An Investigation of the Properties and Potential Applications of Hazelnut Components

Submitted to: Dr. Ron Currie

Submitted by: Anand Batoo, Collin Campbell, Amanda Jack and Beena Jacob

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ABSTRACT

This investigation involves a study of the physical properties of the shell, kernel, and the oil of the hazelnut in order to identify any potential uses for them. The optimal wet ashing process was determined to examine the mineral content of each of the hazelnut fractions. Techniques such as particle size distribution, thermal gravimetric analysis, pyrolysis, and heavy metal adsorption provided valuable information about the properties of the shell. The assessment of the oil involved the extraction of the oil, and oxidation of the oil.

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INTRODUCTION

The hazelnut has a truly delicious history that dates back to ancient times. The earliest known records of the hazelnut can be found in a Chinese manuscript which dates back to the year 2838 B.C.. According to this manuscript, the hazelnut took its place among the five sacred nourishments that God bestowed upon human beings.

About 1800 years ago, the Greek physician, Dioscorides, used hazelnuts in many remedies. Among these was the apparent cure for baldness comprised of burnt hazelnut shells and suet, which was applied to the hairless patches of the head with hope that strands of hair would reappear. He also thought that hazelnuts, mixed with black pepper, cured the common cold. He treated nagging coughs with a mixture of pounded hazelnuts and honey.

Other ancient writings note the hazelnut's curative properties. Hazelnuts mashed along with figs or raisins were used as a paste on the bite of a scorpion to relieve the pain. The leaves of the hazelnut, boiled in water were thought to be a blood purifier. The light coal that is produced from the burning of the hazelnut wood was powdered and eaten to cure stomach problems. There are a countless number of applications and further uses of this magnificent plant that are still being discovered.

The hazelnut may be characterized by a smooth round shell, which sort of resembles a roman helmet. Within the confines of this shell, sits a plump sweet kernel. Its

mouth-watering flavor is surpassed only by its nutritional content and the extent to which the counterparts of the nut may be used in practical situations.

The hazelnut is very nutritious, and is used in a myriad of foods and food additives. They are high in fiber, minerals (calcium, potassium, magnesium), and an excellent source of vitamins, (such as vitamin B6, E). They are also an excellent source of protein (approximately 10% protein) and monounsaturated fats. There are several hazelnut hybrids available on the market, and there are differences evident between the varieties. These differences may lie within the chemical or physical properties of the hazelnut.

The mineral content of the hazelnut is of particular interest. There are several motives for determining the mineral content and uses for the leftover shell and pulp. The primary reason for determining the mineral content of hazelnuts is for nutritional purposes. Is the hazelnut providing sufficient nutrition to the consumer? Are there any aspects of this particular nut that may hold advantages over others? By determining the presence of certain minerals and toxic heavy metals in the hazelnut, these questions can be more effectively answered.

Dundar et al. (2002) studied the influence of variety and geographical region on the mineral contents of hazelnuts in Turkey. Their study involved analyzing the mineral contents of three different varieties of hazelnut, namely Karafindik, Tombul, and Delisava. Using flame atomic absorption spectrometry, they discovered a total of four elements: iron, copper, manganese and zinc in the hazelnut kernels. There was a definite relation between the composition of the minerals found in the hazelnut varieties, and the region from which they were taken.

Analysis of both the shell and the kernel are of great interest. Size reduction of the shell was performed to attain a homogenous sample for further analyses on the shell. Tests were performed using different varieties of the hazelnut and it was investigated whether the initial mass of shells affected the distribution during Tyler Screening. The thermal gravimetric analysis was performed on the shell in order to distinguish if any composition differences existed between the particle sizes. Currently, scientists are investigating whether the hazelnut shells can be used to provide hydrogen, a requirement for fuel cells along with other commodities. Conducting a pyrolysis test helped determine the amount of volatile components emitted from the shells. The hazelnut shell was also assessed for its ability to adsorb heavy metals. By performing adsorption of

heavy metals, it can be deduced whether the shell is capable of removing toxic heavy metals from aqueous solutions. This would be useful in the disposal of heavy metals and possibly in clean up of toxic spills in industry.

The oil was extracted from the hazelnut kernel using a non-destructive procedure to improve its yield. This was accomplished using the cold press method.

In order to determine the effects of oxidation on the oil, a thermal gravimetric analysis was performed on two varieties of hazelnut oils, and olive oil. The samples were run under both inert and oxidative conditions in order to determine which changes in mass were occurring as a result of oxidation.

To determine the mineral content of a substance, in the absence of organic matter, the wet ashing technique was optimized. Wet ashing involves digestion with nitric acid, sulfuric acid or perchloric acid at temperatures reaching up to ~400^{o}C. This latter method was employed in the determination of mineral content of the hazelnut shell, kernel, and oil. Elemental analysis was performed using the ICP (inductively coupled plasma). ICP is a technique that uses inductively coupled argon plasma in its atomic emission. ICP instruments utilize the high temperature and chemically inert environment of an argon plasma as the atomization and excitation source. A high resolution UV-visible spectrometer equipped with the ICP, allowed resolution and multiple elemental analyses with minimal spectral interference. This allowed for the quantitation of eleven metals present in the hazelnut shell, kernel, and oil. This included some nutritionally required minerals, and toxic heavy metals.

METHODS AND MATERIALS

Materials List

The samples of hazelnuts used were the locally purchased and the Badgersett bulk, as well as Badgersett hybrid numbers 1 – 5, 7, 12, and 14. Samples 1 and 3 can be identified as an americana – avellana cross. Samples 2, 4, and 5 are a three way cross between americana, avellana, and cortuna. Sample number 14 also contains the three previously mentioned breeds of hazelnut, and may also include some Turkish. Sample 12

is identified only as R – 077. Colavita brand extra virgin olive oil was also used. The Badgersett hybrids were provided by Badgersett Research Corporation.

The concentrated sulfuric acid, 30% hydrogen peroxide, methylene chloride, acetone, and concentrated ammonium hydroxide were products of the Fisher company. The NAIT prep room provided liquid nitrogen, and an assortment of nitrate salts including cadmium, magnesium, calcium, sodium, copper (II), zinc (II), iron (III), manganese (II), mercury (II), lead (II), and potassium.

Digestion

The digestion took place in a Kjeldahl unit using concentrated H_2SO_4 and H_2O_2. Approximately 0.6 grams of each hazelnut component (shell and kernel), and about 0.4 grams of oil (Badgersett and locally purchased hazelnut, and olive) were weighed out for digestion. 10ml of H_2SO_4 was added at the start and digested at 330^{o}C for 45 minutes. To the hot mixture, 5ml of H_2O_2 was added very slowly dropwise along the sides taking care to actively swirl the tube and hold the tube at a 45^{o} angle to reduce splattering. After the first addition of hydrogen peroxide the samples were digested for another ten minutes and the second volume of hydrogen peroxide was added in the exact same way as mentioned earlier. The tubes were then removed from the Kjeldahl unit.

ICP Operating Conditions

A range of calibration standards ranging from 5 to 10000 parts per billion were prepared using 0.04 M HNO_3 is used as the diluent. All samples were analyzed using a 50 second instrument stabilization delay using the wavelengths indicated in Table 1.

Table 1: Wavelengths Used for ICP Analysis of Cations

Cation	Wavelength (nm)
Ca	393.366
Cd	228.802
Cu	324.754
Fe	259.940
Hg	253.652
K	766.490
Mg	279.553
Mn	257.610
Na	589.592
Pb	220.353
Zn	213.856

The Shell

Size Distribution

The shells of the supplied hazelnuts were ground and size reduced to facilitate analyses such as thermal gravimetric analysis, pyrolysis, and wet ashing on the shells. The initial mass of the shells was kept constant. After having frozen them in dry ice, the shells were then sized reduced using a blender. Following the ten minutes of grinding, the shells were then Tyler Screened for ten minutes to separate the fractions.

Thermal Gravimetric Analysis of the Shell

A thermal gravimetric analysis was performed on all six particle sizes of the shell obtained from the Tyler screening. The process involved heating about 20 milligrams of the shell sample to 800^{o}C at a rate of 35^{o}C per minute under inert (N_2) conditions.

Pyrolysis

A mass of ~1.2g of dried, ground shell was accurately measured into a hand glass test-tube, which was connected in series with 2 impingers. Both the impingers contained 25ml of methylene chloride, and were set to be under inert conditions by running

nitrogen through the system at 8cc per minute. The first impinger was at room temperature while the second was a cold trap immersed in a bath of acetone and dry ice. A rotameter was connected to the pyrolysis tube to regulate the flow rate of nitrogen passing through the system. Due to the strong characteristic odor of the volatiles evolved and the pressure buildup within the system, the experiment should be setup in the fume hood.

The sample was pyrolysed for 30 minutes, at which point the tubes were allowed to cool and the remaining residue weighed. The methylene chloride solutions were analyzed using the GC.

The GC was run using the split/splittles injection mode with a split ratio of 30, and a 1μL sample volume. The initial temperature was 40oC with a hold time of 4 minutes, followed by a 10oC/min increase to 20oC which was held for 20 minutes. Both FID and PFPD detectors were used with helium as the carrier gas and makeup gas flow rate of 20 mL per minute.

Adsorption of Metal Ions from Solution

The conditions of the cation adsorption experimentation were set to meet the conditions of maximum adsorption (pH of 4.70) which was adjusted by adding ammonium hydroxide to the 500 ppb mixed metal solution to be analyzed. The locally purchased hazelnut shells of the smallest particle size were then added to the solutions in approximately 4.0 gram aliquots and stirred for about 5 hours in order to promote adsorption. The metal solution was analyzed before and after adsorption using an ICP.

The Oil

Extraction of the Oil

The kernels derived from the Badgersett and locally purchased hazelnuts were sealed in special bags used for the cold press (doubled up to prevent the oil from leaking). Six of the Badgersett nuts or four of the locally purchased were prepared and placed in the cold press at about 6000 pounds of pressure. The resulting oil was then removed from the bag

carefully, using a Pasteur pipette and transferred to a Millipore syringe in order to remove any the particulate matter.

Oxidation of Oils

The experiment was performed on Badgersett and locally purchased hazelnut oil, and olive oil. The program was set to run twice for each oil sample; once under oxidative (O_2) conditions, and once under inert (N_2) conditions. About 20 milligrams of the oil was brought to a temperature of 250^{o}C at a rate of 2^{o}C per minute.

RESULTS AND DISCUSSION

Digestion

In order to perform a mineral analysis, the shell had to be digested in order to remove any interfering organic material. The wet ashing procedure was developed using the procedure given in NAIT course pack 470L*, Food and Agricultural Analysis,* Expt 11*,* and W.R.Morrison, *Microdetermination of the Phosphorous in Biological Material,* and *Anal. Biochem* 7:218-224, 1964.

Since the concentration of minerals in the nut components were not known, the main aim was to digest as much mass as possible. The mass used in the food and agriculture lab was 0.7g and so for a first trial, a mass of 0.8g was used.

About 0.8g of oil, shell and kernel was accurately weighed out into dry Kjeldahl tubes and 10ml of conc. H_2SO_4 and 10ml of 30% H_2O_2 was added and digested at 330^{o}C for 45 minutes. At the end of the 45 minutes, digestion was incomplete and there was loss of final volume. The final solutions were very dark indicating an incomplete digestion process.

Another trial was performed using a similar process only the H_2O_2 was added after 45minutes of digestion. This process showed slightly better results, but there was still a substantial loss of sample volume. The digestion process was still incomplete as the solutions had not become completely colorless.

It was concluded that the mass of oil added was too high, thus variations in the masses of oil were used (0.2, 0.4, 0.6, and 0.8). The samples were weighed out accurately into dry Kjeldahl tubes. The H_2O_2 was added drop-wise to the center of each tube after removing all of the samples from the heat. The reaction was very vigorous and there was a lot of spattering. Most of the sample volume was lost.

For the next trial, the same of oil were accurately weighed out and 10 ml of H_2SO_4 added to each tube. After the 45 minute digestion, 5 ml of H_2O_2 was added to each tube drop-wise. After another 10 minute again the last 5 ml was added down the center of the tube. Digestion was complete, but the loss in volume was very high.

During the next trial 0.4g of oil, and 0.6g of shell and kernel were weighed out accurately. The process took place exactly as before only for this trial the second 5mL addition of H_2O_2 was added while the tubes were still on the Kjeldahl unit. This enhanced the digestion process even more. The digestion was complete as all of the solutions became colorless, but there was still sample loss due to spattering.

Assuming that the temperature was too hot and the H_2SO_4 was boiling off, the temperature was decreased from 330^{o}Cto 300^{o}C. The process used was identical to the one preceding. Better results were obtained with the decreased temperature because there was less sample loss.

The final trial was also conducted at 300^{o}C and this time the tubes were taken of the digester one at a time. The 5ml of H_2O_2 was dropped down the sides while holding the tube at an angle and actively swirling the tube to reduce sample loss due to spattering. This method gave the best results and was used to prepare the solutions for the ICP analysis.

ICP Calibration

Inductively coupled plasma was used in the determination of the mineral content of the wet ashed hazelnut samples. Some of the calibrations were not linear either because of spectral interferences, or due to the fact that some of the calibration standards were below the detection limits. One of the most significant problems encountered was with potassium. Because the ICP used argon as a coolant, the argon electrons become excited and emit at the same wavelengths as the potassium. This caused the calibration

curve to have a negative slope. For this reason, the calibration curves from April first were used. These results are tabulated in Table 2. There was also interference incorporated with the lead and mercury calibration curves, however the reason for this interference is not known.

Table 2: Accuracy and Precision of ICP Calibration

Analyte	R^2	Std. Dev.
Ca	0.9964	0
Cd	0.9973	0
Cu	0.9965	0
Fe	0.9951	0
Hg	0.9640	0
K	0.9871	0
Mg	0.9961	0
Mn	0.9944	0
Na	0.9965	0
Pb	0.7821	0
Zn	0.9976	0

The instrument was run on two separate days. On both days, two trials were run respectively using a 30 second instrumental stabilization delay, and two runs with a 50 second instrumental stabilization delay. The samples were analyzed using the calibrations performed with the 50 second delay since it showed better linearity in comparison to the 30 second delay.

The most difficult part of the ICP analysis was trying to dissolve eleven cations into a single solution. The main problem faced was trying to find salts and metals that were all soluble and would not react to form insoluble salts. This problem was combated by using salts containing a common anion (nitrate). Due to low solubility, some of the ions that were to originally be analyzed could not be put into the mixed standard.

Another challenge was in building an ICP method that would properly detect and calibrate a very wide range of standard concentrations. The lowest concentration standard, 5 ppb, was below the detection limits of some of the cations, causing variation in some of the calibration curves. Another problem was interference. Argon emits light at the same wavelength as potassium, so the calibration curve for potassium could not be used for proper quantitation. Unfortunately, this problem could not be avoided, because argon is the most common noble gas used in ICP instruments.

Finally, the standards had to be matrix matched to the samples that were to be analyzed. Because the digestion process used concentrated sulfuric acid, 75 mL of concentrated sulfuric acid had to be added to each 500 mL calibration standard. The major concern for this was creating insoluble salts, however, this problem never came to pass because the standards were very dilute.

The Shell

Size Distribution

The purpose of size distribution was to obtain a more homogeneous and representative sample in order to facilitate analyses such as thermal gravimetric analysis, pyrolysis, and wet ashing on the shells. Initially, two hazelnut varieties were supplied: locally purchased and Badgersett Bulk Hazelnuts. The locally purchased hazelnuts were used as a reference and a comparison for the Badgersett bulk hazelnuts. The procedure used to size reduce the shells were similar. The objectives were to weigh each individual hazelnut to obtain a weight distribution between the whole nut, kernel and shell. The results obtained for the locally purchased and Bulk Badgersett hazelnuts are listed in Table 3.

Table 3: Shell and Kernel Masses obtained Relative to Whole Nut for locally purchased and Bulk Badgersett Hazelnuts

	Mass Distribution in Grams			Mass Distribution in Percent		
Sample	Whole Nut (g)	Kernel (g)	Shell (g)	Whole Nut (%)	Kernel (%)	Shell (%)
locally purchased Hazelnut	3.6817	1.5830	2.0987	100	43.1430	56.8570
Badgersett Hazelnut	1.1824	0.3491	0.8333	100	28.8647	71.1353

From the results obtained in Table 3, there was a significant difference in the kernel and shell distribution with respect to the whole nut for each variety. The size of each hazelnut could have contributed to this difference. It was visually noticeable that the locally purchased hazelnut was relatively larger in size in comparison to the Bulk Badgersett hazelnut. Also, a larger kernel to shell ratio was obtained for the locally purchased hazelnut. This may be due to the fact that there was a poor harvest for the Bulk Badgersett hazelnut, which affected the growth of the hazelnut.

The shells were then ground and Tyler Screened to obtain six distributed layers, each of different sizes. Table 4 shows the Tyler Screening results for the locally purchased and Bulk Badgersett Hazelnut Shells.

Table 4: Tyler Screening Results of locally purchased and Badgersett shells

Mass Distribution in Grams			Mass Distribution in Percent		
Sample	locally purchased	Badgersett	Sample	locally purchased	Badgersett
Initial Mass (g)	34.8055	35.8012	Initial Mass (%)	100	100
Screen size (inch)			Screen size (inch)		
0.0117	23.3033	23.7433	0.0117	66.9531	66.3200
0.0098	0.9200	1.0600	0.0098	2.6433	2.9608
0.0059	2.1833	2.4467	0.0059	6.2730	6.8340
0.0049	0.5233	0.6033	0.0049	1.5036	1.6852
0.0035	0.3800	0.5233	0.0035	1.0918	1.4618
Below last screen	5.8400	5.4967	Below last screen	16.7790	15.3533
Losses	1.6555	1.9278	Losses	4.7563	5.3848

The results obtained in Table 4 showed a rather similar distribution of the shells for each variety. This indicated that the shell composition were rather similar for the locally purchased and Bulk Badgersett hazelnut shells.

In addition to the locally purchased and Bulk Badgersett hazelnuts, the size distribution analysis was also performed on nine Hybrid Badgersett shells. Their respective size reduced masses as a percent are listed in Table 5.

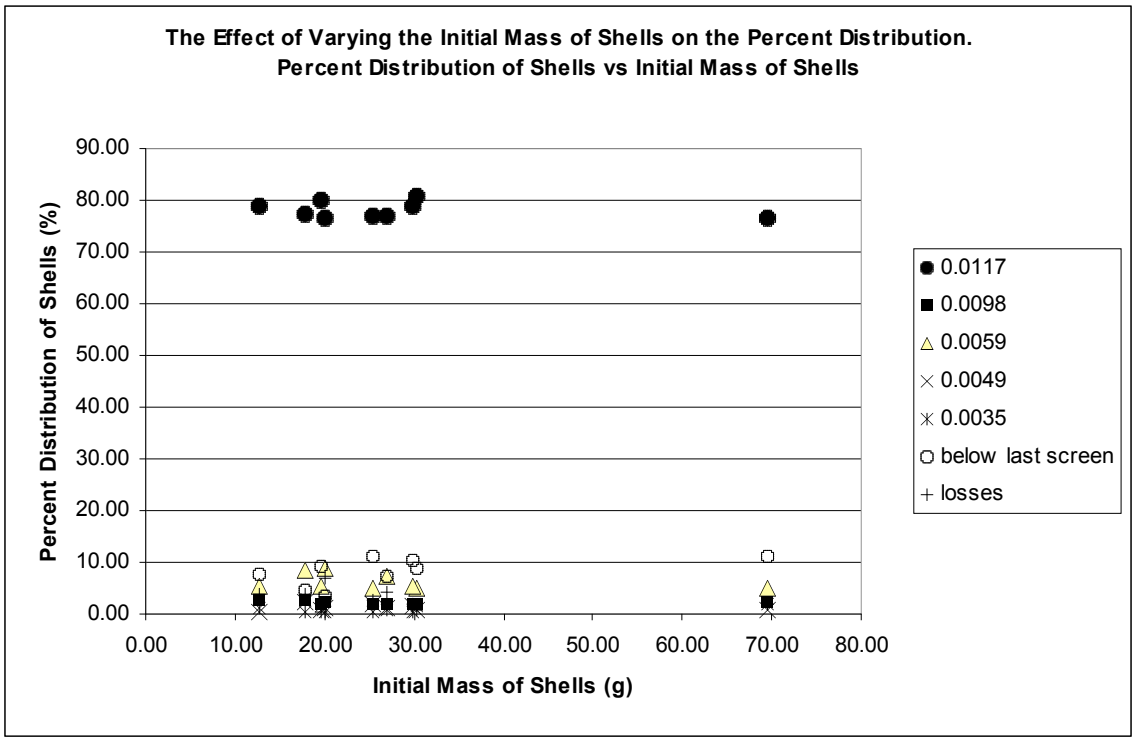
Table 5: Initial Mass and Percent Distribution of Hybrid Badgersett Shells

		Screen Size Results as a Percent						
Hazelnut Variety	Initial Mass (g)	0.0117	0.0098	0.0059	0.0049	0.0035	below last screen	losses
1	69.63	76.50	2.48	5.07	0.93	1.92	11.06	2.02
2	30.22	80.84	2.05	4.90	0.96	1.56	8.77	0.93
3	19.67	80.12	2.03	5.54	0.92	1.63	9.35	0.41
4	25.42	77.07	1.77	4.84	1.73	0.55	11.25	2.79
5	17.74	77.23	2.76	8.57	2.31	0.56	4.79	3.78
7	29.86	78.67	1.77	5.32	1.61	0.30	10.45	1.88
12	12.63	78.94	2.61	5.38	0.40	1.19	7.68	3.80
13	20.01	76.41	2.50	8.90	1.05	0.55	3.55	7.05
14	26.97	76.94	1.82	7.49	1.30	0.93	7.16	4.38

When the shells of the hazelnut samples listed in Table 5 were size reduced, various initial masses were recorded for each variety. This was due to the limited supply of the shells. One concern was to see whether the initial mass weighed out for size reduction had an effect on the percent distribution of the shells during Tyler Screening.

For this comparison, a graph was constructed, shown in Figure 1, plotting the percent distribution on the Tyler Screens versus the initial mass of shells weighed out in grams.

Figure 1: The Effect of Varying the Initial Mass of Shells on the Percent Distribution.



The graph did not conclusively show whether the initial mass had an effect on the percent distribution. As a result, regression analysis was performed on the initial shell mass and the percent particle distribution. If the calculated F-value was less than the F-critical, and if the calculated P-value was greater than 0.05, it would indicate that there was no correlation between the initial mass and the distribution on each screen. The results obtained from regression analysis are tabulated in Table 6

Table 6: Regression Analysis Results for Initial Mass of Shells and Percent Distribution

Screen Size (inch)	F(calc)	F(critical)	P-Value (calc)	P-Value	Conclusion
0.0117	0.637	5.590	0.451	0.050	no correlation between initial mass and % distribution
0.0098	2.02E-03	5.590	0.965	0.050	no correlation between initial mass and % distribution
0.0059	1.01	5.590	0.348	0.050	no correlation between initial mass and % distribution
0.0049	7.60E-02	5.590	0.791	0.050	no correlation between initial mass and % distribution
0.0035	2.51	5.590	0.157	0.050	no correlation between initial mass and % distribution
below last screen	2.60	5.590	0.151	0.050	no correlation between initial mass and % distribution
losses	0.658	5.590	0.444	0.050	no correlation between initial mass and % distribution

The results from the regression analysis proved that there was no correlation between the initial mass of shells weighed out and the percent distribution of the shells. This validated the procedure used for homogenization. It proved that the procedure was robust enough to withstand considerable differences in the amount of shell homogenized.

Another interesting concept was the comparison of the mean distribution of the fractions of the three hazelnut varieties. The ANOVA test allowed the comparison of all three hazelnut varieties: locally purchased, Bulk Badgersett and the Badgersett Hybrids. The results from the ANOVA test are tabulated in the following two tables.

Table7: Results of F-Test on Means comparing Size Distributions of the Three Sources of Hazelnuts

Tyler Screen	F-Test Vs F-Critical	Conclusion
0.0117	72.8>3.89	Significant Difference between the means
0.0098	6.37>3.89	Significant Difference between the means
0.0059	0.236<3.89	Not significant
0.0049	0.990<3.89	Not significant
0.0035	0.573<3.89	Not significant
below last screen	12.32>3.89	Significant difference between the means
losses	2.48<3.89	Not significant

Table 8:Results of ANOVA comparing Size Distributions of the Three Sources of Hazelnuts Shells

Tyler Screen	P-value	Conclusion
0.0117	1.95E-07	Significant difference found in the **Badgersett hybrid varieties**. A **larger** amount is retained for this particle size distribution.
0.0098	0.013	Significant difference found in the **Badgersett hybrid varieties**. A **smaller** amount is retained for this particle size distribution.
0.0059	0.793	No significant difference in the size distribution.
0.0049	0.400	No significant difference in the size distribution.
0.0035	0.578	No significant difference in the size distribution.
below last screen	0.00123	Significant difference found in the **Badgersett hybrid varieties**. A **smaller** amount is retained for this particle size distribution.
losses	0.125	No significant difference in the size distribution.

The results obtained when the means were compared, showed considerable differences between the Hybrids and the locally purchased and Bulk Badgersett shells. A larger mass of shells was collected on Tyler Screen 0.0117 for the Badgersett Hybrids in comparison to the masses that were collected on this screen for the locally purchased and Bulk Badgersett hazelnuts. As expected, less shell fractions were collected on Tyler Screens 0.0117 and below the last screen since a larger mass was retained on the first screen for the Badgersett Hybrids. The size reduction procedure could not reduce the Badgersett Hybrid shells as effectively as it had done with the locally purchased and Badgersett shells. These results confirmed that the Badgersett Hybrids had a tougher shell in comparison to the locally purchased and Badgersett shells.

Thermal Gravimetric Analysis of the Shell

The thermal gravimetric analysis was performed on the shell in order to distinguish what differences (if any) the different particle sizes may possess. The results obtained from the TGA show no consistent relation between particle size and the percent mass loss, because there was not a progressive relation between the two variables. There was, however, a very significant difference in mass loss between the largest and the smallest particle sizes. The extent of mass loss of each particle size can be more clearly observed in figures 2 and 3.

Figure 2: Percent Mass Loss of Various Particle Sizes of Hazelnut Shells

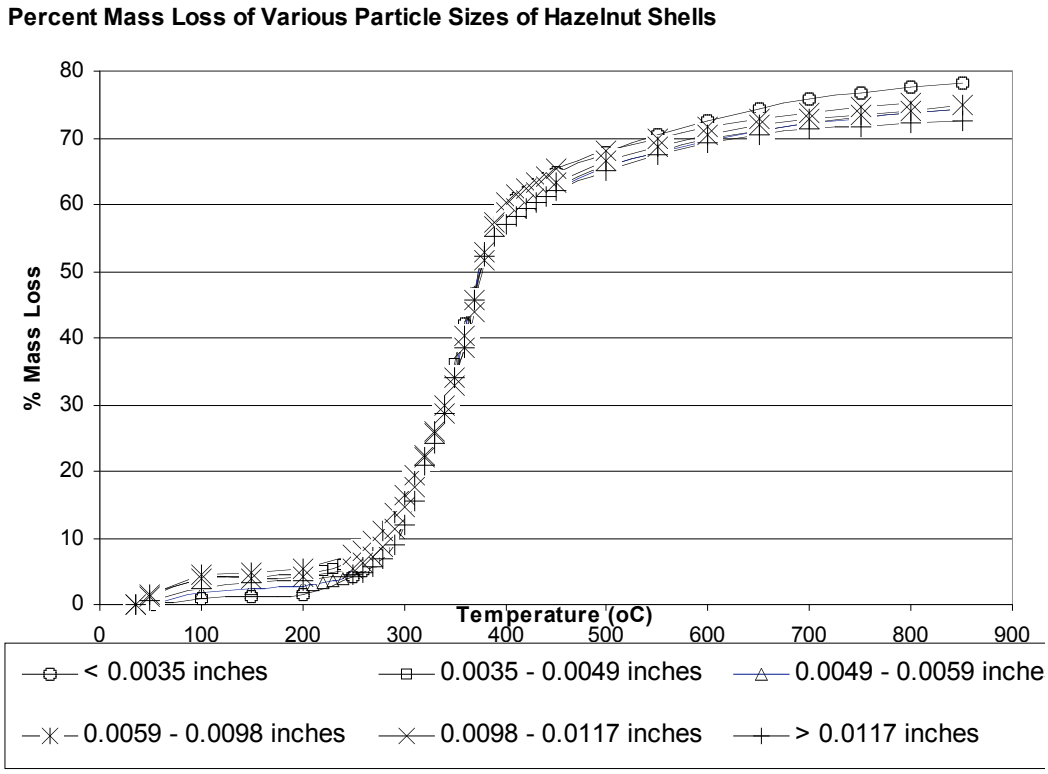
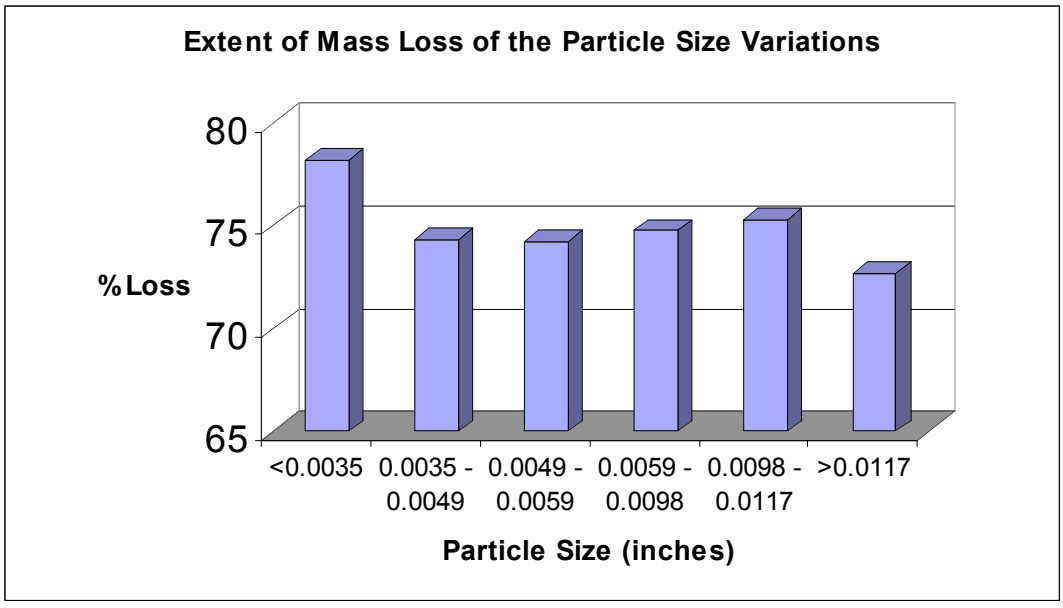


Figure 3: Extent of Mass Loss of the Particle Size Variations



A regression analysis was performed observed to determine if there was a significant relationship between the variables. If the P-value exceeds 0.05 it would indicate that there is no significance between the two factors. The P-value amounted to

0.245, therefore there is no statistical relation between the particle size and the mass loss for the trials performed.

These results are inconclusive because there may be error due to a lack of data. Because there was only a single trial performed for each particle size, it cannot be determined if the fluctuations in mass loss throughout the trials are a result of instrument error, lack of sample homogeneity, or because of the variations in the initial mass of the sample analyzed. If any or all of these factors have any impact on the on the results obtained, there is a possibility that there is composition variation between the different sizes of the hazelnut shell. This would indicate a relationship between the size of the hazelnut shell particle, and the amount of mass loss that occurs. A significant observable difference between the different sizes of the reduced shell implies that this relationship may exist. There was a 78.249% loss when analyzing the <0.0035 inch particles, and a 72.681 % loss was observed when analyzing the particles >0.0117 inches. This means that the distribution of the particle sizes obtained during size reduction is not random. There are certain compounds within different parts of the shell that portray different structural characteristics. This causes some parts of the shell to break down easier than others. Replicate trials must be carried out in order to know for certain if there is a direct relationship between the two factors.

Pyrolysis

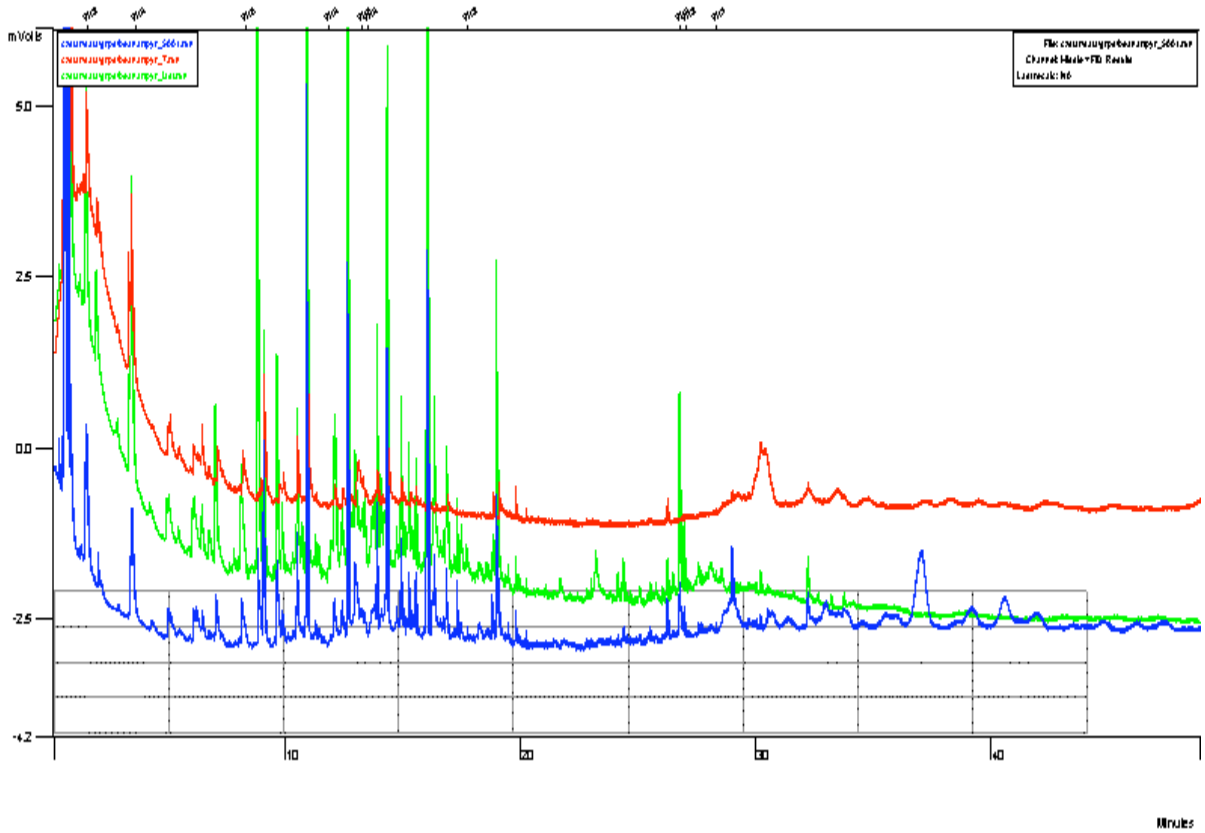
Table 9: Percent Mass Loss After Pyrolysis

Sample #	Initial sample mass	Residual mass	Difference in mass	% Loss
Reference Bottom Layer	1.02	0.35	0.67	65.69
Minesota #1 Bottom layer	1.02	0.37	0.65	63.73
Minesota #5 Bottom Layer	0.53	0.16	0.37	69.81
Minesota #7	1.04	0.35	0.69	66.35

In about a minute after the heating process had begun, brownish vapors were given off. As the vapors were passed through the impingers, the methylene chloride turned yellow. The medium to dark brown powders when pyrolysed were charred to black and the mass loss was significant. These vapors possessed a very strong, pungent odor. Occasionally due to the pressure build up, some of the ground glass stoppers gave way allowing some of the vapors to escape.

The percent mass loss was calculated to be ~65% as seen in Table 9. This low value of residue indicated the ash content could be low as well. The lower the ash content, the better the substance behaves as a fuel. A chromatogram was obtained for three different brands of hazelnuts as shown in Figure 4. The results were very similar as they all showed peaks occurring in relatively the same retention window. This means that the organic material contained within the three hazelnut varieties were very similar to one another.

Figure 4: Gas Chromatogram Results from the Pyrolysis of the Hazelnut Shells



The dry ashing technique was performed in order to determine the ash content of the locally purchased hazelnut shell. The results are indicated in Table 10.

Table 10: Ash Content Obtained from Dry Ashing

Mass of Crucible	Initial mass Crucible+Shell	Final mass Crucible+Ash	% Ash
126.84g	129.65g	126.88g	1.42%

The ash content was determined as 1.42% for the locally purchased hazelnut shells. When compared to the ash content of other common fuels, it can be concluded that this hazelnut shell (and possibly other varieties) may be used as a fuel for stoves. The comparison can be seen in Table 11.

Table 11: Ash Content of Various Fuels

Fuel	**Ash Content**	**Fuel**	**Ash Content**
Alfalfa Seeds	6	Peanut Husks	0.9
Barley Straw	10.3	Rice Hulls	16-23
Charcoal	2-5	Safflower	6
Coffee Hulls	1.3	Wallflower	1.1
Coal	5-17	Wheat Stalks	7.4
Cotton Grin Thrash	17.2	Wood Chips	0.1

Adsorption of Metal Ions from Solution

The disposal of toxic wastewater poses a serious threat in today's excessively polluting society. A major threat which is of ever-growing concern in this respect, is the presence of heavy metals dissolved in water. The methods currently being used in the removal of these cations are either ineffective compared to the guidelines (as in reduction or lime precipitation) or else they are very expensive (ion exchange). A solution to this problem may reside with the hazelnut shell's ability to remove metal cations from solution by adsorption. Cimino et al. (1998) studied the removal of toxic cations and Cr (VI) from

aqueous solution by the hazelnut shell. Further investigation of this property of the hazelnuts has also been performed at NAIT to discover the extent of the removal of these cations.

The adsorption that took place can be seen in table 12. The extent of the removal of these cations from solutions was very significant. Toxic cations among others were being removed from solution in quantities exceeding 90%. Cations such as cadmium, copper, iron and zinc were being removed in the region of about 83% to 97% removal. The lowest amount of adsorption occurred with manganese, which was about 57% removal. This amounts to a range of cation removal from 14.3 to 24.3 milligrams of cation per gram of hazelnut shell.

Table 12: Removal of Cations From Solution by Hazelnut Shells

Metal	Intensity Before Adsorption	Intensity After Adsorption	Percent Removal	Extent of Removal ($mg_{ion}/g_{hazelnut}$)
Cd	14231	1642	88.5	22.1
Cu	2701	191	92.9	23.2
Fe	3384	189	94.4	23.6
Hg	543	43	92.0	23.0
Mn	13730	5903	57.0	14.3
Pb	723	20	97.2	24.3
Zn	4179	686	83.6	20.9

The other amazing feature observed when using the hazelnut shells for adsorption of heavy metals was the fact that ions such as calcium, magnesium, and potassium increased in concentration after the adsorption took place. According to Dr. Decuypere's Nutrient Charts, (www.healthalternatives2000.com) which were described as containing high amounts of calcium, magnesium and potassium (16 mg Ca, 22.8 mg Mg, and 95.2 mg K in 10 hazelnuts). The experimental results do not comply with the literature values for the amount of metals added to solution. The experimental values would indicate hundreds of milligrams of metal added to solution by 10 hazelnuts (depending on the masses of the individual nuts). The extent of the addition of cations to solution is tabulated in table 13.

Table 13: Addition of Cations to Solution by Hazelnut Shell

Metal	Intensity Before Adsorption	Intensity After Adsorption	Percent Addition	Extent of Addition ($mg_{ion}/g_{hazelnut}$)
Ca	1381657	5380971	289.5	72.4
K	919	16586	1704.8	426.2
Mg	7427	16848	126.8	31.7
Na	27393	31114	13.6	3.4

Some of the results listed in tables 12 and 13 cannot be quoted on their values because of their reliability. As the intensities decrease the relative standard deviation increases, as seen in table 14. This is best shown by the mercury analysis where the decrease in intensity from 543 to 43 results in an increase in RSD% from 5.30% to 43%.Some of the values of increased adsorption due to a release of metals into solution show a relatively low deviation. Sodium is the lowest overall with a relative standard deviation of the analyses before and after the adsorption occurred amounting to under 2 percent.

Another factor that is likely to result in an error in quantitation of the metal concentrations after the adsorption trial is the fact that there was no calibration performed for these trials. Therefore it must be assumed that the relation between the concentration and the intensity is linear, and that the resulting curve passes through the origin. This means that the amount of metal removed or added to solution is most likely not accurate, but the removal or addition of the ion can clearly be seen.

Table 14: Standard and Relative Deviation of Adsorption Analysis

	Pre-adsorption			Post-adsorption		
Metal	**Mean**	**SD**	**RSD%**	**Mean**	**SD**	**RSD%**
Cd	14231	1606	11.28	1642	130	7.89
Cu	2701	327	12.10	191	31	16.38
Fe	3384	154	4.56	189	136	71.77
Hg	543	29	5.30	43	19	43.32
Mn	13730	361	2.63	5903	494	8.37
Pb	723	55	7.63	20	6	30.00
Zn	4179	84	2.01	686	45	6.60
Ca	1381657	4176	0.30	5380971	384790	7.15
K	919	46	4.98	16586	420	2.53
Mg	7427	1	0.02	16848	786	4.67
Na	27393	354	1.29	31114	609	1.96

Although this did not provide any definitive evidence of the identity of the molecule that was removing the cations from solution, it showed that the removal of these metals is occurring, possibly as a result of an exchange of the unwanted cations with Ca^{2+}, Mg^{2+}, and K^{+}, or because of an organic chelating agent within the hazelnut. Further investigation may be performed to determine the source of adsorption and how effective it is.

Mineral Analysis

Table 15: Mineral Analysis of the Hazelnut Shell

	Concentration (ug/g)						
Analyte	**Variety 1**	**Variety 4**	**Variety 5**	**Variety 7**	**Variety 12**	**Variety 13**	**Variety 14**
Ca	1542.6	1095.3	3394	2913.7	3222.3	4123.1	2259.2
Cd	ND	ND	ND	ND	ND	ND	ND
Cu	20.43	8.35	7.67	23.96	34.71	58.86	2.98
Fe	3.83	8.55	25.67	ND	ND	46.95	65.6
Hg	ND	116.8	175.1	237.6	976.4	282	1151.7
K	3297.2	3476	2336.8	ND	809.1	ND	515.3
Mg	177.4	138.5	324.9	554.6	506.8	793.8	451.2
Mn	112.7	70.36	230.8	311	121.2	180	47.83
Na	575.7	955.7	514.5	456.8	250.2	275.2	446.5
Pb	ND	ND	ND	ND	ND	ND	ND
Zn	25.68	12.75	16.66	18.39	25.08	30.36	24.49

ND = None Detected

The results show that there are large concentrations of calcium and potassium in the shells of the hazelnuts. The results also show that there is a significant difference of metal concentrations between the varieties of hazelnuts.

The Kernel

Mineral Analysis

Table 16: Mineral Analysis of the Hazelnut Kernel

	Concentration (ug/g)
Analyte	**Variety 1**
Ca	3645
Cd	ND
Cu	27.36
Fe	51.16
Hg	ND
K	22335
Mg	3102
Mn	407
Na	203
Pb	ND
Zn	41.19

ND = None Detected

The results from the kernel analysis show that the hazelnut kernels have the highest concentration of potassium. The kernels also show high concentrations of calcium and magnesium.

The Oil

Extraction of the Oil

The results of the cold press method differed for each type of hazelnut. The Badgersett hazelnuts provided about 1mL of oil for each 8 kernels pressed (or 0.125mL per kernel). This oil was a very cloudy, light yellow even after 2 filtrations. The locally purchased hazelnuts on the other hand, presented a much higher yield of 1mL of oil for each 3 kernels (or 0.333mL per kernel). The locally purchased oil was also a much clearer, brighter yellow with absolutely no visible suspended particulate matter. From this information it can be established that the locally purchased hazelnuts are much better for their oil content, as far as quantity and clarity are concerned.

Oxidation of Oils

The reasoning behind the analysis was to investigate the presence and stability of unsaturated fatty acids in the oil, which would oxidize in an oxygen rich environment such as the one we live in. The oxidation reaction is assisted by heat, and the increased concentration of oxygen (pure O_2 is used). The result is an increase in mass followed by a drastic decrease in mass. This is unwanted as it leads to the rancidity of oils.

Figure 5: Thermal Gravimetric Analysis of locally purchased Hazelnut Oil

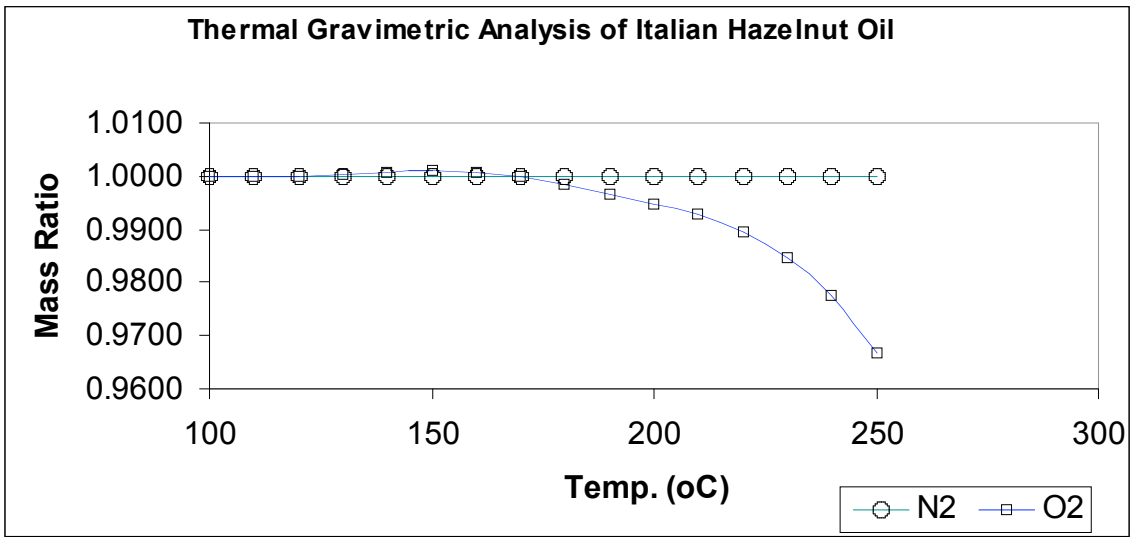


Figure 6: Thermal Gravimetric Analysis of Badgersett Hazelnut Oil

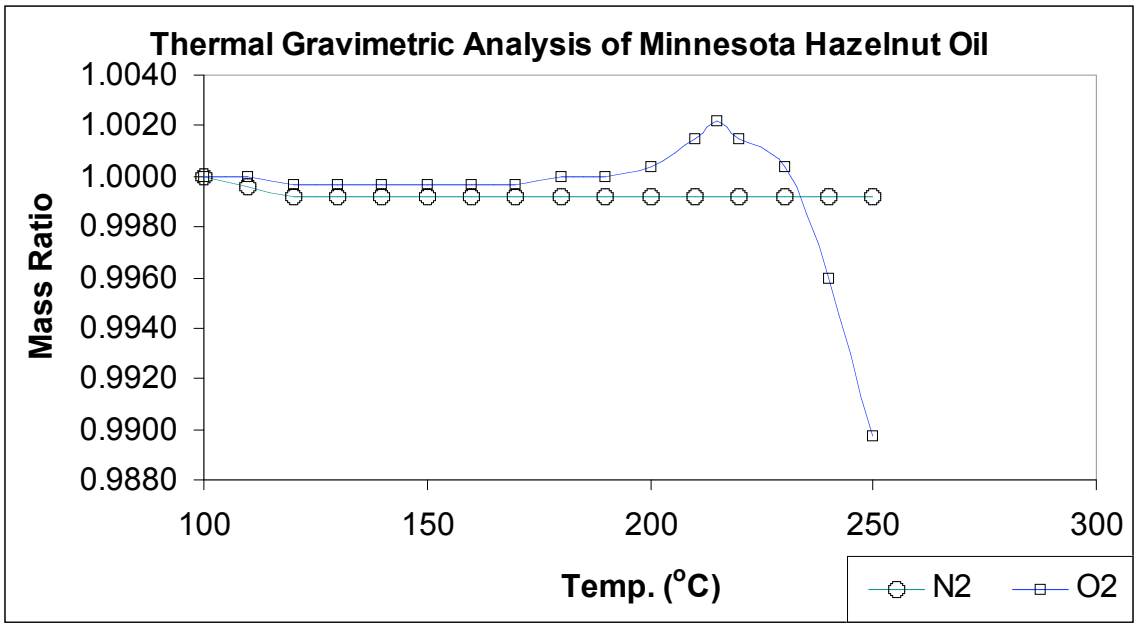
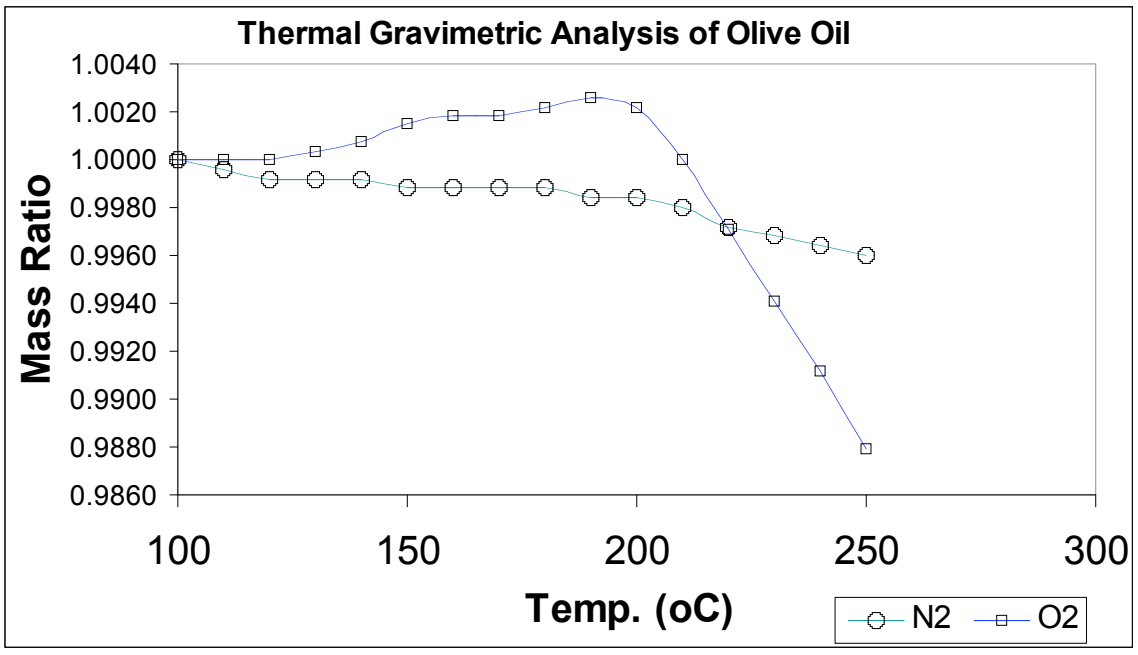


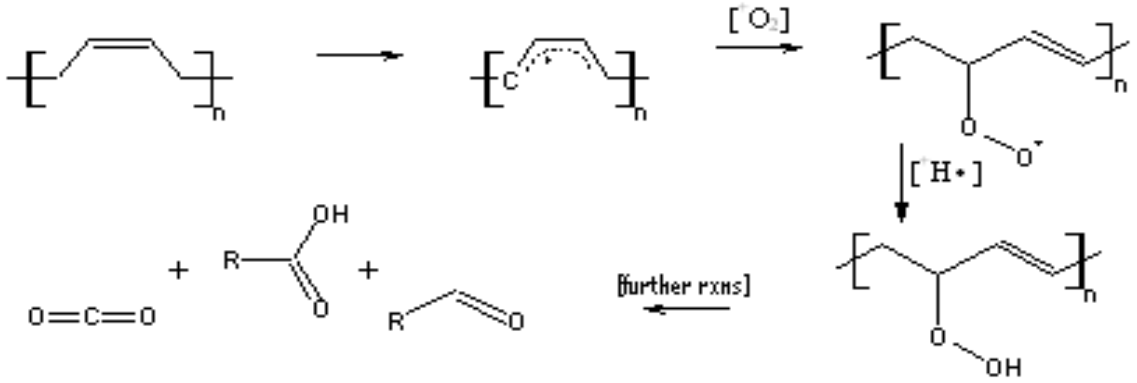
Figure 7: Thermal Gravimetric Analysis of Olive Oil



The results (shown in Figures 5 through 7) were all very unique in their own respect with one common similarity; they all yielded very different results with nitrogen as opposed to oxygen, which meant there was oxidation occurring! The locally

purchased hazelnut oil showed signs of oxidation early in the run, steadily gaining mass from ~120°C to ~170°C. The increase in mass seen in this trial was very small (0.0017% mass gain considering the loss during the nitrogen trial at the same temperature). The cause of this is the formation of oxygenated compounds such as hydroperoxides in the presence of oxygen. This gain in mass is followed by a drastic loss in mass due to the decomposition of the substance with further exposure to oxygen. An example of the reaction occurring is illustrated in Figure 8.

Figure 8: Oxidation of Unsaturated Fatty Acids



The same type of relation was observed during the Badgersett hazelnut run, only the initial oxidation for this oil occurred much later in the temperature program. The initial increase in temperature happened at ~ 180°C. This is approximately the point at which the shift from mass loss to mass gain took place in the locally purchased Hazelnut oil. This mass loss (0.3001%) was much larger than that occurring with the locally purchased oil, but took place over a very low temperature range (~25°C). This means that the Badgersett hazelnut oil has a much higher thermal stability than the locally purchased oil.

The olive oil is even more unstable than either of the hazelnut oils. It showed an exceptionally large mass gain (0.4202%), over an unusually wide temperature range (120-170°C). This proves that it would be much more practical to cook with the Badgersett hazelnuts or their oil, rather than using the locally purchased hazelnuts or olive oil.

Mineral Analysis

Table 17: Mineral Analysis of the Hazelnut Oil

	Concentration (ug/g)	
Analyte	locally purchased Oil	Badgersett Oil
Ca	61.72	66.44
Cd	ND	ND
Cu	47.24	59.32
Fe	ND	ND
Hg	ND	ND
K	ND	ND
Mg	1.76	2.99
Mn	2.27	3.13
Na	285.2	318
Pb	ND	ND
Zn	22.87	27.2

ND = None Detected

The oil samples showed higher concentrations of sodium, but little else. Once again, the concentrations varied according to variety.

CONCLUSION

Bulk Badgersett shells. The Hybrids were then analyzed solely to investigate whether there was a correlation between the initial mass of shells used for particle distribution. From the results, it was concluded that the initial mass did not have an effect on the percent distribution of the shells.

The procedure developed for the digestion of the hazelnut components is a quick and inexpensive process. Although there are no toxic chemicals used or emitted during the process, the addition of hydrogen peroxide to the hot sulphuric acid produced a very vigorous and violent reaction. The two most crucial factors in achieving success of the method are; mode of hydrogen peroxide addition, (i.e.; size of droplets) and the

temperature. In order to make the process a complete success, a system should be developed where the hydrogen peroxide when added can be done consistently with the same droplet size and mixing rate. The system should incorporate a cover to prevent sputtering.

The various particle sizes were tested for any difference in structural properties by testing their reaction to extreme temperatures via the thermal gravimetric analyzer. The results show that there is no significance between the size of the hazelnut particle and the mass loss.

The results obtained from the TGA and the pyrolysis tend to agree with each other based on the mass loss. The TGA indicates a mass loss of ~75%, while the pyrolysis shows a mass loss of ~65%. The difference between the two may be due to the fact that some residue was lost on the walls of the apparatus and therefore can't be accounted for. The experiment leads to the conclusion that the hazelnut shell can be used as a potential fuel. However further research should be done using a GC mass spectrometer to analyze what compounds are really in the shells and which ones are responsible for the strong odor during combustion. Work has to be done to see if they would still have the same characteristics if the odor causing compounds are removed. If the odors are not eliminated, the chances of using the shell as fuel are scarce or it will have to be heated in a closed system. Research has also to be done in the area of transferring these shells into a user friendly pellets or artificial logs.

The locally purchased hazelnut shells proved very effective in removing heavy metals from an aqueous solution by adsorption. All toxic cations initially present in solution were removed in exceptionally large amounts (most over 85%). This process also proved very effective in increasing the concentrations of minerals such as calcium, magnesium, and potassium in the solution. Unfortunately, these values cannot currently be quantitated accurately because a calibration involving an identical matrix was not performed.

The oil was extracted by cold press and filtered through a Millipore syringe. This was a lengthy and tedious process, and the yield was approximately 0.125mL per Badgersett kernel, and 0.333mL per locally purchased kernel.

The oil was tested in the thermal gravimetric analyzer to determine the ability of the oil to resist oxidation. The Badgersett possessed the greatest thermal stability by far,

while the olive oil was the least thermally stable. The Badgersett hazelnut oil would therefore be the most appropriate oil to cook with.

The results of the mineral analysis show that the kernels are very high in potassium. The shells and kernels also have significantly higher metal concentrations than the oil. Finally, the mineral content of a hazelnut depends on its variety. There is no evidence that any of the toxic cations examined are present in the hazelnut shell, kernel, or oil.

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