols, the number of bonds formed also increases and hence the value of enthalpy of combustion increases because more energy is required to break these new bonds. For instance, to break one additional C-H bond, the heat energy required is 414 kJ/mol. Therefore, because tertiary alcohols have a greater number of C-H bonds than primary alcohols, the enthalpy of combustion value increases down the series.

However, the data does not clearly show a significant or rising increase as we move through the three types of alcohols and the data chart plotted against the number of carbon atoms below is a much clearer interpretation of the data. Thus, this could be an area for further study.

Part (ii) Effect of the number of carbon atoms on the enthalpy of combustion values:

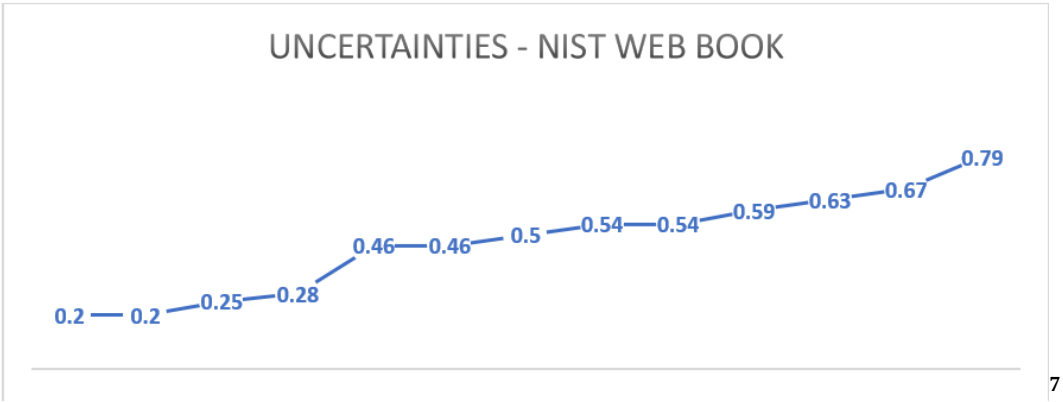


	1	2	3	4	5	6
NIST	725.7	1367.6	2021.31	2670	3330.91	3984.37
UCDSB	726	1367.3	2021	2675.6	3328.7	3983.8
MIT	726.13	1367.54	2028.19	2673.58	3324.61	3982.33

In graph 2, we can see the relationship between the enthalpy of combustion values and the number of carbon atoms, and it is evident that an increase in carbon atoms increases the heat of combustion values. The values in all the three databases that were plotted have more or less overlapped each other due to slight differences in between them. The line graph depicts a linear relationship with little anomaly from a few data values, thereby ensuring the accuracy of this analysis.

As mentioned in the hypothesis, as the number of carbon atoms increase in an organic compound, the heat energy required to break and form bonds increases and hence the heat of combustion also increases. It will take more heat energy to break the extra bonds as you add one more carbon atom to each consecutive compound. The positive sloping graph shows the relation between the number of carbon atoms and the heat of combustion of the organic compounds. Right from methanol to hexanol, the Hcø values rise from 725 kJ/mol to 3984 kJ/mol, which is approximately a percentage increase of 450%.

Part (iii) Graph for uncertainties



[7]

The graph above shows the uncertainty in the values taken from the NIST Web book, since I was only able to find uncertainties for this particular database, I could not include the other databases in this graph. It can be inferred from the graph above that the heat of combustion values used from the NIST web book, especially for the values of the compound, n-butanol range in accuracy from ± 0.2 to 0.79. This tells us that the values are precise and thus improves the results and analysis done in this investigation.

Conclusion:

The result obtained helps us provide evidence to support the hypothesis as both the changes in the position of the hydroxyl group and the number of carbon atoms effect the enthalpy of heat values. To be able to answer both the parts of the research question stated above –

1. Changes in the position of the hydroxyl group by changing the number and position of carbon atoms from primary alcohols to secondary and tertiary has shown an increase in the enthalpy values.
2. There is a positive sloping relationship between the number of carbon atoms and the enthalpy of combustion. As the number of carbon atoms increase from 1 to 6, the enthalpy of heat rises significantly from 700 kJ/mol to 4000 kJ/mol. This is because

[7] (Afeefy, Liebman and Stein)

an increase in carbon atoms means that the number of bonds broken or formed also increases.

Hence, these conclusions form a basis to thereby answer the research question for this investigation.

Further Investigation:

These two questions have not been answered in this research and hence can be the basis for further study.

1. **Investigating the effect of bond chain length on the enthalpy of combustion values.**
2. **Investigating the effect of boiling and melting points of homologous series on the enthalpy of combustion values.**

Bibliography

Afeefy, Hussein Y., Joel F. Liebman and and Stephen E. Stein. *Neutral Thermochemical Data*. 2018. Eds. P.J. Linstrom and W.G. Mallard. WebBook. October 2020.

Boudreaux. *Alcohols - Organic Chemistry*. n.d. October 2020. <https://www.angelo.edu/faculty/kboudrea/molecule_gallery/05_alcohols/00_alcohols.htm>.

Derry, Lanna, et al. *Chemistry for use with the IB Diploma Programme - Standard Level*. Melbourne: Pearson Education Australia, 2008. Document.

Education, Owlcation -. *Butanol Isomer Structure*. 17th December 2016. November 2020. < https://owlcation.com/stem/Heat-Energy-produced-by-Fuel-Butanol-and-its-Isomers>.

EndMemo. n.d. 23 October 2020.

GCSE Science - Products of oil. 2015. Html page. 17 October 2020.

H. A. Skinner, A. Snelson. "The heats of combustion of the four isomeric butyl alcohols." *Transactions of the Faraday Society* (1960): 1776-1783. Paper.

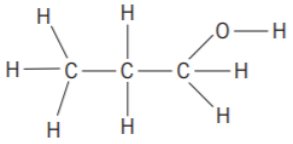
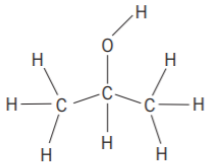
Owen, Steve. *Chemistry for the IB Diploma*. 2nd. Cambridge University Press, 2014. Document.

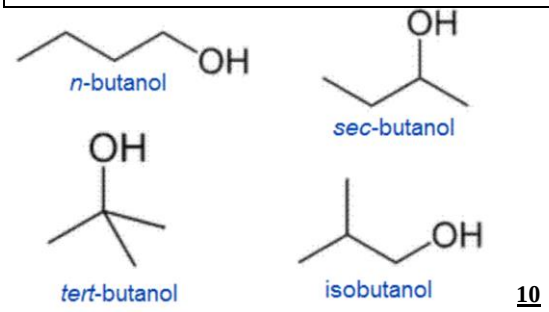
Rossini, Frederick D. "HEATS OF COMBUSTION AND OF FORMATION OF THE NORMAL ALIPHATIC ALCOHOLS IN THE GASEOUS AND LIQUID STATES, AND THE ENERGIES OF THEIR ATOMIC LINKAGES." *Journal of Research of the National Bureau of Standards* 13 (1934): 190-201. Research Paper. October 2020. <https://nvlpubs.nist.gov/nistpubs/jres/13/jresv13n2p189_A2b.pdf>.

Stretton, Tom. *Organic Compounds: Physical and Thermochemical Data*. October 2004. 18 October 2020.

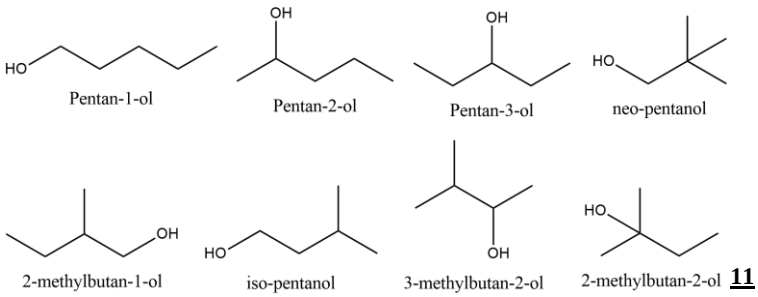
Vedantu. *Structural Isomers of Pentanol*. n.d. November 2020. < https://www.vedantu.com/question-answer/alcohols-are-structural-isomers-of-c5h11oh-class-12-chemistry-cbse-5f853c454dddb9022398bb0c>.

Appendix 1: Propanol, Butanol and Pentanol Isomers

 propan-1-ol [8]	 propan-2-ol [9]
1-propanol (n-propanol)	2-propanol (iso-propanol)



10



11

Appendix 2

[8] (Derry, Connor and Jordan)
[9] (Derry, Connor and Jordan)
[10] (Education)
[11] (Vedantu)

Important Definitions of terminology:[12]

1. **Standard enthalpy change of combustion (ΔHc)** is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.
2. **Structural isomers** are two or more compounds that have the same molecular formula but different structural formulas – the atoms are joined together in different ways.
3. **A homologous series** is a series of compounds that have the same functional group. Each member differs from the next by a common structural unit (usually –CH2–).
4. **A functional group** is the atom or group of atoms in a molecule that gives it its characteristic chemical properties – this is the reactive part of a molecule.
5. Primary, Secondary and Tertiary Alcohols: Alcohols are described as **primary, secondary or tertiary** depending on the number of carbon atoms attached to the carbon with the –OH group.
    a. Ethanol is a **primary alcohol** because it has one carbon atom attached to the C with the –OH group. Hence, a primary alcohol contains the –CH2OH group**.**
    b. Propan-2-ol is a **secondary alcohol** because it has two carbon atoms attached to the C with the –OH group. Hence, secondary alcohols contain the –CHOH group.

[12] (Owen)

c. 2-methylpropan-2-ol is a **tertiary alcohol** because it has three C atoms attached to the C with the –OH group.

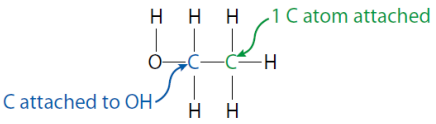


Figure 10.16 A primary alcohol – ethanol.

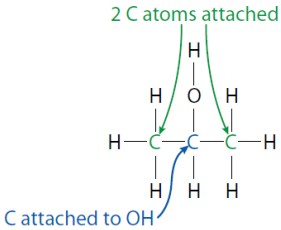


Figure 10.17 A secondary alcohol – propan-2-ol.

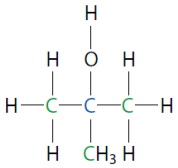


Figure 10.18 A tertiary alcohol – 2-methylpropan-2-ol.

13

Appendix 3:

n-butanol table values[14]		
SR No.	**Enthalpy Values – Heat of Combustion, $\Delta H_{c,liq}$ (kJ/mol) of: n-butanol**	**Uncertainty**
1.	-2676.18	± 0.24
2.	-2640.00	± 0.120
3.	-2675.61	± 0.45
4.	-2676.01	± 0.24
5.	-2677.40	± 0.63
6.	-2674.90	± 0.84
7.	-2670.40	± 0.42
8.	-2670.44	-
9.	-2676.00	-
10.	-2670.77	-
Average:	-2670.00	± 0.20

[13] (Owen)
[14] (Afeefy, Liebman and Stein)