Results:

Table 1. Experimental and AM1 *model chemistry* calculated bond angles, bond lengths, and vibrational frequencies.

Compound	Experimental Bond Angles/ Lengths [1]	AM1 Bond Angles/Lengths	Experimental Vibrational Frequencies (cm^{-1})	AM1 Vibrational Frequencies (cm^{-1})
Carbon Dioxide	180º/ 1.163 Å	180º / 1.189 Å	1333; 2349; 667	511, 1480, 2565
Water	104.474º/ 0.9584 Å	103.53º / 0.961 Å	3657; 1595; 3756	1829.25; 3908.43; 3999.83
Oxygen	180º/ 1.28 Å	180 º /1.086 Å	1580.2	2429.67

To begin the comparison of AM1 calculations to experimental values, the experimental and AM1 calculated bond angles, bond lengths, and vibrational frequencies were tabulated (Table 1.)

Table 2. The experimental and AM1 and PM3 *model chemistry* calculated ΔH_C for several organic compounds arranged by molecular weight.

Compound	Exp. ΔH_C (kJ/mol) [1]	AM1 ΔH_C (kJ/mol)	PM3 ΔH_C (kJ/mol)	Molecular Weight (g/mol)
Ethylene	-2307.88	-2010.83	-2186.26	28.05
Methanol	-886.91	-630.27	-505.09	32.04
Propane	-2742.04	-2225.67	-2252.36	44.10
Ethanol	-1978.94	-1622.26	-1647.91	46.07
Butane	-2767.57	-1972.93	-2633.55	58.12
Propanol	-2334.32	-1960.05	-1514.97	60.10
Cyclopentane	-3100.35	-2838.69	-3262.53	70.13
Benzene	-3228.19	-3247.51	-2292.67	78.11
Cyclohexane	-3656.75	-2696.63	-3019.06	84.16
Hexane	-4194.62	-3621.74	-4275.61	86.18
Toluene	-5194.48	-5247.25	-6203.84	92.14
Phenol	-3122.16	-2690.23	-3255.71	94.11
Cyclooctane	-5228.46	-4607.82	-6169.09	112.21
Octane	-5314.11	-4312.34	-11406.07	114.20
Napthalene	-5661.84	-4618.92	-6014.82	128.17
Phenanthrene	-5546.98	-5993.68	-3839.87	178.23
Anthracene	-7594.06	-7095.49	-10811.15	178.23
Kerosene	-3693.30	-3569.20	-3693.00	~180
Pyrene	-7748.00	-6945.44	-8142.46	202.25

Table 2 shows that there are differences between the experimental ΔH_C and the PM3 and AM1 methods. In order to better compare these variations and determine any correlations, a

scatter plot of the data (Fig. 1) was constructed. A linear trend line was fit to this data for both AM1 and PM3. A slope of 1 would indicate that the experimental and calculated ΔH_C had the same values, while the R^2 values are a measure of how well the lines fit the data. *Model chemistry* AM1 produced a trend line with a slope of 0.9578 and an R^2 value of 0.9529. The slope of the PM3 method was 1.4301 with an R^2 value of 0.7385.

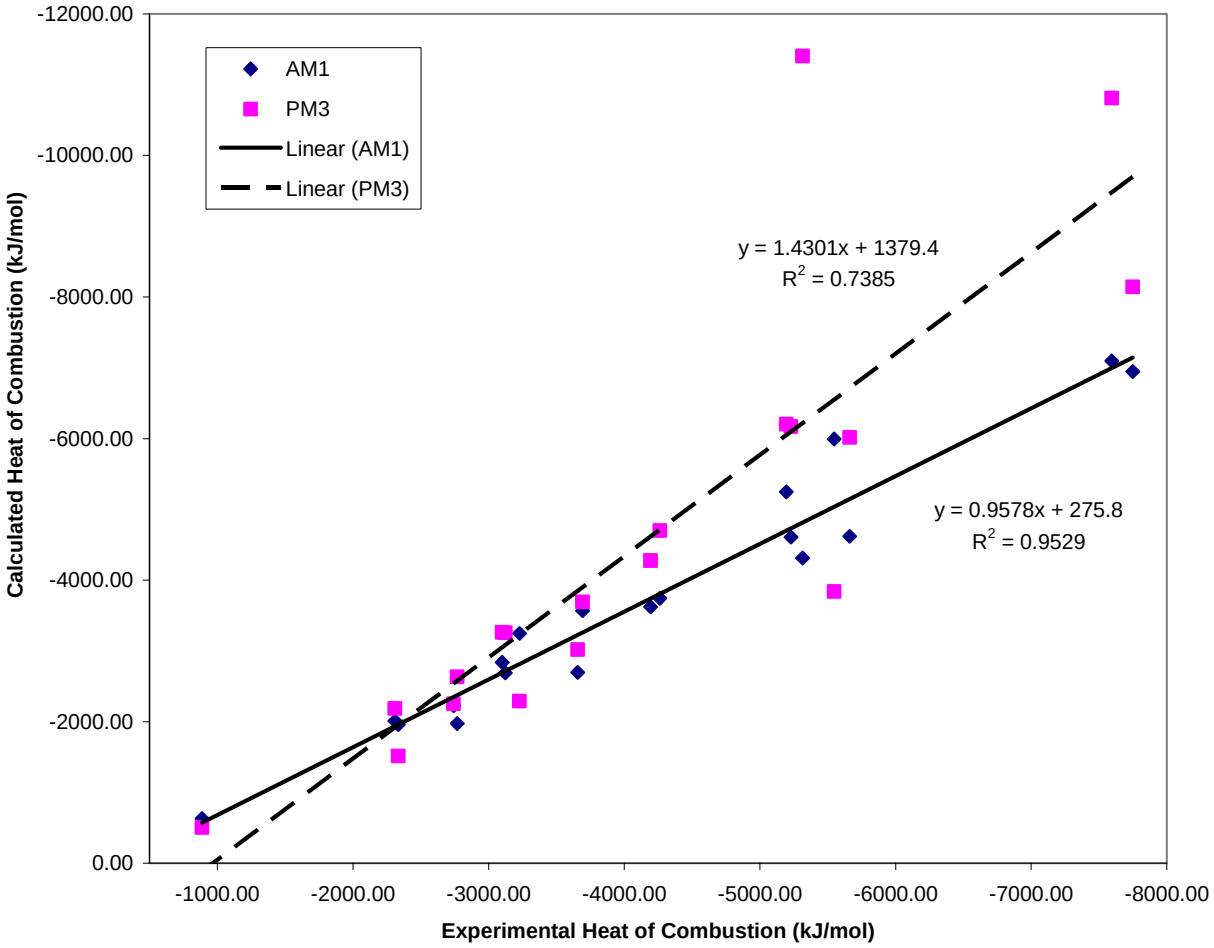

Figure 1. Experimental ΔH_C vs. the AM1 and PM3 calculated ΔH_C with trend lines.

Comparing molecular weights to the ΔH_C reveals that they are generally proportional to each other; as the molecular weight increases so does the ΔH_C. Also, as the ΔH_C increases, the AM1 and PM3 values vary much more significantly from the trend line than they do at lower molecular weights (Fig. 1).

The ΔH_C for all compounds were also calculated in kJ/g and tabulated (Table 3.)

Table 3. The experimental, AM1, and PM3 calculated heats of combustion in kJ/gram for each hydrocarbon.

Compound	Exp. Heat of Combustion (kJ/gram)	AM1-Heat of Combustion (kJ/gram)	PM3-Heat of Combustion (kJ/gram)
Phenanthrene	-23.4	-22.8	-21.2
Kerosene	-23.6	-22.8	-21.3
Methanol	-27.7	-21.1	-16.3
Phenol	-33.2	-28.6	-34.6
Ethanol	-38.2	-44.2	-92.3
Pyrene	-38.3	-34.4	-40.3
Propanol	-38.8	-32.6	-25.2
Benzene	-41.3	-33.5	-21.1
Anthracene	-42.7	-39.8	-60.7
Cyclohexane	-43.5	-32.0	-35.9
Napthalene	-44.2	-36.0	-46.9
Cyclopentane	-44.2	-40.5	-46.5
Butane	-45.7	-33.9	-45.3
Octane	-46.5	-37.8	-100.0
Cyclooctane	-46.6	-41.1	-55.0
Hexane	-48.7	-42.0	-49.6
Toluene	-56.4	-57.0	-67.4
Propane	-62.2	-50.5	-51.1
Ethylene	-82.3	-71.7	-77.9

Discussion:

Except for the bond angles of oxygen and carbon dioxide, the AM1 calculations for bond angles, bond lengths and vibrational frequencies for water, carbon dioxide, and oxygen were all much higher than the experimental values. As such, AM1 is not a perfect method for calculating these values.

As Table 2 shows, increases in molecular weight logically correlate to an increase in ΔH_C. Because these are all hydrocarbons, any increase in molecular weight is mainly due to an increasing amount of carbons and thus, bonds, which increases the energy stored in the molecule.

The slopes from Figure 1 show that both AM1 and PM3 are fairly accurate in calculating ΔH_C; both are close to experimental values. However, there are several factors that show AM1 is

the better choice between the two *model chemistry's*. For example, AM1's slope of 0.9578 is closer by ~10% to the ideal slope of one as compared to PM3's slope of 1.4301. Also, the y-intercept would ideally cross through 0 kJ/mol. AM1 is the closest at 275.8 kJ/mol, while PM3's y-intercept is a much higher 1379.4 kJ/mol. One last indication that PM3 is less accurate than AM1 is the R^2 values. The closer these values are to one, the better the line fits the data. AM1's value is ~20% closer than PM3. This is visible in the graph as there are several PM3 data points that deviate from the trend line substantially more than any of the AM1. These points may have been calculated incorrectly, and in the future it would be interesting to repeat them and compare the values. Overall, AM1 should be used in future calculations as it is significantly more accurate than the PM3 *model chemistry*.

Error within the individual *model chemistry* calculations is also prevalent as the several compounds that were calculated more than once vary significantly. Each calculation should have started with the same molecule entered into WebMO and a very similar heat of formation value obtained through NIST. However, there were great differences within the calculations. For example, within the experimental ΔH_C values for Benzene there was a standard deviation of 85.6 kJ/mol and the AM1 and PM3 standard deviations were 553.0 kJ/mol and 983.4 kJ/mol, respectively. There were also great deviations within the lower molecular weight compounds despite being the relatively more accurate compounds. Methanol, the compound with the second lowest molecular weight, has an experimental ΔH_C standard deviation of 401.4, but the AM1 and PM3 are less at 301.1 and 300.7. Therefore, the ΔH_C's vary within the methods and no pattern seems to be discernable (e.g. PM3 does not always deviate the most.)

Combustion reactions are exothermic and represented with negative ΔH_C's. The more exothermically a compound combusts, the more efficient it will be as a fuel. Efficiency is best determined by observing ΔH_C in kJ/g (see Table 4). According to the experimental values in

Table 4, ethylene is the most efficient fuel at -82.3 kJ/gram followed by propane (-62.2 kJ/gram) and toluene (-57.0 kJ/gram.) These fuels are also the top three for AM1, but PM3 has much higher values for ethanol and octane. These PM3 values are over twice as large as the experimental and AM1, so they are probably miscalculated and will not be considered. The least efficient fuels were phenanthrene (Experimental: -23.4 kJ/g, AM1: -22.8 kJ/g), kerosene (Experimental: -23.6 kJ/g, AM1: -22.8 kJ/g), and methanol (Experimental: -27.7 kJ/g, AM1: -21.1 kJ/g).

Ethanol is the fifth least efficient fuel when comparing the experimental ΔH_C's of Table 4. But, using it as a fuel has several advantages. First, it is currently created from corn, a renewable resource. This decreases our dependence on the ever-diminishing supply of petroleum gas. Also, it lessens our economic dependence on foreign countries that are not always reliable (e.g. Venezuela used to export the largest amount of oil to the U.S., but has currently severed all ties.) These positive aspects are why it's used to create 85% ethanol and 10% ethanol blends. It's difficult to say which the most advantageous is as the 10% ethanol is more efficient, and thus, would get better mileage in a vehicle; but, 85% ethanol would greatly decrease our dependence on an unrenewable resource obtained from other countries.

References:

(1) NIST. NIST Chemistry WebBook, 2005; Vol. 2007.