



April 2011 Teacher's Guide

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About the Guide

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Articles from past issues of *ChemMatters* can be accessed from a CD that is available from the American Chemical Society for \$30. The CD contains all *ChemMatters* issues from February 1983 to April 2008.

The *ChemMatters* CD includes an Index that covers all issues from February 1983 to April 2008.

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Student Questions

Tanking Up with Cooking Oil

1. What is meant by the term “hydrocarbon”?
2. What is the difference in composition between a gasoline molecule and a diesel molecule?
3. Why is diesel fuel more viscous than gasoline?
4. If fats and oils are both lipids, what is the difference in the terms?
5. What are the two major differences between the burning of gasoline and the burning of diesel fuel in an internal combustion engine?
6. Why is the burning of vegetable oil in a diesel engine considered to be “carbon neutral”? What is meant by the term “carbon neutral”?
7. What are the several environmental advantages gained from using vegetable oil rather than gasoline as fuel in an engine?
8. What is biodiesel fuel?

H₂GO: Hydrogen In, Water Out

1. Which is more efficient, a gasoline-powered car or a hydrogen-powered car? Cite evidence from the article.
2. If the hydrogen-fuel-cell-powered car doesn't have an engine, what drives this car?
3. List and describe the role of each of the three parts of a fuel cell.
4. Write the equation describing the reaction occurring at the anode.
5. Write the equation for the reaction occurring at the cathode.
6. Write the equation for the overall reaction.
7. What are the three problems cited by the author preventing hydrogen-powered cars from being used in large numbers?
8. Given the problems involved with hydrogen, are there any advantages to using it as a fuel? Explain.
9. Has the federal government done anything to encourage research into hydrogen cars?
10. Now that the federal government has scaled back on hydrogen vehicle research, are the car companies following suit? Explain.

A Single Ignition: A Cautionary Tale

1. How many gallons of oil were in the Carnes tank when the explosion occurred?
2. Name and describe the process by which crude oil is refined.
3. The article says there are three things required for something to burn. Name them.
4. In the article the equation for the combustion of octane is given. Name the products of combustion.
5. What are the requirements of an explosion?
6. What factors affect the rate of a chemical reaction?

Sweet but Good for You?

1. What food and drink ingredient is in almost every non-diet soft drink, lots of sweet foods, like cookies and cakes, and also some lunch meats, pasta sauces, and breads?
2. Which part of the corn kernel contains the key ingredient used to make high fructose corn syrup? What key ingredient does this portion of the corn contain?
3. What large family of molecules does starch belong to? What purpose do these types of molecules serve in our bodies?
4. How are the two varieties of starch molecules alike? How do they differ?
5. Describe the three enzymatic processes starch undergoes to transform it into high fructose corn syrup.
6. How do types of high fructose corn syrup differ?
7. Why is high fructose corn syrup an ingredient in foods that don't even taste very sweet, such as processed meats, pasta sauces, and bread?
8. How is sucrose similar to high fructose corn syrup? How does it differ?
9. What is the problem with ingesting too much of a sweetener such as sucrose or high fructose corn syrup?

Authentic or Not? Chemistry Solves the Mystery

1. What method of analysis was used to study the "French" canvas in the van Gogh F 614 case?
2. What is the name of the type of canvas that van Gogh used and what allowed modern scientists to use this canvas to prove that the F 614 in question was a fake?
3. Name the German art dealer in the van Gogh case described in the article.
4. Name the paint pigment used to discredit the Jackson Pollock paintings.
5. Name the type of spectroscopy used by James Martin to identify a paint pigment used in the fake Pollock paintings.

Answers to Student Questions (from the article)

Tanking Up with Cooking Oil

- 1. What is meant by the term “hydrocarbon”?**
A hydrocarbon is a molecule composed of only hydrogen and carbon atoms.
- 2. What is the difference in composition between a gasoline molecule and a diesel molecule?**
A gasoline molecule contains between 5 and 10 carbon atoms while a diesel molecule contains between 10 and 24 carbon atoms.
- 3. Why is diesel fuel more viscous than gasoline?**
Diesel fuel is more viscous because its longer molecules provide more places for intermolecular bonds, hence stronger bonds between molecules compared with the shorter gasoline molecules.
- 4. If fats and oils are both lipids, what is the difference in the terms?**
Fats are considered to be lipids that are solid at room temperature and have an animal origin, whereas oils are liquid at room temperature and usually are from plants.
- 5. What are the two major differences between the burning of gasoline and the burning of diesel fuel in an internal combustion engine?**
Gasoline is introduced into an engine’s cylinders as a vapor mixed with air. It is ignited by an electrical discharge from a spark plug. For diesels, there is no spark plug to ignite the fuel. And the fuel is not introduced with air as a mixture of vapors. Rather air is first introduced and compressed to heat the gas. Then the diesel fuel is introduced as a vapor which is ignited by the hot air, not by a spark plug—because there is no spark plug in the diesel engine.
- 6. Why is the burning of vegetable oil in a diesel engine considered to be “carbon neutral”? What is meant by the term “carbon neutral”?**
Since the oil comes from plants that utilize photosynthesis which requires the uptake of carbon dioxide, the oil when burned produces carbon dioxide that came from plant material produced from the photosynthetic products. If the uptake and output of carbon dioxide are equal, then the burning process does not add additional carbon dioxide to the atmosphere. The two processes cancel each other out in terms of carbon dioxide; this is what’s meant by “carbon neutral”. The entire cycle of photosynthesis and burning is carbon neutral.
- 7. What are the several environmental advantages gained from using vegetable oil rather than gasoline as fuel in an engine?**
 - a) Burning vegetable oil is carbon neutral.*
 - b) Using vegetable oil produces fewer pollutants such as carbon monoxide, hydrocarbons, and sulfur oxides.*
- 8. What is biodiesel fuel?**
Biodiesel fuel is any diesel fuel that is made from a biological source, particularly plant material, including oils and cellulose (through special bacterial action).

H₂GO: Hydrogen In, Water Out

- 1. Which is more efficient, a gasoline-powered car or a hydrogen-powered car? Cite evidence from the article.**

The hydrogen-powered car is more efficient—80% efficient, versus 15-20% efficiency for the gasoline-powered car.

2. **If the hydrogen-fuel-cell-powered car doesn't have an engine, what drives this car?**

An electric motor uses the electricity produced by the hydrogen fuel cell to drive the car.

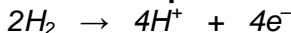
3. **List and describe the role of each of the three parts of a fuel cell.**

a) *The anode is the site at which oxidation occurs, which releases electrons.*

b) *The cathode is the site where reduction occurs, which uses the electrons produced at the anode.*

c) *The polymer electrolyte membrane allows the protons (H^+ ions) to pass through from the anode to the cathode.*

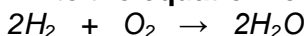
4. **Write the equation describing the reaction occurring at the anode.**



5. **Write the equation for the reaction occurring at the cathode.**



6. **Write the equation for the overall reaction.**



7. **What are the three problems cited by the author preventing hydrogen-powered cars from being used in large numbers?**

The three main problems holding back the development of hydrogen-powered cars are:

a) *hydrogen is only present in compounds on earth and elemental hydrogen must be produced through chemical reactions. These reactions produce pollution,*

b) *storing hydrogen onboard the car is difficult because it is a gas and occupies so much space, and*

c) *right now we don't have a way of distributing hydrogen fuel on a large geographic scale, as we do for gasoline.*

8. **Given the problems involved with hydrogen, are there any advantages to using it as a fuel? Explain.**

Despite the problems with hydrogen fuel, there are several advantages:

a) *it is abundant (think water in the oceans as a source),*

b) *it contains a lot of potential chemical energy,*

c) *it is non-polluting (remember, the product of the reaction is simply water), and*

d) *it is a very efficient energy-conversion process (80% for hydrogen fuel in electrical fuel cells vs. 20% for burning gasoline). Much less energy is lost as heat.*

9. **Has the federal government done anything to encourage research into hydrogen cars?**

The US Department of Energy instituted a program in 2005, the National Hydrogen Learning Demonstration, to get the automobile industry and energy companies to begin working together toward hydrogen vehicles.

10. **Now that the federal government has scaled back on hydrogen vehicle research, are the car companies following suit? Explain.**

Even though DOE cuts have been made on hydrogen vehicle research, automobile companies have agreed to continue their research, saying that it will eventually bear fruit.

A Single Ignition: A Cautionary Tale

1. **How many gallons of oil were in the Carnes tank when the explosion occurred?**

There were 588 gallons of oil in the tank. The article says there were 14 barrels and each barrel is equal to 42 gallons.

2. **Name and describe the process by which crude oil is refined.**

The process by which crude oil is refined is called fractional distillation and involves heating the crude so that each of the hydrocarbon compounds in the mixture boils off, is cooled and collected in separate fractions.

3. **The article says there are three things required for something to burn. Name them.**

The three conditions listed in the article are fuel, heat, and oxygen. In the case of the explosion in the article the fuel was the hydrocarbon vapors that make up crude oil. The heat source was unknown, but the article says it could have been a match, a lighter or a spark caused by two pieces of metal scraping each other or from static electricity. The oxygen, of course comes from the air.

4. **In the article the equation for the combustion of octane is given. Name the products of combustion.**

The products are given on the right hand side of the equation. They are carbon dioxide and water. Energy, usually in the form of heat and light, is another product of combustion, which is always exothermic.

5. **What are the characteristics of an explosion?**

The article lists these two requirements—production of a gas or gases and the production of heat, which causes the gases to expand. In the equation for the combustion of octane, for example, there are more total moles of gases on the products side than on the reactants sides. If there are more moles produced the products will occupy greater volume. The heat produced in the explosion also serves to raise the temperature of the gaseous products and increases their volume according to Charles Law.

6. **What factors affect the rate of a chemical reaction?**

The factors listed in the article that affect the rate of reaction are:

- a) the nature of the reactants,
- b) the physical state of the reactants (solid, liquid, or gas),
- c) temperature,
- d) pressure, and
- e) the amount of surface area—the area of exposed surface of chemical substances.

Sweet but Good for You?

1. **What food and drink ingredient is in almost every non-diet soft drink, lots of sweet foods, like cookies and cakes, and also some lunch meats, pasta sauces, and breads?**

High fructose corn syrup is often present in all of the foods and drinks listed.

2. **Which part of the corn kernel contains the key ingredient used to make high fructose corn syrup? What key ingredient does this portion of the corn contain?**

The part of the corn kernel called the endosperm contains the key ingredient—starch—used to make high fructose corn syrup.

3. **What large family of molecules does starch belong to? What purpose do these types of molecules serve in our bodies?**

Starch belongs to a large family of molecules called carbohydrates that help the body store and transport energy.

4. **How are the two varieties of starch molecules alike? How do they differ?**

Both amylose and amylopectin are polymers of the monosaccharide glucose. Amylose is a long, linear chain structure, while amylopectin's structure branches.

5. **Describe the three enzymatic processes starch undergoes to transform it into high fructose corn syrup.**

An enzyme called alpha amylase is added to a slurry mixture of starch and water. The enzyme breaks the carbon bonds that hold the repeating units of glucose in the amylose

form of starch, leaving behind only glucose. Next, a second enzyme called glucoamylase is added, which breaks up the branch points of amylopectin, leaving behind only glucose. A third enzyme called glucose isomerase then converts a portion of the glucose to fructose.

6. **How do types of high fructose corn syrup differ?**

The type of high fructose corn syrup depends on the amount of fructose present. One standard type of high fructose corn syrup has a ratio of 42% fructose and 55% glucose, while another type has a ratio of 55% fructose and 42% glucose. The type with a higher ratio of fructose tastes sweeter.

7. **Why is high fructose corn syrup an ingredient in foods that don't even taste very sweet, such as processed meats, pasta sauces, and bread?**

Adding high fructose corn syrup to processed meats and sauces covers up any bitter tastes that might be present, since our tongues pick up sweet tastes before they detect bitter ones. High fructose corn syrup also makes foods brown more easily, contributing to a nicely browned bread crust.

8. **How is sucrose similar to high fructose corn syrup? How does it differ?**

Sucrose and high fructose corn syrup are both made of the monosaccharides glucose and fructose, in nearly half-and-half proportions. Sucrose is a single molecule made of the monosaccharides joined together, making it a disaccharide. High fructose corn syrup is a mix of glucose and fructose, with the monosaccharides floating free.

9. **What is the problem with ingesting too much of a sweetener such as sucrose or high fructose corn syrup?**

These two sweeteners "...have 4 kilocalories per gram, and no other nutrients. These calories can add up fast, making it harder to burn as many calories as you take in. They can also edge out other foods that have more nutritional value..."

Authentic or Not? Chemistry Solves the Mystery

1. **What method of analysis was used to study the "French" canvas in the van Gogh F 614 case?**

Because the canvas itself was not visible, X-ray analysis was used to "see" the thread count and texture of the canvas. X-rays are able to penetrate the pigment layer (except for pigments that contain lead or other heavy metals) and reach the canvas layer.

2. **What is the name of the type of canvas that van Gogh used and what allowed modern scientists to use this canvas to prove that the F 614 in question was a fake?**

Vincent van Gogh used a type of canvas called a French canvas which, according to letters between him and his brother, he purchased in Paris.

3. **Name the German art dealer in the van Gogh case described in the article.**

The German art dealer's name was Otto Wacker. Eventually he was convicted of fraud and sentenced to 19 months in prison.

4. **Name the paint pigment used to discredit the Jackson Pollock paintings.**

The pigment in the Pollock painting case is known by several names—Ferrari red, Red 254, or its chemical name, 3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

5. **Name the type of spectroscopy used by James Martin to identify a paint pigment used in the fake Pollock paintings.**

James Martin used Fourier-Transform Infrared Microspectroscopy to determine that the paint chip was a synthetic pigment not available in Pollock's lifetime.

ChemMatters Puzzle: Dial-an-Organic

Shown below is the typical telephone layout. Notice that three letters are associated with each of the numbers 2 through 9. It's easy to imagine that baseball player Roger Clemens might have the telephone number 254-6367, since one can spell out CLEMENS by those numbers. Being told that he is a famous pitcher helps out in this identification.

Listed below are twelve names or terms, each seven letters long, all from the field of *organic chemistry*. All are likely discussed in a chapter on that subject in any first year high school chemistry textbook. They are in no special order. About half are IUPAC names of compounds.

We'll provide for each one a "phone number" and a clue to help identify it. For example, if the first two digits are 7 and 7, the first two letters must be either P, R, or S, in some combination.

Continuing, **776-7263** contains the letters **PROPANE**, with "barbecue grill gas" as a clue. See if you can identify all the remaining ones below with just the information provided .

Good luck with your phoning; don't get any wrong numbers!

<u>PROPANE</u>	776-7263	barbecue grill gas
_____	223-8663	the simplest ketone
_____	476-6377	butanol-1 and diethyl ether are said to be ___ of one another
_____	437-8263	is ZERO on the gasoline <u>octane rating scale</u>, by definition
_____	384-2665	when "denatured", this compound is quite poisonous
_____	737-8433	the link between two amino acids in a protein chain
_____	849-6463	one of the four nucleotides used in DNA
_____	672-4825	place where a shared pair of electrons is likely to be found
_____	384-2625	a product of the oxidation of ethyl alcohol
_____	765-9637	a long chain of repeating structural units
_____	776-7963	a member of a family of formula C_nH_{2n-2}, molmass 40 μ
_____	458-2673	one of two compounds that make up a molecule of table sugar

Here's the telephone layout:

1	ABC 2	DEF 3
GHI 4	JKL 5	MNO 6
PRS 7	TUV 8	WXY 9
*	0	#

Answers to the *ChemMatters* Puzzle

PROPANE	$\text{CH}_3\text{CH}_2\text{CH}_3$
ACETONE	$(\text{CH}_3)_2\text{C}=\text{O}$
ISOMERS	Both compounds have the same formula, $\text{C}_4\text{H}_{10}\text{O}$, but quite different structures: Butanol-1 is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ while the ether is $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$.
HEPTANE	n- heptane, C_7H_{16} (with no branches) is 0, and 2,2,4 trimethyl pentane is 100, by definition to calibrate this scale.
ETHANOL	$\text{C}_2\text{H}_5\text{OH}$; it's distilled from grains or grapes to make tax-able whiskey, wine , etc, Denatured alcohol is much cheaper to purchase, but undrinkable. Note that "alcohol" has seven letters but does <u>not</u> match given telephone number.
PEPTIDE	H-N to C=O connection between two adjacent amino acids
THYMINE	The other three nucleotides do not have seven letters in their names.
ORBITAL electrons.	ex: the C atom in methane has 4 sp^3 orbitals , each with a shared pair of electrons.
ETHANAL	first step of oxidation yields the aldehyde ; further oxidation produces ethanoic acid (i.e. acetic acid). Wine turns into vinegar in air over time!
POLYMER	ex: starches are polymers of $\text{C}_6\text{H}_{12}\text{O}_6$ units.
PROPYNE	$\text{CH}_3\text{C}\equiv\text{CH}$, a member of the <u>alkyne</u> family of hydrocarbons
GLUCOSE	$\text{C}_6\text{H}_{12}\text{O}_6$. "table sugar" is sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, a disaccharide. In it glucose is one unit, fructose the other.

NSES Correlation

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	Cooking Oil	Hydrogen	Single Ignition	Sweet but Good for You?	Authentic or Not?
Science as Inquiry Standard A: about scientific inquiry.			✓		✓
Physical Science Standard B: of the structure and properties of matter.	✓	✓		✓	✓
Physical Science Standard B: of chemical reactions.	✓	✓	✓	✓	
Physical Science Standard B: of the interaction of energy & matter					✓
Science and Technology Standard E: about science and technology.	✓	✓		✓	✓
Science in Personal and Social Perspectives Standard F: of personal and community health.			✓	✓	
Science in Personal and Social Perspectives Standard F: about natural resources.			✓		
Science in Personal and Social Perspectives Standard F: about environmental quality	✓	✓			
Science in Personal and Social Perspectives Standard F: about natural and human-induced hazards.			✓		
Science in Personal and Social Perspectives Standard F: about environmental quality.	✓				
Science in Personal and Social Perspectives Standard F: of science and technology in local, national, and global challenges.	✓	✓		✓	✓
History and Nature of Science Standard G: of science as a human endeavor.		✓			✓
History and Nature of Science Standard G: of historical perspectives.					✓

Anticipation Guides

Anticipation guides help engage students by activating prior knowledge and stimulating student interest before reading. If class time permits, discuss students' responses to each statement before reading each article. As they read, students should look for evidence supporting or refuting their initial responses.

Directions for all Anticipation Guides: *Before reading*, in the first column, write "A" or "D" indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Tanking Up with Cooking Oil

Directions: *Before reading*, in the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Diesel fuel has more carbon atoms than gasoline.
		2. Diesel fuel flows more easily than gasoline.
		3. Vegetable oil contains carbon, hydrogen, and oxygen atoms.
		4. Gasoline and diesel engines are both internal combustion engines.
		5. Diesel engines depend on a spark to ignite the fuel vapors.
		6. Both gasoline and diesel engines can be converted to use vegetable oil for fuel.
		7. Heating fuel decreases its viscosity.
		8. Cars burning vegetable oil are carbon-neutral, meaning they produce the same amount of CO ₂ that plants use to grow to make the vegetable oil.
		9. Cars burning vegetable oil produce just as much carbon monoxide as cars burning conventional fuels.

H₂GO: Hydrogen In, Water Out

Directions: *Before reading*, in the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Most cars on the road today use only 20% or less of the energy in gasoline.
		2. Hydrogen cars have engines similar to today’s internal combustion engine.
		3. Both the oxidation and reduction reactions in a hydrogen fuel cell use a platinum catalyst.
		4. Hydrogen fuel cells do not produce any carbon emissions.
		5. The process in a hydrogen fuel cell is faster than the process in a gasoline engine.
		6. Most hydrogen comes from natural gas or coal.
		7. Hydrogen cars will be commercially available within five years.
		8. In a national race, a group of high school students designed and entered a car that scored more than 1000 miles per gallon.

A Single Ignition: A Cautionary Tale

Directions: *Before reading*, in the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Crude oil from different areas has different composition.
		2. Crude oil is very flammable.
		3. The refining process separates crude oil into different compounds.
		4. In fractional distillation of crude oil, the lightest molecules are found at the bottom of the tower.
		5. Gasoline is composed of only octane, C_8H_{18} .
		6. When gasoline burns, the moles of gaseous reactants outnumber the moles of gaseous products.
		7. As a general rule, gases react more quickly than liquids or solids.
		8. Deaths from oil field tank explosions occur because a spark ignites the vapor in the top of the tank.

Sweet but Good for You?

Directions: *Before reading*, in the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. High fructose corn syrup is made from sweet corn.
		2. Simple sugar molecules have five or six carbon atoms.
		3. The difference between the starch molecules amylose and amylopectin is that amylose is a linear chain and amylopectin is branched.
		4. All of a corn kernel’s starch is found in the pericarp.
		5. The same enzyme works to break down amylose and amylopectin.
		6. Corn syrup (brand name Karo) is not as sweet as table sugar, but high fructose corn syrup is sweeter than table sugar.
		7. High fructose corn syrup is used only to make products we eat sweeter.
		8. High fructose corn syrup and table sugar are both made of glucose and fructose.
		9. High fructose corn syrup and table sugar both provide 4 kilocalories of energy per gram.
		10. Humans and chimpanzees have the same level of amylose to break down starch present in their saliva.

Authentic or Not? Chemistry Solves the Mystery

Directions: *Before reading*, in the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Most scientific techniques to detect art forgeries are based on chemistry at the molecular level.
		2. X-rays can be used to determine the properties of the canvas underneath the paint of famous paintings.
		3. The authenticity of some paintings by Van Gogh and others is still in doubt despite chemical analysis.
		4. When molecules absorb radiation from a laser or other source of electromagnetic radiation, the electrons within the molecule move to an excited state.
		5. Electrons emit light when they move from an excited state to the ground state.
		6. The paint pigment Red 254 (“Ferrari red”) contains carbon, hydrogen, oxygen, chlorine, and nitrogen.
		7. Every chemical compound has its own spectrum, different from the spectra of other compounds.
		8. National galleries such as the National Gallery in London do not keep fake paintings.

Reading Strategies

These matrices and organizers are provided to help students locate and analyze information from the articles. Student understanding will be enhanced when they explore and evaluate the information themselves, with input from the teacher if students are struggling. Encourage students to use their own words and avoid copying entire sentences from the articles. The use of bullets helps them do this. If you use these reading strategies to evaluate student performance, you may want to develop a grading rubric such as the one below.

Score	Description	Evidence
4	Excellent	Complete; details provided; demonstrates deep understanding.
3	Good	Complete; few details provided; demonstrates some understanding.
2	Fair	Incomplete; few details provided; some misconceptions evident.
1	Poor	Very incomplete; no details provided; many misconceptions evident.
0	Not acceptable	So incomplete that no judgment can be made about student understanding

Notes regarding the articles:

1. The April 2011 issue of *ChemMatters* includes articles about hydrocarbon and carbohydrate compounds that will fit in nicely with units on biochemistry and organic chemistry often taught near the end of the school year.
2. When students read “Sweet but Good for You?” remind them that 1 science kilocalorie = 1 food Calorie.

Tanking Up with Cooking Oil

As you read the article, complete the chart below to compare the advantages and disadvantages of using gasoline, diesel fuel, and vegetable oil for fuel in internal combustion engines. Use bullets to separate each new idea.

Fuel	Advantages	Disadvantages
Gasoline		
Diesel fuel		
Vegetable oil		

- Would you use vegetable oil for fuel to run your car, now or in the future? Explain your reasoning in the space below.

H₂GO: Hydrogen In, Water Out

As you read the article, complete the charts below. The first chart compares the reactions at the anode and cathode of a hydrogen fuel cell, while the second chart describes the advantages of hydrogen fuel cells, along with an explanation for how this is done and why it is an advantage.

Hydrogen Fuel Cells	Anode	Cathode
Chemical reaction		
Oxidation or reduction?		
Where do electrons go after leaving?		

Advantages of hydrogen fuel cells	How is this accomplished?	Compare to internal combustion engines
More efficient		
Abundant		
Non-polluting		

A Single Ignition: A Cautionary Tale

As you read the article, complete the chart below describing the possible sources of fuel, oxygen and heat that produced the explosion described in the article. Use bullets for each new idea.

Ingredients necessary for fire	Possible sources
Fuel	
Heat	
Oxygen	

- **Use your knowledge of chemical reactions to write a short warning message to teenagers about the dangers of hanging out at oil production sites. Use the space below.**

Sweet but Good for You?

As you read the article, complete the chart below describing the steps used to produce high fructose corn syrup.

Process	What?	Description
Extraction		
Separation		
First enzyme		
Second enzyme		
Third enzyme		
Result		

Authentic or Not? Chemistry Solves the Mystery

As you read the article, complete the diagram below to describe how the art forgeries were detected.

	Van Gogh F614	Pollock
When did the real artist live?		
Where did the forged or misattributed paintings come from?		
What part of the painting was examined scientifically?		
Describe the critical scientific evidence to detect the forged or misattributed painting.		
Where are the forged or misattributed paintings now?		

Tanking Up with Cooking Oil

Background Information (teacher information)

More on Biofuels

The *ChemMatters* article focuses on the use of cooking oil as a fuel for a car, in particular, a car with a diesel engine. Therefore, we are talking about the oil used in place of diesel fuel derived from refining petroleum. Putting used cooking oil into an unmodified diesel engine is a novel but not practical idea. One of the problems with using waste cooking fat from restaurants, as mentioned in the article, is that the oil is quite viscous and must be either heated and/or mixed with actual petroleum-derived diesel fuel before using the untreated cooking oil (and after, to flush out the fuel line). In colder climates, cooking oil as a fuel has its limitations, again due to the viscosity of the oil, which increases even more with decreasing temperature.

The more serious approach to using alternative fuels that are not petroleum-based comes under the rubric of biofuels or bioenergy, most of which is derived from plants (biomass). The more familiar biofuel of the last decade is ethanol, derived primarily from corn. This process has been promoted and, therefore, subsidized by the federal government, artificially supporting the true price of producing the alcohol. There are many critics of this alternative fuel promotion with a whole host of questions including whether or not it takes more energy to produce the ethanol than is contained in the fuel itself, how much carbon dioxide is put into the atmosphere from the cultivation and processing of the corn as well as from the actual combustion of the alcohol in an automobile or truck engine. One issue that is not in dispute is the effect of producing ethanol on food prices because of growing a food crop (animal feed) that is then diverted to fuel production. When there is competition for a food crop as in food versus fuel, the price and availability of food is affected. There is ample evidence for that. To reduce this impact, there has been research into using cellulose rather than the starch of plants for producing, through fermentation, ethanol and methanol fuels. Cellulose comes from those parts and kinds of plants that are normally not associated directly or indirectly with human consumption. The source of this cellulose is often from the part of plants not eaten by animals. This includes the stems of grass plants such as switchgrass or the waste products from wood processing (think wood chips).

What is becoming of more interest is to find other types of fuels for combustion that are not derived from petroleum and do not depend on food crops as the carbon source. Again, we are talking about fuels that are derived from non-food plants, hence biofuels. More specifically, oils found in plants can be converted to a fuel with the properties of diesel fuel and is called biodiesel.

More on Biodiesel

It is possible, through fairly simple processes, to change plant-derived oils into diesel fuel. There are many different plants that can provide the oil- this is nothing new. We are all familiar with cooking oils such as canola and soybean oil. But again, if one wants to convert these oils into biodiesel, we are diverting a food crop to a transportation fuel. And that continues to be a problem as has been clearly delineated with the promotion of ethanol from corn. But there are currently non-food crops that produce oil, specifically single cell algae.

In the government publication *Renewable Fuels Standard (RFS)* mentioned previously a detailed and documented argument is set out for developing biodiesel derived from non-food algae to replace petroleum-based diesel fuel.

The U.S. government has actively promoted the development and use of biofuels and other alternative fuels over the last 20 plus years. (Alternative fuels include hydrogen, electricity, natural gas, propane, ethanol and biodiesel) The idea of course is to find fuel sources to replace those that come from fossil fuels, particularly petroleum. Information about the *Renewable Fuels Standard (RFS)* is found in a publication, "The Promise and Challenge of Microalgal-derived Biofuels" from the National Renewable Energy Laboratory, available at (http://www.afdc.energy.gov/afdc/pdfs/microalgal_biofuels_darzins.pdf). Excerpts containing important information follow.

The RFS calls for the production of 36 billion gallons by 2022 of which at least 21 billion gallons must be advanced biofuels (i.e., non-corn ethanol). While cellulosic ethanol is expected to play a large role in meeting the EISA goals, a number of other advanced biofuels show significant promise in potentially helping to achieve the 21 billion gallon mandate. Of these candidates, biofuels derived from algal biomass feedstocks are generating considerable interest around the world. It is with this in mind that microalgal-derived lipids could serve as a major contributor to our goal of energy independence. There are several aspects of algal biofuel production that have combined to capture the interest of researchers and entrepreneurs around the world.

These include:

i) high per-acre productivity, ii) algal feedstock based on non-food resource, iii) use of otherwise nonproductive, non-arable land, iv) utilization of a wide variety of water sources (fresh, brackish, saline, and wastewater), v) mitigation of GHG release into the atmosphere, and vi) production of both biofuels and valuable co-products.

The development of biofuels from traditional oil crops and waste cooking oil/fats cannot realistically meet the demand for transportation fuels. If the entire 2007 U.S. soybean oil yield, representing almost 3 billion gallons produced on 63.6 million acres of farm land (Soy Stats™, American Soybean Association, available at <http://www.soystats.com>) was converted to biofuel, it would replace only about 4.5% of the total petroleum diesel (~66 billion gallons).

If that much land were used to cultivate algae, the resulting oil could, even at a conservative projected productivity (10g/m²/day at 15% triacylglycerols or TAG), replace approximately 61% of the petroleum diesel used annually (Table 1), as well as capturing approximately 2 billion tons of CO₂ in the biomass. CO₂ capture, however, should not be confused with CO₂ sequestration since a portion of the CO₂ captured and partitioned in the oil will be released when the algal-derived fuel is combusted, and the remaining biomass will likely be used as a feedstock for a byproduct that will ultimately be converted to CO₂. Algal capture of CO₂ for biofuels applications really amounts to a 'recycling' of the CO₂ for at least one additional use prior to being released during burning of the fuel. Under this scenario, there is no permanent CO₂ capture unless the algal biomass is completely isolated from the environment and stored."

(http://www.afdc.energy.gov/afdc/pdfs/microalgal_biofuels_darzins.pdf (pp 432, 433))

Data comparing productivity of soybeans vs. algae:

	Soybean	Algae		
Productivity		Low Productivity	Medium	High
		10 g/m ² /day	25 g/m ² /day	50 g/m ² /day
		15% TAG	25% TAG	50% TAG
Gal/acre	48	633	2637	10,549
Total Acres	63.6 million	63.6 million	25 million	6.26 million
Gal/Year	3 billion	40 billion	66 billion	66 billion
%Petrodiesel	4.5%	61%	100%	100%

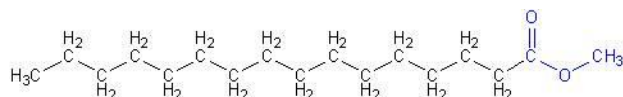
(Ref: http://www.afdc.energy.gov/afdc/pdfs/microalgal_biofuels_darzins.pdf (p.434)

NOTE: TAG is Triacylglycerols

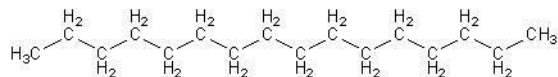
More on the Chemistry of Biodiesel

Biodiesel from plant-derived oils is based on the standard chemical process of esterification. Essentially, one combines an oil with an alcohol in the presence of some alkali such as sodium or potassium hydroxide. Heating the mixture converts the oil into an ester (the biodiesel) and glycerol. As will be referenced later, students can easily perform this experiment in the laboratory. [Reaction of vegetable oil with alkali is shown below.]

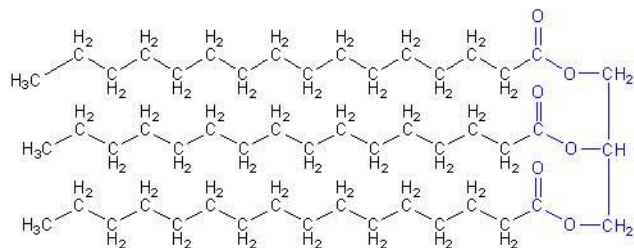
Vegetable oil, like biodiesel, belongs to a category of compounds called *esters*.



Molecule of biodiesel (with ester group in blue):



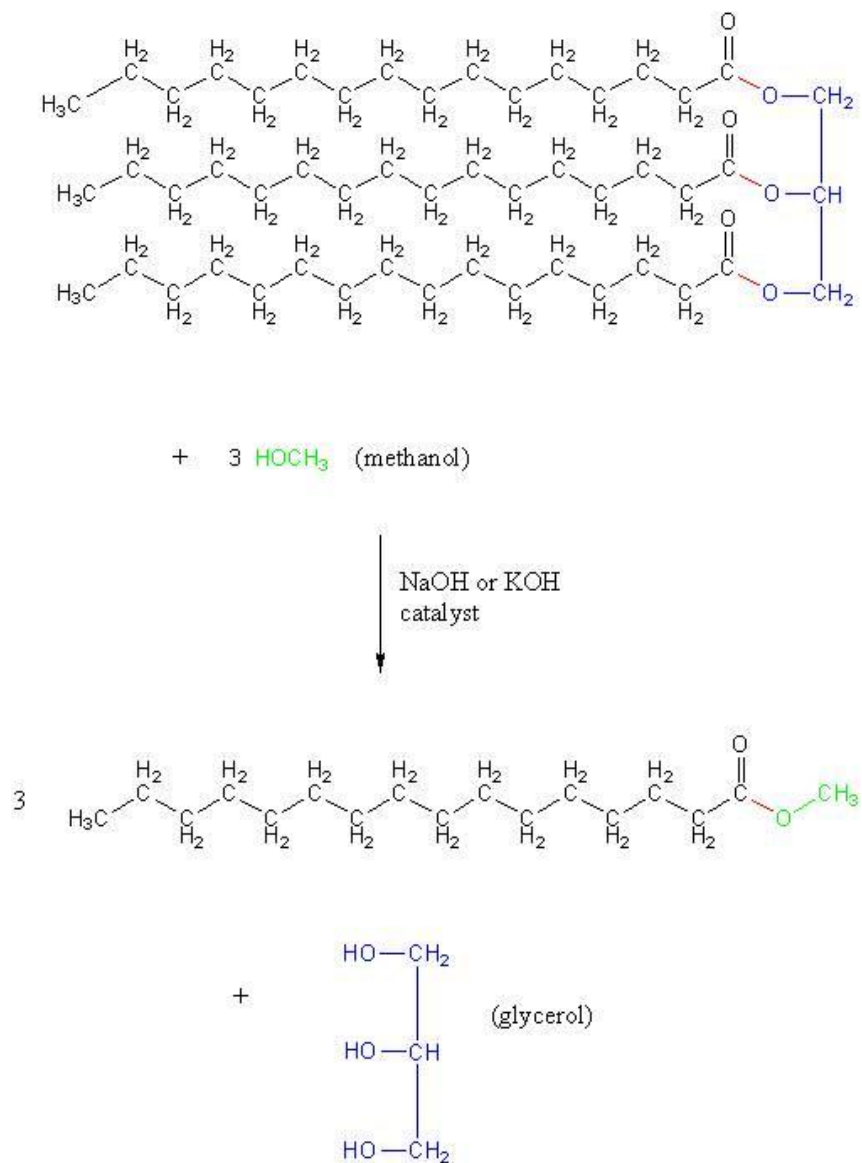
Molecule of regular diesel, a hydrocarbon



Molecule of vegetable oil

“Therefore, converting vegetable oil into biodiesel is called a *trans-esterification reaction*. Doing this reaction requires using methanol (shown in green [in the diagram below]), which causes the red bonds in the structure below to break. This breaks off the blue section, like a backbone on the molecule, which becomes glycerol. The red bonds that did go to the glycerol

backbone are placed with bonds to methoxy groups (shown in green in the final structure) that came from the methanol:"



(Source: Goshen College Department of Chemistry website, <http://www.goshen.edu/chemistry/biodiesel/chemistry-of/>)

Currently, the search is on for the most economical methods for both producing the oil and converting it to biodiesel. As mentioned, there is currently keen interest in the use of algae rather than food crops such as soybean and canola seed. Further there is a good argument to locate these algae-culturing units close to a source of carbon dioxide such as a power-generating plant that burns coal, oil, or natural gas. The algae cultures become a carbon sink for the emissions of the electricity generating plant, therefore adding a second dimension to developing oils for fuel. One of the current U.S. government policies concerning the production and use of biofuels is that these fuels must achieve at least a 50% reduction in life-cycle greenhouse gas emissions. This is not possible using fossil fuels since these fuels, although plant derived, are not currently utilizing carbon dioxide in their production! They simply produce

carbon dioxide in their combustion. Presently living plants that eventually become biofuels absorb as much if not more carbon dioxide than they eventually produce if “burned” or biologically decomposed.

More on Biodiesel from Algae

There are many benefits from using algae as the source of plant lipids for conversion to biodiesel. Cultivation of algae is done in water rather than growing on land, obviously. The cultivation is done in closed-loop structures to eliminate contamination from other air-borne algae. With these closed loop set-ups, cultivation is under controlled conditions of temperature, light intensity, carbon dioxide concentrations (higher than from the normal atmosphere), pH, and nutrient levels. Certain physical arrangements also increase the surface area exposed to light using transparent vertical growing tubes. There is a good video on the production of algae under controlled (indoors) and more efficient (vertical tubes, multiple-side exposure) conditions than open ponds; see <http://www.5min.com/Video/Algae-as-a-Green-Solution-to-the-Worlds-Energy-Problem-255719725>.

Land-based crops require much more acreage than algae cultivation apparatus, even if in the form of covered ponds. Further their growth time to produce an amount of oil when compared with land-based crops is significantly less. The Department of Energy (DOE, USA) reports that algae yield 30 times more energy per acre than land crops such as soybeans. Some numbers suggest 100,000 barrels of oil per acre from algae versus 20,000 barrels of corn-based ethanol per acre. Considering just oil production from various crops, the numbers below make the case for algae-produced oil.

Organism	Lipid production ($L ha^{-1} yr^{-1}$)
Photosynthetic microbes	72,000-130,000
Sunflower	570-1,030
Soybean	380-650

Table 1. Comparison of lipid production ranges per hectare per year for microalgae and oil-producing plants.

(Source: <http://biofuels.asu.edu/tubes.shtml>)

More on Extraction Techniques for Algae-based Biodiesel

Extraction of oil from algae can be done one of three ways—use of an oil press, use of supercritical fluids, and use of the solvent hexane.

The oil press is the most direct and easiest method. As in extracting oil from olives, the process yields up to 75% of the oil found in the algae.

The use of supercritical fluids extracts up to 100% of the oil in the algae. In this process, carbon dioxide is used. It is pressurized and heated to produce a liquid as well as a gas. The algae are mixed with the supercritical carbon dioxide and the algae turn completely into oil. The equipment required for this process makes it a less popular option for extraction.

The use of hexane as a solvent is a two-part process. First the algae are put through the presses. The leftover algae are then mixed with hexane and the mix is filtered, separately removing the residual hexane.

More on Alternate Methods for Converting Waste Vegetable Oil

Some investigators have been exploring more efficient ways to convert plant oils to biodiesel by operating at lower temperatures with the use of two catalysts, bismuth triflate and scandium triflate, which eliminates the need to use, in separate reactions, sulfuric acid and potassium hydroxide. A description of the technique can be found at <http://www.futurity.org/earth-environment/kinder-faster-biodiesel-conversion/>. The sulfuric acid converts the fatty acids in the vegetable oils to biodiesel, and the potassium hydroxide converts triglyceroles to biodiesel.

Connections to Chemistry Concepts (for correlation to course curriculum)

1. **Lipids**—Are biomolecules which include both fats (animal source) and oils (plant source). Both are starting molecules to be converted to biodiesel through the ester formation process (esterification).
2. **Esterification**—Because lipids contain triacylglycerols or triglycerides, these molecules can be broken apart using an alcohol in a basic reacting environment (the esterification process) to form a molecule dubbed biodiesel (the ester), and glycerin which can be used in the soap-making industry as well as an additive to animal feed.
3. **Combustion**—Fuel, oxygen and kindling temperature are the basic ingredients of burning or combustion, and explosions occur as a result of rapid combustion reactions.
4. **Explosions**—Explosions are merely rapid combustion reactions that happen in an enclosed space where pressure can build up. This is the basis for creating motion within the internal combustion engine that is translated to additional mechanical motion of a vehicle.
5. **Rates of Reactions**—The rate of a combustion reaction is determined by the amount of fuel, the size of the fuel particles and the availability of oxygen.
6. **Thermodynamics/Thermochemistry**—Explosions are prime examples of heat production and the rate of heat production in chemical reactions. These reactions can be related to the relatively high heat content of the reactants compared to the much lower heat content of the products.
7. **Petroleum**—Petroleum is a mixture of different kinds of hydrocarbons and other organic molecules that can be separated out by distillation. Petroleum has been produced most likely from extreme pressure on dead and decaying plant material, including algae. Some species of algae found as fossils in petroleum (and coal) are the same type now being used to produce the oil for biodiesel synthesis.
8. **Viscosity**—Because of the viscosity of diesel fuel, provision must be made to warm the fuel in order to flow better to the engine as well as to vaporize the fuel.
9. **Hydrocarbons**—These types of molecules are good fuels because of the carbon-hydrogen content that leads to production of water and carbon dioxide with a net ΔH that is negative. Coal, which is essentially pure carbon and not a hydrocarbon, produces less energy per mole because of the lack of hydrogen for producing water.
10. **Kinetic molecular theory**—Molecular collisions cause bonds to break and new ones to form, resulting in chemical reactions.

Possible Student Misconceptions (to aid teacher in addressing misconceptions)

1. **“The energy produced by burning biodiesel or other fuels comes from the breaking of chemical bonds, releasing bond energies.”** *Burning a fuel is a combustion reaction which, like other exothermic reactions, results in a net output of energy (heat, light) due to both the breaking of chemical bonds (input of energy or endothermic reaction) and the making of bonds (output of energy or exothermic reaction). The sum of these two energy changes equals the net energy change in the system. In the case of combustion, the net energy change is exothermic or a net output of energy in the system.*
2. **“If chemical bonds produce heat when broken, they must contain heat.”** *Chemical bonds between atoms within a molecule are due to the sum of the forces of attraction and repulsion, creating positions with distance between the atoms. These atomic bonding positions determine the bond’s potential energy or energy of position. A change in the distances between the atoms means a change in potential energy which is associated with the making and breaking of bonds. The sum of the potential energy changes in making and breaking of bonds results in heat energy of the combustion reaction.*
3. **“Temperature and heat are the same thing.”** *Temperature is a measure of molecular motion. Heat is a form of energy that flows across a conducting boundary from the higher to the lower temperature.*
4. **“If a reaction mixture gets hot, the reaction mixture must be endothermic.”** *If a reaction mixture becomes hot, it is not due to absorbing heat but because the reaction is generating heat (exothermic) in the mixture. Heat flows out of the system into the surroundings. One needs to distinguish between system (loses energy) and surroundings (gains energy and becomes warmer).*

Anticipating Student Questions (answers to questions students might ask in class)

1. **“How is oil from plants different from oil out of the ground (petroleum)?”** *Oil from the ground or petroleum is a mixture of different organic compounds that can be separated out by distillation. The origin of these compounds is thought to be from the chemical conversion of plant material, particularly different types of algae including the single celled algae used to provide the oils used in biodiesel conversion. Oil in plants is also a mixture of different organic compounds with the predominant molecule being a mono-alkyl ester of long chain fatty acids. The major difference as it relates to global warming is that burning oil from petroleum releases massive amounts of carbon dioxide into the environment, while burning oil from plants growing today results in carbon-neutrality—the amount of carbon absorbed from the air by the plant as it grew just balances the amount of carbon dioxide that is released back into the air when we burn the plant-derived oil.*
2. **“Why is biodiesel considered to be a cleaner fuel than diesel derived from petroleum?”** *Burning biodiesel produces fewer unburned hydrocarbons, carbon monoxide and particulate matter compared with petroleum-derived diesel. In addition, exhaust emissions of sulfur oxides and sulfates are essentially absent from biodiesel.*
3. **“If biodiesel contains carbon, why is it considered a better fuel for reducing carbon emissions and its contribution to global warming than regular diesel?”** *It is estimated that biodiesel reduces net carbon emissions by 78 per cent due to biodiesel’s closed carbon cycle, that is, the carbon dioxide given off originally came from the atmosphere and was*

incorporated into the plant tissue that produced the oil used to make biodiesel; the carbon dioxide emitted when the biodiesel is burned will again be taken up by plants. Petroleum did not remove carbon dioxide in recent times as biodiesel-producing plants have done. So petroleum is simply adding carbon dioxide to the atmosphere, not recently removing carbon dioxide in the formation of petroleum.

4. **“Does biodiesel take more energy to make than it gives back?”** Calculations suggest that for every unit of fossil fuel energy used to make biodiesel, 4.5 units of energy are gained when it burns. This takes into account the planting (growing), harvesting, fuel production and fuel transportation to the end user.

In-class Activities (lesson ideas, including labs & demonstrations)

1. It is not difficult to make biodiesel* in the school laboratory. After making it, students can test the energy value of the biodiesel and compare with some other fuels, including ethanol and a higher carbon fuel such as kerosene or candle wax. They could also compare the energy value of cooking vegetable oil which is used to make the biodiesel. The standard method for determining the joule value of each fuel is to set up a calorimeter, using a soda can suspended over the fuel source. For the liquid ethanol, biodiesel and kerosene, use flint glass “alcohol” burners available from school science supply companies. (* A simple procedure for making biodiesel can be found in the most recent *Chemistry in the Community (ChemCom)* textbook (5th ed., 2006, ISBN 0-7167-8919-1; pp 286-288). A more involved biodiesel laboratory exercise is found at [http://www.teachbiofuels.org/biodiesel%20lessons%202007/Stoichiometry_%20Making%20Biodiesel%20\(single%20phase\).pdf](http://www.teachbiofuels.org/biodiesel%20lessons%202007/Stoichiometry_%20Making%20Biodiesel%20(single%20phase).pdf).
2. Students could produce the biofuel ethanol through the fermentation process. In this exercise, students could determine the optimum conditions for fermentation including pH, temperature, type of substrate (various sugars including glucose, sucrose, lactose, fructose) keeping the same type of yeast. Determining the optimum conditions means that students would measure the rate of fermentation, using computer-based lab probes to measure gas pressure over a short period of time (roughly 10 minutes). This would be a closed system. If your lab probe program includes real time graphing, the data can also be used by the students to produce a hard copy of the data and graph for analysis (rate also calculated by the computer program). What are the optimum conditions for fermentation with each type of sugar? Does the size of the sugar molecule have any relationship to the rate?
3. If students do the fermentation lab (#2), they could also isolate the alcohol using small scale distillation (250 ml flask with delivery tube and thermometer); the ethanol could be evaluated for density, flammability, boiling point (temperature data from the distillation process) and its joule value, using the procedure in #1 above.
4. Demonstrate the principal of the diesel engine (compression ignites fuel) with a fire syringe (available at Educational Innovations, <http://www.teachersource.com/Energy/EnergyConversion/FireSyringeDemo.aspx>). Several videos show the fire syringe in operation, including one at the above website; see other examples at <http://video.google.com/videoplay?docid=5308173995304909609#> and <http://www.youtube.com/watch?v=MnpvQvCTj90>.
5. The effect of the number of hydroxyl groups on viscosity due to the increasing number of intermolecular bonds can be shown by slowly pouring, separately, several three-carbon alcohols with different numbers of hydroxyl groups. Use 1-propanol, 1,2-propanediol, (propylene glycol), and 1,2,3-propanetriol or glycerol (one of the products resulting from the trans-esterification of plant oils when making biodiesel).

6. An interesting video that combines some elements on the periodic table with future material generation using non-petroleum sources (focus is on the car—its fuel and structural materials) comes from the current (2011) PBS NOVA program on “Stuff”, in particular, the second program titled “Making Stuff Cleaner”. The program can be viewed at any PBS station’s website under NOVA programs. (<http://video.pbs.org/video/1768954299>)
7. Several videos that show the cultivation of algae and its attendant technical problems can be found at the following websites: <http://www.youtube.com/watch?v=k4z7p8-4oGo&NR=1>, <http://www.youtube.com/watch?v=hGcLgE52rzv&feature=fvw>, and <http://www.youtube.com/watch?v=EmiNcxbpFnI>.
A video of a college PowerPoint lecture (7 minutes) on algae culture that is very comprehensive can be found at <http://www.youtube.com/watch?v=cAVJN0-gUTw&feature=related>.
8. If your course includes a discussion of bond energies and estimating enthalpies of reaction from bond energies, you could assign the following problem
9. A Web Quest on “Alternative Biofuels” by high school chemistry teacher Ron Brandt is available at <http://web-prod-1.shu.edu/~brandtro/indexAF.html>. The student is tasked with working as part of a team of four students to research and report to the President (of the U.S.) about either ethanol or biodiesel as an alternative to fossil fuels. A 3-week timeline is given, with interim reports required at specified intervals. This is very professional looking, with specific requirements for each step, and an evaluation rubric included. An added feature to this site is a blog students can access to discuss their findings with others and the “President”, and to report progress. (Unfortunately, this is an in-school feature and not available to outside access; nonetheless, it is a worthwhile item to consider in your own class work.)
10. The density of gasoline is 0.78 g/mL. The density of regular diesel fuel is 0.85 g/mL. A gallon is equal to about 3.8 L. Given the following average bond dissociation energies:
 - C-C (347 kJ/mol)
 - C-H (413 kJ/mol)
 - O=O (495 kJ/mol)
 - C=O (799 kJ/mol)
 - H-O (467 kJ/mol)

and assuming that gasoline can be represented by the formula C_8H_{18} and diesel fuel by the formula $C_{14}H_{30}$, estimate the number of Joules of energy that would be released when one gallon of gasoline and one gallon of diesel fuel are burned. Assume the only products of the reactions are gaseous carbon dioxide and water vapor.

Alternately, even less information could be given and students could be expected to look up or calculate some of the required information. Stating the problem with minimal information one might ask:

Using average bond dissociation energies, estimate and compare the amount of energy released when one gallon of gasoline and one gallon of diesel fuel are burned. Assume their respective formulas are C_8H_{18} and $C_{14}H_{30}$ and the only products of the reactions are carbon dioxide and water vapor.

Out-of-class Activities and Projects (student research, class projects)

1. Students could evaluate what parts of the visible spectrum are most effective (efficient) in photosynthesis of algae. First they need to establish how the photosynthetic process can be evaluated in terms of rate of reaction. To do this, large size test tubes are used as algae incubators, with a delivery tube attached to each test tube through a one-hole stopper. The

delivery tube will be attached to an oxygen sensor (computer-based lab probe) for measuring rate of production of oxygen gas during photosynthesis. The individual tubes will be placed in a water bath, preferably in a transparent rectangular container that can hold water to maintain a constant temperature. Between a strong light source (flood lamp) and the water bath container will be placed various cellophane filters (see your local theater department; otherwise, check with Kodak for known filter values that are available) Source of inexpensive cellophane paper is <http://www.hyglassproducts.com/Cello-Wrap-Rolls-p/71501-1.htm>. Students must make sure the intensity of the various wavelengths of light is constant through the use of a light meter, varying distance from light source to reacting chamber.

Also there is an abstract of a student's photosynthesis experiment at <http://www.usc.edu/CSSF/History/2006/Projects/J1610.pdf>. It provides the set-up details including the chemical environment provided for photosynthesis to take place.

An excellent simulation (animation) of the photosynthesis process at the cellular level with the ability to manipulate the intensity of light and the particular wavelengths used can be found at http://www.mhhe.com/biosci/genbio/biolink/j_explorations/ch09expl.htm. There is an accompanying lab exercise (including scoring rubric) using the data collected in the simulation that can be found at

http://www.biologycorner.com/worksheets/photosynthesis_sim.html.

Another lab exercise reference that could be used to set up the original experiment to see the effect of various wavelengths of light on photosynthesis, using various probes for light intensity, % oxygen produced and temperature range used is found at http://www.fourier-sys.com/pdfs/new_experiments/nova_biology/photosynthesis.pdf. There is a very good picture to show the setup of the equipment.

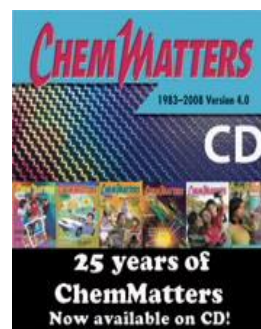
2. Students could research the various alternate fuels for transportation, including biofuels, in terms of cost, and viability (why they could be useful or possible). Start with the government website on Alternate Fuels <http://www.afdc.energy.gov/afdc/about.html>, and <http://www.afdc.energy.gov/afdc/fuels/index.html>. Another site is found at <http://www.rsc.org/chemistryworld/Issues/2009/April/Thebiofuelfuture.asp> and <http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/> (biodiesel performance, costs, and use)
3. Students could research the various commercial cultivation methods and parameters for algae at <http://www.oilgae.com/algae/oil/biod/cult/cult.html>.
References for extraction of oils from algae (chemical, mechanical) can be found at <http://www.oilgae.com/algae/oil/extract/mec/mec.html> and <http://www.oilgae.com/algae/oil/extract/che/che.html>

References (non-Web-based information sources)

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site:

<http://www.acs.org/chemmatters>. (Part way down the website screen, click on the *ChemMatters* CD icon like the one here at the right.)

Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)



Schirber, M. Green Gasoline: Fuel from Plants. *ChemMatters* **2010**, 28 (1), pp 13-15. The author discusses the chemical processes by which the cellulose of plant material is converted to various compounds found in gasoline.

Kirchhoff, M. Do You Want Biodiesel with That? *ChemMatters* **2005**, 23 (2), pp 7-9. The author discusses the chemistry of biodiesel, its synthesis and its use as a fuel to be blended with petroleum-derived diesel fuel. Discussion focuses on soybean oil as the source for conversion (trans-esterification) to biodiesel, with chemical (structural formulas) reaction diagrams. Current thinking is not to use soybeans since they are a food source also (see background information).

Alper, J. Rudolph Diesel's Engine, *ChemMatters*, **1990**, 8 (4), pp 11-13
This is a complete biography on Diesel's life, including the design and use of his invention, the diesel engine.

Chemistry in the Community (ChemCom) textbook has a unit on Petroleum (includes alternate fuels and a biodiesel lab exercise): *Chemistry in the Community*, American Chemical Society: Washington DC, 2006

Web sites for Additional Information (Web-based information sources)

More sites on biofuels from biomass

A comprehensive overview of converting biomass to useful fuels, particularly ethanol, is found at <http://www.rsc.org/chemistryworld/Issues/2009/April/Thebiofuelfuture.asp>.

A government roadmap for using algae as the source of biofuels is found at <http://www.technologyreview.com/energy/25695/page1/>

A very extensive collection of references (links) on fuels from biomass can be found at <http://www.altenews.com/biomass.htm>.

More sites on biodiesel

All the facts about biodiesel including the entire commercial process (flow chart) as well as its physical and chemical properties can be found at http://www.biodiesel.org/pdf_files/fuelfactsheets/prod_quality.pdf.

More sites on algae production using nanoparticle-enhanced light

An interesting idea using nanoparticles to enhance the photosynthesis process through the selective reflection of the most efficient wavelengths of light in an algal culture is described at Futurity's website, <http://www.futurity.org/earth-environment/grow-light-may-give-algae-biofuel-edge/>.

More on alternate methods for converting waste vegetable oil

Some investigators have been exploring more efficient ways to convert plant oils to biodiesel by operating at lower temperatures with the use of two catalysts, bismuth triflate and scandium triflate, which eliminates the need to use, in separate reactions, the sulfuric acid and potassium hydroxide. A description of the technique can be found at <http://www.futurity.org/earth-environment/kinder-faster-biodiesel-conversion/>. The sulfuric acid converts the fatty acids in the vegetable oils to biodiesel, and the potassium hydroxide converts triglyceroles to biodiesel.

More on alternate microorganisms (*E. coli*, algae) to produce biodiesel

<http://www.scientificamerican.com/article.cfm?id=bacteria-transformed-into-biofuel-refineries> provides an article on bioengineering the bacterium *E. coli* for biofuel synthesis, eliminating both the oil extraction process and the subsequent esterification procedure for algal oils. The engineered *E. coli* first enzymatically digests/converts plant cellulose into sugar molecules that are then converted to biodiesel directly. The biodiesel floats to the top of a bioreactor vat, where it can be physically removed rather than depending on distillation for separation, which is an additional energy expenditure.

A similar biological approach using genetically altered algae rather than bacteria is detailed in the following articles: <http://green.blogs.nytimes.com/2010/05/04/banking-on-fuel-sweating-flora/?scp=1&sq=%22%20...%20Fuel-Sweating%20Flora%22&st=cse> and <http://www.technologyreview.com/energy/25077/>.

More sites on integrating algae cultivation with waste treatment plants (municipal and industrial)

Using algae for wastewater treatment offers some interesting advantages over conventional wastewater treatment. The advantages of algae-based treatment include: cost effective treatment, low energy requirement, reduction in sludge formation and production of algal biomass. See the following website for additional references that elaborate on the above rationales for algae-based waste treatment from which algae can be harvested for oil extraction: <http://www.oilgae.com/algae/cult/sew/sew.html>.

An excellent Power Point, with good explanatory details that could be used in classroom shows the pluses and minuses of a scheme for using algae in waste treatment plants. The power point can be accessed at <http://www.nrel.gov/biomass/pdfs/lundquist.pdf>.

More sites on algae cultivation near power plants

Algae cultivation near fossil-fuel burning power plants allows for capture of carbon dioxide emissions that normally would go into the air, and using the gas for photosynthesis in algae for oil production and subsequent biodiesel production. A complete description of this arrangement and rationale can be found at <http://www.oilgae.com/algae/cult/cos/pow/pow.html>. The site includes a flowchart that illustrates the capture of carbon by algae, and then collection and trans-esterification of the algae oil to produce biodiesel.

More sites on Ethanol Feedstock Resources

http://www.afdc.energy.gov/afdc/ethanol/feedstocks_resources_national.html is a website from the U.S. government that provides an extensive amount of data on the potential U.S. biomass feedstock resources that could be used in place of food crops for producing ethanol biofuel.

<http://www.nrel.gov/gis/biomass.html> is a website that provides a U.S. map for location and details of biomass available for biofuel production, particularly ethanol.

A complementary map showing biomass resources per square kilometer in the U.S. is found at http://www.afdc.energy.gov/afdc/ethanol/feedstocks_resources_state.html.

More sites on the workings of an internal combustion engine

If students are interested in seeing the internal workings of the 4-stroke internal combustion engine, you can show them the “real deal” in an animation at http://www.carbibles.com/fuel_engine_bible.html. It can even be enlarged to full-screen mode! And the text is there to describe what’s happening.

Another source of information and animations about car engines is the “How Stuff Works” site at <http://auto.howstuffworks.com/engine.htm>.

H₂GO: Hydrogen In, Water Out

Background Information (teacher information)

“I believe that water will one day be employed as fuel; that hydrogen or oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable.”

~ Jules Verne, *The Mysterious Island* – 1874

More on the history of fuel cells

Fuel cells are not a new invention. The first fuel cell was made in 1839 by Sir William Grove, a Welsh lawyer, turned scientist. He had worked with wet-cell batteries and was known for his “Grove cell”, a battery that consisted of a platinum electrode in nitric acid and a zinc electrode in zinc sulfate. The battery generated ~12 amps at ~1.8 volts. He experimented with platinum electrodes in sulfuric acid, and found that he could use oxygen and hydrogen to generate electricity, producing water in the process. He realized that this was essentially the reverse of electrolysis, and saw that if he were to place several of these cells in series, he might generate enough electricity to “effect the decomposition of water by means of its composition”. He did this and produced a “gas battery”—the first fuel cell. His cell was experimental only and produced too little electricity to be useful for any commercial purpose.

Research on fuel cells spurred research into batteries and electrochemistry in general. Two different theories arose about current flow between substances: the contact theory, proposed by Alessandro Volta, and the chemical theory, championed by Christian Schönbein (who is credited with first describing the first theoretical fuel cell). The contact theory stated that there had to be a physical contact between materials to produce electricity, while the chemical theory explained that a chemical reaction was happening to produce the electricity. Much debate and discussion resulted in much research that furthered our understanding of the interaction between matter and electricity. The goal of this research was then, unlike today, to better understand the basic science behind electrochemistry; hence, fuel cell development was science-based, rather than technology-based.

This approach changed in the 1880s and beyond into the 20th century; as we learned more about the chemistry behind fuel cells, scientists began researching ways to improve the fuel cell to make it a more practical source of electricity. Ludwig Mond and his assistant Carl Langer experimented with gas derived from coal as a source for their fuel cell. They were able to produce almost 1 volt of electricity at a current of 6+ amps. Mond is credited with the origin of the term “fuel cell” in 1889 (50 years after Grove’s original discovery).

Several teams of scientists working with similar cells at the time noted that the technology of the time was such that combining cells in series never gave them an actual voltage that would have matched the potential voltage. There was always loss of voltage. These groups concluded separately that, if expense were no object, these problems could be overcome and that fuel cells could produce required voltages, but solving the established

problems was not likely to happen any time soon. This was especially true since precious metals were usually required for the electrodes, making commercial production impractical. So, for many years, fuel cell technology reached a standstill.

Then in the late 1930s Francis Bacon, a direct descendant of **the** Francis Bacon, began researching alkali fuel cells, believing they would be a useful source of power for Royal Navy submarines, rather than storage batteries then in use. He worked on alkaline cells, rather than acid cells, as had been used since Groves' cell. The alkali material, KOH, was less corrosive to the electrodes. Bacon was successful in producing sufficient electricity in his fuel cells to power lights and motors, attracting the attention of commercial developers. His alkali fuel cell eventually became part of NASA's space program and was used in the Apollo spacecraft and eventually in the Space Shuttles.

PEM fuel cells

General Electric had developed PEM fuel cells in the early 1960s as a power source for electronic gear on the battlefield. PEM fuel cells were tried in NASA's Project Gemini, preceding Apollo Project, but they developed contamination and leakage. Batteries were used on Gemini flights 1-4, until the PEM could be improved. Refinements allowed them to be used on the remaining Gemini flights. Alkali fuel cells were chosen for the Apollo flights and the remainder of the space program to-date.

General Electric continued improving their PEM cells and in the 1970s developed PEM water electrolysis technology for underwater life support, resulting in the US Navy Oxygen Generating Plant. This technology was adopted by the British Royal Navy for their submarine fleet. Other research ensued. In the 80s and 90s, Los Alamos National Lab and Texas A & M University developed methods to reduce the amount of platinum needed for the cells.

Space and underwater technologies are not the only areas of PEM research. In the mid-1990s Ballard Systems tested fuel cell buses in Vancouver and Chicago. This was followed by a joint venture with Daimler Chrysler to build experimental vehicles. Other areas of use include unmanned blimps and ocean buoys that emit and receive sonar signals.

Long-duration-flight, small aircraft was another area of research. In the early 2000s, AEROVIRONMENT used PEM technology to provide nighttime power for its solar-powered aircraft. Photovoltaic panels absorbed sunlight during the day to power the electric motors and to electrolyze water, which was then used as fuel for the PEM cells to provide power at night. Today, AEROVIRONMENT has a working drone, the Global Observer, that can stay aloft for a week at a time. (*Fortune*, February 28, 2011, p 32.)

Probably the biggest area of research for PEM fuel cells has been the automotive industry, especially since new regulations for clean air have gotten more stringent. Major automotive manufacturers like Ford, Volkswagen, Mercedes-Benz, GM and Honda all have PEM research projects.

In 1998, Iceland announced plans to create a hydrogen economy, in cooperation with German car-maker Daimler Benz and Canadian fuel cell developer Ballard Power Systems. The plan was to convert all transportation vehicles, including Iceland's fishing fleet, to fuel cell powered vehicles. (Source for much of the above information: "Collecting the History of Fuel Cells", The Smithsonian National Museum of American History, <http://americanhistory.si.edu/fuelcells/>)

The goal of the Hydrogen Future Act of 1996 was "...to direct the Secretary of Energy to conduct a research, development, and demonstration program leading to the production, storage, transport, and use of hydrogen for industrial, residential, transportation, and utility applications..." (http://www.hydrogen.energy.gov/pdfs/hydrogen_future_act_1996.pdf) The bill also contained revisions/additions to previous energy bills requiring more direct focus on hydrogen fuel research and development.

Prior to this in 1991, a Hydrogen Technical Advisory Panel had been established by the U.S. DOE to "1) raise the visibility of hydrogen as a key part of the nation's energy agenda and 2) advise DOE on the conduct of its hydrogen R&D activities". (http://www.hydrogen.energy.gov/pdfs/htac_pres_alan_lloyd.pdf)

In 2003, in his State of the Union address, President Bush unveiled a program, the Hydrogen Fuel Initiative (HFI). This program was further "...supported by legislation in the Energy Policy Act of 2005 (EPACT 2005) and the Advanced Energy Initiative of 2006...to develop hydrogen, fuel cell and infrastructure technologies to make fuel-cell vehicles practical and cost-effective by 2020." So far, the U.S. has spent more than \$1 billion on fuel cell research and development. ("How Fuel Cells Work", *How Stuff Works* website, <http://auto.howstuffworks.com/fuel-efficiency/alternative-fuels/fuel-cell.htm>.)

In keeping with these initiatives, car manufacturers continued anew their research into fuel cell cars. Some interesting information from the December 2000 issue of the *ChemMatters* Teacher's Guide will show the progress (or lack thereof) of research/development of the hydrogen fuel cell powered car:

General Motors predicts that by the end of the decade [2010], 10 percent of new cars will run on combinations of fuel-cell technology and hydrogen. They predict that by 2025 that figure could rise to 25 percent of the world market.

BMW presented what they referred to as the world's first production-based hydrogen car in May, 2000, the BMW 750 hL ... BMW claims that they will be the first automobile manufacturer in the world to offer series production hydrogen cars. They plan to open hydrogen fuel stations throughout Europe by the year 2010, when they plan to have sold several thousand hydrogen-powered cars priced competitively with similar conventional cars.

Needless to say, neither of these predictions had come to fruition by 2010, although significant progress has been made in terms of development of prototype fuel cell-powered cars. Another interesting tidbit is that the BMW 750 hL used an onboard 140-L cryogenic tank (think 33-gallon, over-sized Thermos® bottle) to store the hydrogen at -250 °C!

Closed loop regenerative fuel cell

NASA's Glenn Research Center in Cleveland, OH has produced a hydrogen fuel cell that can use electricity from an outside source to electrolyze water into hydrogen and oxygen, and then using those elements in a fuel cell to produce electricity, which can then be used to re-electrolyze the water into its elements, etc., effectively making it a closed loop system.

The original research was done to power a high-altitude solar-electric airplane. It was never used for that purpose but, prior to the recent budget cuts, was being developed for use on

the moon. NASA's plan was to have a lunar colony within 20 years, and that colony would need a power source that was not dependent strictly on solar power, and that would last a long time (batteries don't last long enough). Solar energy is available on the moon, but not on a constant basis. The sun rises and sets on the moon, so there are extended periods of darkness, perhaps as long as 330+ hours at a time. A power source is needed for those dark times.

The closed loop regenerative fuel cell is a completely sealed system. No fuel needs to be added, as in a regular hydrogen fuel cell that constantly needs refueling as it operates. The same hydrogen and oxygen can be reused over and over again in the closed loop cell, to produce water and then can be decomposed back into hydrogen and oxygen. The original "kick" to start the system would come from the sun providing light energy to a series of solar panels to produce electricity to start the electrolysis of water. Once that process is started, the cell will use the hydrogen and oxygen produced to generate electricity for the colony. In 2005, trials were made that showed the cell to work for at least 5 complete synthesis/decomposition cycles, with no loss of material or efficiency. Improvements have been made since then to increase the reaction cycles of the cell. This research might not be used any time soon on the space program, since NASA's emphasis short-term is for unmanned probes; however, the closed loop cell may find uses on submarines. For the record, the Mars missions all seem to be using solar panels as their power sources, with lithium batteries to store the electrical energy.

More on Iceland's hydrogen economy

Iceland is the first country to fully embrace hydrogen technology. The country is in a unique position to make use of hydrogen fuel. Its population of approximately 300,000 is entirely dependent on foreign oil to run its cars and buses (gasoline is >\$8/gal) and has almost no coal or even forests for fuel. But it does have a large supply of geothermal energy from hot springs heated by underground volcanic magma, and a vast amount of hydroelectric potential from its many rivers and waterfalls, fed by melting glaciers. The Icelandic government is building an infrastructure that can use this geothermal and hydrodynamic energy to generate electricity.

Presently, steam-powered turbines produce electricity and hot water, which are piped all over the country. Almost all buildings on Iceland are heated with this technology.

But moving forward, this practically free (and nonpolluting) electricity can be used to electrolyze water into hydrogen and oxygen. They will then use the hydrogen in fuel cells to propel cars and buses. From 2003, the government began converting many of its transit buses to hydrogen fuel cell power, and they are working to convert automobiles the same way. Their fishing fleet also depends on fossil fuel, and boats and ships also will eventually be converted to fuel cell-power. Automobile companies from around the world approached Iceland's government to provide funds for research and development. Hydrogen-powered buses are already in use in the Iceland transit system. The government also proposes to generate hydrogen that could then be exported to other countries, thus creating a total hydrogen economy that would reap huge monetary rewards to Iceland residents.

Alcoa Aluminum Company is also working with the Icelandic government to use their abundant cheap electricity to smelt aluminum from ore found in Iceland's remote regions. Iceland could then export the aluminum, adding a huge amount of money to government coffers. They "are exporting electricity in the form of aluminum."

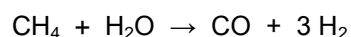
You can view several videos explaining these developments in our "More sites on Iceland's hydrogen economy", below.

More on hydrogen

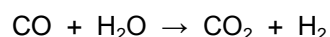
“It is interesting to compare some of the properties of hydrogen to that of gasoline. In terms of energy content, it only takes about 9.5 kg of hydrogen to produce as much energy as 25 kg of gasoline. But because of the low density of hydrogen, storing 9.5 kg of hydrogen requires a 55-kg tank, whereas storing 25 kg of gasoline only requires a 17-kg tank. Hydrogen fuel typically takes up about four times as much space as gasoline to deliver the same energy content.” (December 2000 *ChemMatters* Teacher’s Guide)

So, where does the hydrogen come from that hydrogen fuel cell cars require?

The U.S. produces about 9 million tons of hydrogen per year, enough to power more than 5 million homes. Most of it is produced in just three states—California, Louisiana and Texas. Elemental hydrogen cannot be isolated from natural sources, so it is produced chemically from hydrogen compounds. About 95% of all hydrogen is produced by a process called steam reforming of natural gas (CH₄). In the first step in this process, steam is passed through the natural gas to produce hydrogen and carbon monoxide:



A second step produces more hydrogen by exposing the CO to additional steam:



Some hydrogen is also produced by electrolyzing water.

Hydrogen can be used as an energy fuel, both as a primary fuel for rockets (as liquid hydrogen) and in fuel cells. NASA is the largest user of fuel cells, which are the electrical sources for spacecraft. In industry, hydrogen is used in refining, metal treating and in food processing. For more on fuel cells, see the article in this edition of *ChemMatters*.

In 1671, Robert Boyle reported the results of a reaction between dilute acids and iron filings in which a flammable gas was produced. The gas was hydrogen. Nearly a century later, Henry Cavendish recognized the gas to be a distinct element and that it produced water when burned. In 1783, Lavoisier reproduced Cavendish’s work and named the gas hydrogen.

Also in 1783, the Montgolfier brothers achieved the first manned hot air balloon flight, and about 10 days later Jacques Charles flew in a balloon filled with hydrogen. Both flights occurred in Paris. By the 1790’s hydrogen was being used in balloon flight on a regular basis.
(*ChemMatters* Teacher’s Guide, December 2007)

One of PBS’s NOVA 53-minute-long videos in the “Making Stuff” series, “Making Stuff: Cleaner”, focuses on alternate sources of energy. The first half of the video deals with alternate sources of fuel for cars. It covers electric cars, hydrogen fuel cell cars, and biofuels fueling existing internal combustion engines. The video also discusses carbon neutrality. The second half of the video covers using renewable resources for various purposes: tires, car interiors made of biopolymers, degradation of polymers into carbon nanotubes to make batteries (“upcycling”), generating electricity by burning trash, excess electrical storage in batteries made

of aluminum from the ground, methane fuel cell batteries, and flexible solar fuel cells using “artificial photosynthesis”. (<http://video.pbs.org/video/1768954299>)

More on other ways to store hydrogen

Storing gaseous hydrogen under pressure is not an efficient method, due to the great pressure and low temperature required. Both conditions require energy, reducing the efficiency of the hydrogen fuel cell. The best way to store hydrogen would be in the liquid phase, as that contains the highest energy density. Here again, low (cryogenic) temperatures and high pressures are required to maintain the liquid phase.

One other way to store hydrogen is to actually combine it with metals to form metal hydrides or other hydrogen-storing compounds. These can then be transported relatively easily, as they are liquids or solids. The advantage to this system is that the hydrogen is stored in a condensed phase, thus increasing its energy density immensely. A drawback to this method is that high pressures are required to force the hydrogen gas to react with the metals to form the hydride structure in the first place. Another problem of this storage method is that high temperatures are needed to force the release of the hydrogen from these structures (a chemical reaction), again reducing overall efficiency.

Another approach is to adsorb molecular hydrogen onto the surface of a solid storage material. In this situation, hydrogen doesn't break apart and recombine when charging or discharging the storage system. It's a physical change, rather than a chemical change. Hence, the energy requirements are much smaller, making this a much more efficient storage method. Current research suggests that two types of materials can be useful for this purpose: metal-organic frameworks and nanomaterials such as carbon nanotubes and nanometallic hydrides.

Wikipedia states that “metal-organic frameworks (MOFs) are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous.” These pores are the sites of hydrogen gas (and other substances) adsorption onto the solid structure. The metal ions or clusters are linked to the organic molecule. The choice of metal and linker directly influence the type of substance absorbed into the MOF, which makes these compounds extremely versatile as adsorbents. They must have large surface areas in order to adsorb as much hydrogen as possible. You can read more about hydrogen storage in MOFs here: http://en.wikipedia.org/wiki/Metal-Organic_Framework.

Nanomaterials have a very large surface to volume ratio, making them ideal for adsorption media. Buckyballs, C60 structures were originally thought to be great potential adsorbent materials, as they could theoretically contain as many as 60 hydrogen molecules inside the buckyball structure. Recent research suggests that many fewer molecules are practically possible, although work on carbon nanotubes continues to look somewhat promising. For a list and brief description of each of many hydrogen storage methods, visit http://en.wikipedia.org/wiki/Hydrogen_storage.

Part of the PBS NOVA 53-minute-long video in the “Making Stuff” series, “Making Stuff: Cleaner”, discusses the storage of the hydrogen and the potential dangers of high-pressure storage. Then they show research into using chicken feathers as a way to store the hydrogen gas, instead of putting it under extreme pressure. The feathers are heated to 750 °F. This results in the fibers becoming super-absorbent, 200 times as porous

("nanoporous"), and they can then contain hydrogen at atmospheric pressure. View the video at <http://video.pbs.org/video/1768954299>.

More on alternatively-powered vehicles

The US DOE Hydrogen Program compares all types of vehicles to each other. In a "well to wheels" analysis—comparing the costs and benefits from drilling for oil (the "well" part of the analysis) to the actual driving of the vehicle (the "wheels" part)—the hydrogen fuel cell powered car does very well when compared to any other type of propulsion system for automobiles. This analysis is "...a sub-set of life cycle assessments which attempt to look at a product, system, or technology in its totality to determine the full cost and benefit to society, from the raw materials to the end of life disposal. A "well-to-wheels" analysis looks at the overall efficiency of transportation fuels from well-head to operations in a vehicle." (http://www.hydrogen.energy.gov/pdfs/9002_well-to-wheels_greenhouse_gas_emissions_petroleum_use.pdf) This site contains tables of comparisons of all types of powered automobiles.

More on vehicle efficiency (inefficiency)

Fuels cells are much more efficient than internal combustion engines, that is, they convert more of the energy available in the chemical bonds of a fuel into useful kinetic energy that actually ends up moving a car down the road. There are three main sources of inefficiency in internal combustion engines. The first is that most of the energy released in an internal combustion engine is released as heat. Some of this heat makes gases in the cylinders expand, pushing the pistons, and ultimately, turning the wheels of the car. However, pushing the pistons doesn't use nearly all the heat produced. When the gases are through pushing, they are still very hot, and much of the heat is sent out the tailpipe of the car with the hot exhaust gases. What's more, a lot of the heat released doesn't do any useful work at all, but just makes the metal in the engine hot. This is the nature of heat, to flow from hot objects to cold objects, so containing it requires a fight against the second law of thermodynamics. A fuel cell releases most of its energy as electrical current rather than heat, reducing this kind of inefficiency.

The second source of inefficiency is friction. An internal combustion has lots of moving parts. Pistons slide up and down in cylinders, the crankshaft moves in its bearings, and so forth. Every time moving parts move in contact with non-moving surfaces, the moving parts must overcome friction. There is plenty of friction in an internal combustion engine, cutting its efficiency. Fuel cells, on the other hand, have few moving parts, and therefore little loss of energy due to friction.

The third source of inefficiency in an internal combustion engine has to do with the way pistons move. In an internal combustion engine, pistons are constantly moving back and forth, accelerating to very high speeds, coming to a stop, and then accelerating in the opposite direction. When the fast-moving piston comes to a stop, a lot of its kinetic energy is converted to heat rather than being used for work. Some clever designs, like the Wankel rotary engine used by Mazda in several models, eliminate this problem. Needless to say, fuel cells have no pistons and no such energy losses.

(*ChemMatters* Teacher's Guide, December 2007)

See also “Anticipating Student Questions” #1, below, for a brief discussion of the efficiency of an all-electric vehicle.

More on other uses of fuel cells

NASA has been using fuel cells to power manned and unmanned space vehicles and all their electronic gear since the 1960s. NASA scientists found that batteries didn't last long enough for long flights in space. Another source of energy, nuclear power—the major viable long-term power source—involved too much risk to the health of astronauts from radiation damage. Shielding for the nuclear power source would also have added excessive weight to the space capsule. So fuel cells made more sense. Also, in addition to providing electrical power for the spacecraft, the fuel cell also produces water, a necessary ingredient for maintaining life in space vehicles.

Besides outer space, “inner” space can use fuel cells, too. Companies are researching into fuel cell motors that can drive submarines. Fuel cells can also be used to generate electricity to run the technological applications onboard the sub as well. Unmanned aircraft also use fuel cells to power their engines, especially useful for long-term (>24-hour) flights.

Fuel cells can be used for portable power in almost any device in which we presently use batteries. They are useful as power back-ups, for both military and civilian purposes. The benefit of a fuel cell over a conventional battery is that a fuel cell can operate as long as it is supplied with fuel, whereas a battery will cease to function as soon as the reactive chemicals stored inside the battery are used up in the normal functioning of the battery to generate electricity.

Fuel cells can also be used in stationary mode. They can be used as electrical generating stations, especially in areas that are in remote locations not supplied by an electrical grid, or as a backup system in case of disruption of the main electrical supply (e.g., in a hospital). They can be used to power communication devices in remote areas, and they can be used to generate power from landfills and waste water treatment plants.

More on PEMs and catalysts

One of the key polymers used in the proton exchange membrane, or polymer electrolyte membrane, is Nafion®, a modified form of Teflon®, polytetrafluoroethylene. Both were developed at DuPont. The Teflon® was changed by adding sulfonic acid groups, which are strongly ionic. This gave ionic properties to an otherwise non-conducting polymer. Developed in the late 1960s by Dr. Walther Grot, this was the first conducting polymer, or ionomer, ever produced.

Since it has the Teflon® polymer backbone, it is extremely chemically inert, subject to chemical degradation only by alkali metals, sodium in particular. Like Teflon®, it is capable of working at fairly high temperatures, in some cases, up to 190 °C. The added sulfonic acid groups, however, make it highly conductive (unlike Teflon®), and it functions as a cation exchange polymer. The sulfonic acid groups make Nafion® a very strong proton donor. It is very permeable to water, and selectively so. The sulfonic acid groups efficiently absorb water, and the water can transfer rapidly through the Nafion®. It is also susceptible to proton transfer, and it is this property that is utilized in the fuel cell. The partially negative oxygen ends of the sulfonic

acid groups weakly attracts protons, but the near proximity of other oxygen atoms on nearby sulfonic acid groups allows for easy transfer along the polymer chain.

The catalyst for the electrodes for PEM fuel cells has traditionally been platinum. This does not mean, though, that the electrode is solid platinum. Rather, it has been a platinum-coated electrode, often consisting of carbon. Standard electrodes may consist of very tiny (from 2-5 nanometers, or 4-20 atoms across) pieces of platinum, embedded on tiny, but larger (~1 micrometer) pieces of carbon (called “carbon black”), which are attached to a carbon “cloth”. Carbon is neutral, but conductive and also porous, allowing gases and ions to flow through. Research seems to be showing that larger catalyst particles can result in longer fuel cell life.

The high cost of platinum has led researchers to test other non-precious metals for catalytic activity. Nickel, or at least a nickel-platinum alloy ($\text{Pt}_3\text{Ni(III)}$), seems to work for the cathode catalyst in the hydrogen fuel cell. This particular alloy is said to have increased the catalytic activity of the fuel cell cathode by more than 90-fold, compared to the platinum-carbon cathode catalyst. Platinum-ruthenium alloys have also shown promise, although ruthenium itself is rather expensive. To eliminate the high cost of these metals, other researchers are experimenting with non-metallic catalysts to do the same job.

Connections to Chemistry Concepts (for correlation to course curriculum)

1. **Oxidation-Reduction**—The electrical energy produced by the hydrogen fuel cell comes from an oxidation-reduction reaction.
2. **Half-reactions**—The two half-reactions, one oxidation and the other reduction, for the hydrogen fuel cell are given in the article
3. **Anode**—The anode, where oxidation occurs, for the hydrogen fuel cell, involves changing H_2 molecules to H^+ ions.
4. **Cathode**— The cathode, where reduction occurs, for the fuel cell, involves changing O_2 to O^{2-} ions, with the subsequent combination of the O^{2-} ions with 2 H^+ ions to produce water.
5. **Catalyst**—Platinum is the catalyst used in most hydrogen fuel cells, although other, cheaper metals are being studied to at least partially replace platinum. A catalyst is needed at both the anode and the cathode.
6. **Adsorption/absorption**—In the fuel cell, oxidation and reduction both occur as gas molecules adsorb onto the catalyst surface. The molecules are not absorbed into the bulk catalyst.
7. **Electrochemical cell**—The overall hydrogen fuel cell reaction is an electrochemical cell, producing electricity from the chemical reaction between hydrogen and oxygen gases.
8. **Reduction potential**—The reduction potentials of the half-cell reactions in the hydrogen fuel cell (or any cell) can be used to calculate its theoretical voltage.
9. **Ions**—Hydrogen ions and oxygen ions carry charges through the cell. Discussion in class could focus on the semi-permeable PEM and why hydrogen ions can get through, while oxygen ions cannot (in the opposite direction). Pore size in the PEM is one reason.
10. **Polymers**—Proton exchange membranes (PEMs), also called polymer exchange membranes, use polymers that selectively conduct positively charged ions through the cell. Of course, polymers are used throughout any car produced today—whether it’s a fuel cell car or the standard internal combustion engine—in the car tires, the car body, and throughout the interior of the car.

- 11. Atomic structure**—Atoms and ions are crucial to the working of the fuel cell. Understanding the adding or removing of electrons to or from atoms to form ions is central to atomic structure.
- 12. Gases and liquids**—Gaseous hydrogen occupies a large volume because it is a gas. Liquefying the gas would result in a much denser, more easily transportable fuel, but the requisite temperature and pressure become problematic.
- 13. Elements/compounds**—The fuel cell begins with two elements and results in the formation of a compound. The element hydrogen, though, began the process as a part of a compound, most likely methane, other hydrocarbons or water.
- 14. Thermochemistry**—One can calculate the amount of energy (thermal or electrical) potentially available for fuel cells from thermochemical data.
- 15. Thermodynamics and efficiency**—Heat loss in the various types of vehicle propulsion systems can be compared, and this can be related to the efficiency of the system.
- 16. Safety**—The need to reduce the volume of hydrogen to store it in a tank on the vehicle relates to safety due to the need to pressurize the tank. Students will also think of the flammability of hydrogen as an inherent safety issue, although they'll probably overlook the flammability of gasoline as an identical safety issue in gasoline-powered vehicles.

Possible Student Misconceptions (to aid teacher in addressing misconceptions)

- 1. “Hydrogen fuel cells burn hydrogen, right?”** *No. Hydrogen fuel cells convert hydrogen and oxygen directly into water, generating electricity in the process. It is a direct oxidation-reduction reaction; there is no burning, in the sense of combustion, occurring. The result is that very little heat is produced in fuel cells, since almost all the energy is generated as electricity (with just a bit of heat), unlike a combustion reaction, in which almost all the energy of the reaction is produced as heat (and a little light).*
- 2. “If we can get hydrogen from water, then we have an almost unlimited source of hydrogen—for FREE!”** *This is almost true. We do have the water source almost for free—and lots of it, but it takes a large amount of electricity to coerce oxygen atoms into releasing their hold on hydrogen atoms in water molecules. This energy needed to produce pure hydrogen gas is **not** free and, indeed, is a major stumbling block to putting the hydrogen fuel cell into widespread use in many applications, even beyond automobiles.*
- 3. “An all-electric car is better than a fuel cell car.”** *Many factors need to be taken into consideration in deciding what type of car is “better”. All-electric cars, like fuel cell cars have a limited distance they can travel before needing recharging/refueling. Recharging an electric car may take hours (best done overnight), while refueling hydrogen takes mere minutes. See “Anticipating Student Questions” #1, below for a discussion of fuel efficiency.*
- 4. “In an accident, a fuel cell car is extremely dangerous because its hydrogen tank will rupture and explode.”** *See “Anticipating Student Questions” #2 and “In-class Activities” #3 below for a discussion of and teaching ideas about this misconception.*
- 5. “Wait, don’t NASCAR race cars already use fuel cells?”** *Actually, NASCAR cars **do** use “fuel cells”, but their definition of a fuel cell differs dramatically from the one used by scientists. NASCAR “fuel cells” are merely their gasoline tanks, usually containing 22 gallons of gasoline. The gasoline (or other liquid fuel, for example, ethanol) is still burned in an internal combustion engine to provide power for these race cars.*
- 6. “Electrodes in a fuel cell absorb molecules and ions.”** *The process involved here is adsorption, not absorption. Adsorption is defined as “the adhesion of a chemical species onto the surface of particles” (Chemistry Glossary Definitions, About.com), while absorption is defined as “the process by which atoms, molecules, or ions enter a bulk phase (liquid,*

gas, solid)". Adsorption, as happens on the electrodes of a fuel cell, is a surface phenomenon. Hydrogen and oxygen adhere to the platinum surface of the electrodes. They do not penetrate into and become part of the substrate of the electrodes. It is important for students to understand the difference between these two very similar-sounding, but very different-meaning terms.

Anticipating Student Questions (answers to questions students might ask in class)

1. But what about electric cars, like the Chevy Volt or the Nissan Leaf? Aren't they really efficient?

An all-electric car is very efficient (~90%), if one only considers the electricity used to drive the vehicle. But if one also considers the production of that electricity—obtaining and burning fossil fuel to produce the electricity, transporting that electricity long distances, and distributing that energy to the rechargeable car battery, the efficiency drops dramatically. This excerpt is taken from the April, 1993 issue of the *ChemMatters* Classroom Guide:

Two issues are pertinent to electric cars: pollution and energy efficiency. *Chem Matters [past]* editor David Robson has investigated the efficiency of electric cars and reports some interesting numbers. It is startling to learn that a modern gasoline engine converts only 20% of the energy in gasoline into motion of the car; a modern electric motor can convert 90% of the electrical energy into useful motion. However, to compare the two vehicles fairly, one should examine the full cycle of extraction of fossil fuels through the final disposal of waste products. In the case of the electric vehicle, there are many other less obvious and less efficient steps. The electricity must first be generated at a generating plant that typically burns coal and is only 35% efficient: starting with 100 joules of heat of combustion in coal and oxygen, the plant produces 35 joules of electricity and 65 joules of heat. The electricity is delivered by a grid of power lines that is 95% efficient; it flows through a battery charger, 95% efficiency; the battery charge/discharge process, 85%; the vehicle's electric power controller, 93%; and, finally, the electric motor, 90%. Sadly, the overall efficiency is 22%—only slightly better than the gasoline car.

Of course, much research has been done since 1993. Today, slightly more than 11% of our domestic energy production comes from renewable sources. This will increase the overall efficiency of the all-electric vehicle.

2. Won't the hydrogen tank in a hydrogen fuel cell car explode if it's ruptured in an automobile accident?" *This question relates to "Possible Student Misconception" #4, above, and to "In-class Activity" #3, below. While the rupture of a hydrogen tank will result in the sudden release of the pressurized gas in the tank, and the hydrogen might even ignite, there won't be a chemical explosion. An explosion requires the production of lots of heat in a rapid combustion reaction in an enclosed space that produces gases and rapidly builds up pressure to the bursting point. This can't happen in the hydrogen tank for several reasons. First, combustion requires a fuel, oxygen, and an ignition source. The hydrogen in the tank cannot burn to produce heat because there is no oxygen in the tank that it can combine with to burn. Also, inside the tank there is no ignition source. No burning, no heat—no explosion. Second, if the tank ruptures first, the hydrogen can burn if it is ignited as it exits the tank, but the tank has already burst, so even if the hydrogen does ignite, it's already escaped from the tank, so no pressure can build up to produce an explosion. There may be a huge fireball, but the heat will quickly dissipate as the hot gases rise away from the site of ignition. Note*

that the same thing would happen if a gasoline tank was ruptured, the vapors might ignite. The difference here is that the hydrogen gas would quickly burn in a fireball and the fuel would be gone, unlike gasoline, which as a liquid would remain at the accident scene and continue to burn until it was all burned up.

Since this idea of non-explosiveness can be difficult for students to comprehend, see “In-class Activities” #3 below for two demonstrations you can do to illustrate this scenario.

3. **“If platinum is the catalyst at both the anode and the cathode, why do you need a membrane between the anode and cathode?”** *The membrane separates the electrons at the anode from the electron-seeking oxygen molecules at the cathode and forces them to go through the wire to the motor and back to the cathode. If there were no separator between the anode and the cathode, the electrons would transfer by contact, directly from the anode to the cathode. The chemical oxidation-reduction reaction, oxidation from the anode and reduction from the cathode, would both take place at the anode-cathode interface. There would be no separation of charges and thus no electric potential. The electrons would never reach the motor and hence would do no work. Electrons travel the path of least resistance, and the resistance between the anode and cathode would be zero, so they’d go directly from anode to cathode; the cell would, in short, short out. The membrane separating the two electrodes allows the tiny protons (hydrogen ions—hydrogen atoms minus their sole electron) to pass through from anode to cathode, while not allowing the larger oxygen molecules at the cathode to travel back to the anode.*
4. **“We’ve made hydrogen from water by electrolysis in the lab, why can’t we use water as the source of hydrogen for these fuel cells?”** *Actually, about 10% of all hydrogen used in the US comes from electrolysis, but it is a very expensive and energy-intensive process. Most of the electricity used for electrolysis comes from electrical generating plants that burn fossil fuels, so the process adds to pollution and decreases the desirability of hydrogen fuel cell cars. As the amount of electricity produced worldwide by renewable sources (think wind, solar) increases, electrolysis becomes a more “green” method of producing hydrogen.*
5. **“Will the DOE cut the hydrogen program altogether in the new budget? And if that occurs, will the car companies drop their research, also?”** *The answers to these questions are unknown at present. As of the writing of this Teacher’s Guide (February, 2011), the budget for the next fiscal year was still being formulated (and argued). It is unlikely, however, that car companies will cease research, considering the amount of funding they’ve spent on research and the progress they’ve made so far.*

In-class Activities (lesson ideas, including labs & demonstrations)

1. The Web-based Inquiry Science Environment group (WISE) has a project on the hydrogen fuel cell car (among many other projects). You can view the project at <http://wise4.telscenter.org/webapp/vle/preview.html?projectId=73>, or you can register with WISE to allow you access to all the teacher materials and teacher management tools that accompany all their projects at <http://wise4.telscenter.org/webapp/index.html>. A nice worksheet that takes students through an animated sequence inside a hydrogen fuel cell (from SEPUP) can be found on the fuel cell project site (the URL ending in 73, above). Once there, click on the “Hydrogen Fuel Cells” pull-down tab, at the bottom, left). Then click on 6.5, “How Do Car Fuel Cells Work?” The worksheet is there, along with the URL for the animation. This might be good for an emergency lesson for a substitute teacher to handle, although this worksheet probably won’t take the whole class period. Although the project uses inquiry methods and modeling techniques to assess student understanding, I can’t recommend using the entire project as it stands, because there are a

few problems at this time. The narrative text for this project has a few incorrect statements, like, "...hydrogen fuel cell cars...use liquid hydrogen as fuel...", and "Hydrogen and oxygen react and the released heat changes to electrical energy stored in fuel cells to power cars." The complete project contains parts (called "steps") involving background information on gasoline engines, energy transfers, combustion, both of gasoline and hydrogen (not sure why hydrogen is included here), and finally the hydrogen fuel cell. The content seems to be aimed at grades 6-8, although it is a bit mixed. Although the project is not yet a cohesive unit, changes are being made to improve the content. You can pick and choose the parts you want to use in your classes.

2. HyTEC, Hydrogen Technology and Energy Curriculum, from SEPUP, the Science Education for Public Understanding Program by the Lawrence Hall of Science is a curriculum project that contains both student and teacher versions of the materials. It was to be published in the Fall of 2010. You should be able to purchase the online textbook from Lab-Aids. You can view much of the information at the HyTEC site, including video clips and simulations. (<http://sepuplhs.org/high/hydrogen/index.html> and http://www.sepuplhs.org/hytec/fuel_cells.html)
3. Here is another brief simulation of a hydrogen fuel cell: <http://wise.berkeley.edu/upload/18292/FuelCellAnimation.gif>
And here is a good PBS video that shows an analogy using a tennis court to explain how a hydrogen fuel cell works: <http://www.pbs.org/wgbh/nova/tech/fuel-cells.html>.
4. **Electrolysis experiments/ demonstrations**
 - a. Students can duplicate on a small scale the production of hydrogen by the process of electrolysis. You can find a good basic lab experiment for electrolysis at <http://galileo.phys.virginia.edu/outreach/8thGradeSOL/ElectrolysisFrm.htm>. If you wish, save the gases produced from this reaction for the next activity, or review what happened when the gases reacted when you get to activity 3b, below. A video showing a very simple electrolysis apparatus using a 9-volt battery, a plastic cup, two thumb tacks and two test tubes, can be found at <http://www.teachingvideos.co.uk/index.php/videos/viewvideo/1359/chemistry/water-electrolysis>.
 - b. Mickey Sarquis from Terrific Science shows teachers in a teachers' workshop how to build and use their very own simple electrolysis apparatus. View it at <http://www.terrificscience.org/freebies/movies/>. Scroll to the bottom of the page for the video on electrolysis (or go directly to <http://www.youtube.com/watch?v=R15W3jV1tkk> to view it there.)
 - c. For a microscale version of electrolysis, see <http://www.slcc-science.org/chem/labs/chem1225/1225experiment12.pdf>. This activity uses a 9-volt battery, plastic straws, straight pins, pencil leads and 24-well micro plates to obtain the gases. The text of the web page contains calculations of E° and experiments that involve electrolysis of other compounds, besides water—which you may or may not want to include in your lesson.
 - d. You might prefer to do electrolysis in a Hoffman apparatus as a class demonstration. For a thorough discussion of this demonstration, see David Brooks' Doing Chemistry web page at <http://dwb.unl.edu/chemistry/dochem/DoChem044.html>. It includes a complete package of teacher information, including materials, procedure, hints, safety, disposal, etc., and a short video showing how the demonstration is done. To show a video of the entire process, see <http://www.teachingvideos.co.uk/index.php/videos/viewvideo/1359/chemistry/water-electrolysis>.
 - e. The California Fuel Cell Partnership has two lessons, one on fuel cells and one on hydrogen. The lesson on hydrogen

(<http://www.cafcp.org/sites/files/Hydrogen%20Lesson.pdf>) contains a student electrolysis experiment, and the lesson on fuel cells

(<http://www.cafcp.org/sites/files/Fuel%20Cell%20Lesson.pdf>) has an activity to construct a rudimentary fuel cell from platinum (or platinum-coated) wires, a volt meter and a reverse electrolysis experiment.

5. **To demonstrate that a hydrogen fuel tank cannot explode upon impact/ rupture**, do the following experiments/ demonstrations for students. (related to “Possible Student Misconception” #4, above, and “Anticipating Student Questions” #2, also above)

- a) Prepare three inflated balloons, as follows. The first should contain plain air. The second should contain pure hydrogen gas, while the third should contain a mixture of air and hydrogen gas in the approximate ration of 2.5 volumes of air to 1 volume of hydrogen. This approximates the stoichiometric ratio of 1:2, oxygen to hydrogen. (Air is 1/5 oxygen, so 1/5 of 2.5 is 0.5, and 0.5 volume of oxygen to 1 volume of hydrogen is 1:2.)

Ignite the plain air balloon first and ask students to observe. They will note a loud “pop”. Explain that the balloon bursts due to the heating and tearing of the elastomer of the balloon, and the ensuing rush of escaping air results in a loud “pop”, but this is **not** an explosion in the chemical sense, 1) because there is no combustion, and 2) because no new gases are produced to build up new pressure.

Now ignite the second balloon, containing pure hydrogen. This time students will observe a large fireball, in addition to the “pop”. Again, this is not an explosion. It is combustion, but it is **not** an explosion, because the burning only takes place **after** the balloon has burst and the hydrogen has escaped into the air (which contains oxygen and allows the hydrogen to burn). The fireball rises because the hydrogen/air mixture is less dense than the surrounding air. It’s less dense for two reasons: first, hydrogen is less dense than air, so a mixture of the two will also be less dense than just air and second, the gas mixture is burning and hot, and hot gases are less dense than cooler gases (of the same type).

Now, prepare to ignite the third balloon. Before you do this, however, warn students to cover their ears because this reaction might be quite loud. **WARNING:** this reaction **will** be quite loud! When you ignite this balloon, students will probably be shocked at the decibel level of the explosion. They may miss the light given off when the hydrogen/air mixture explodes. The explosion occurs because the gases are heated to their ignition point. They ignite **inside** the balloon, creating hot gas which rapidly expands and blows the balloon apart explosively. See **NOTE** below.

Safety must be your first consideration in igniting the hydrogen-oxygen balloon. You might want to take a look at this article before you do the demonstration: “Auditory Risk of Exploding Hydrogen-Oxygen Balloons” in the October 2010 issue of the *Journal of Chemical Education*, pp 1039-1044.

- b) See <http://www.practicalchemistry.org/experiments/exploding-balloons.47.EX.html> for a description of a student experiment involving these balloons. (You may still wish to do this as a demonstration only—imagine a whole class of exploding balloons!) See **NOTE** below.
- c) OK, if you don’t want to actually **do** the balloons demonstration, you can show students this video instead: “Combustible Gases in Balloons”, at <http://www.youtube.com/watch?v=7UoFNdp0UYg&feature=related>. It shows balloons of oxygen, hydrogen, and a mix of hydrogen and oxygen. The instructor ignites all three, one at a time, and the video shows all of them in slow motion, also. Note that the hydrogen balloon seems to do a bit of exploding itself. I suspect a little air infected the all-hydrogen balloon. Nevertheless, the video shows the differences in combustibility of all three. See **NOTE** below.

- d) If you prefer a smaller-scale demonstration of the non-explosive nature of pure hydrogen, simply perform the classic burning-splint test on a sample of pure hydrogen, or allow students to do the test on the hydrogen they produce from the electrolysis experiment/ demonstration discussed in #2, above. Make sure that students see that the hydrogen only burns at the lip of the collecting tube—where air/ oxygen mixes with the hydrogen to allow burning—and not inside the tube, where oxygen is not present. You might want to demonstrate to them that if the splint is thrust into the tube of pure hydrogen (held with the open end down, so that the hydrogen doesn't escape as readily), the flame will actually be extinguished inside the tube because there is no air inside the tube, so the hydrogen (and the wood splint) cannot burn. Be sure that no air has mixed in with the hydrogen inside the tube, and ensure that students are wearing appropriate personal safety equipment and that they (and you) are taking all relevant safety precautions. See **NOTE** below.

You might also want to demonstrate what happens to the splint if it is placed in the relatively pure oxygen environment of the other gas collection tube from the electrolysis experiment. Explain that, in this tube, the abundance of oxygen increases the rate of combustion of the wood splint. This shows the necessity for the presence of oxygen in order for combustion to occur. See **NOTE** immediately following.

NOTE: No matter which version of the experiment/demonstration you choose, you need to follow up with a discussion to make sure students understand the analogous situation with a hydrogen fuel cell tank. The hydrogen tank is analogous to the second balloon, with just hydrogen inside. It did **not** explode because no air/oxygen was inside the tank to allow combustion to occur. Without combustion, there is no source of extra heat and no build-up of instantly heated gas. The third balloon is an example of what **cannot** happen in a hydrogen tank. The first balloon was just used as a control of sorts, to show students the difference between a “pop” and a real explosion.

“Because of the potential danger if the collected hydrogen becomes mixed with oxygen, you should consult any reliable source of demonstration activities for specific directions and safety considerations. One excellent source of such a demonstration is Shakhshiri, Bassam Z. *Chemical Demonstrations, Volume 2*; The University of Wisconsin Press: Madison, 1985; pp 128–136.” – *ChemMatters* Teacher's Guide, December 2000.

6. You could probably build several lessons on hydrogen fuel cell vehicles based on the information contained in the California Fuel Cell Partnership's fuel cell booklet, *Driving for the Future*. You can download the pdf file of this 7-page, well-illustrated booklet at http://www.fuelcellpartnership.org/sites/files/20081015_Fuel%20Cell%20Booklet.pdf. This booklet could also serve as a very good summary of the material contained in the *ChemMatters* article, and you could easily generate a series of questions based on the booklet to serve as an emergency lesson plan for a substitute teacher.
7. You can find a single class period lesson to introduce students to the hydrogen fuel cell at Cornell University's “Cornell Center for Materials Research” web page, <http://www.ccmr.cornell.edu/education/modules/documents/IntrotoFuelCells.pdf>. This 10-page lesson, “Intro to Fuel Cells”, includes six pages of teacher material and a 4-page student worksheet to accompany the lesson. The lesson uses an inquiry approach, focusing on the 5 Es. The only drawback is that, again, it requires the availability of an actual hydrogen fuel cell. Also, note that the author occasionally uses the term “hydrolysis” when he means “electrolysis.”
8. **Students can build their own fuel cell**
- a) Planet Green.com has a very simple, one-page description of how to build your own hydrogen fuel cell at <http://planetgreen.discovery.com/tech-transport/build-hydrogen-fuel-cell.html>. Everything needed comes from around the house—except for the platinum wire.

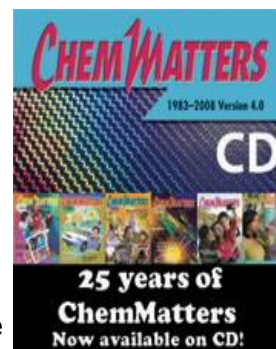
- eHow has a similar set of instructions: http://www.ehow.com/how_7257042_build-simple-hydrogen-fuel-cell.html.
- b) This site has a set of directions for building a microbial fuel cell—this one from Jell-O, dry yeast and carbon paper. Check it out at <http://www.instructables.com/id/Lime-Jello-Yeast-and-Carbon-Paper-Fuel-Cell/>.
 - c) The *Journal of Chemical Education* contains a tested demonstration to build a “Thin-Layer Fuel Cell for Teaching and Classroom Demonstrations” in its March 2009 issue. If you subscribe to *JCE* you can find it at the JCE website: <http://jchemed.chem.wisc.edu/>. Authors Shirkhazadeh and Maynard show you how to use the cell as both an electrolyzer (with a DC power source) to produce hydrogen and then as a fuel cell using the produced hydrogen to fuel the cell to produce electricity. The article is referenced in the References section of the Teacher’s Guide.
9. You can have students construct simple galvanic cells as a way to reinforce the concept that chemicals can produce electricity directly. The similarities between fuel cells and galvanic cells can help students better understand what’s happening in both cells. The December 2007 issue of the *Journal of Chemical Education* contains a student activity to build an “Aluminum-Air Battery” (pp 1936A and B). The advantage to this battery is that it produces enough current to actually turn a motor or light a bulb. Students construct the battery and measure its electrical output. The chemistry of the battery is discussed. At the end of the article, one of the questions posed is: “How is the battery you made like or unlike a fuel cell?” This helps students make the connections between galvanic cells and fuel cells. Student and teacher sheets are provided in the article.

Out-of-class Activities and Projects (student research, class projects)

1. Ask students to research and report their findings on the following statement: “Hydrogen fuel cell-powered cars are cleaner for the environment than gasoline-powered cars.” Insist that they include consideration of all factors, including: engine/motor efficiency, pollution involved in the chemical process that produces the energy (combustion or oxidation-reduction), pollution involved in producing the fuel, energy content of the fuel, “miles per mole”(?) (or miles per gram), etc. You could have students choose “sides” of this statement and stage a debate, based on their research. You might want to send them to “Increase Your H₂IQ”, a web page of the EERE division of DOE for a start. This site has almost a dozen non-technical basic fact sheets regarding hydrogen and fuel cell technology. (<http://www1.eere.energy.gov/hydrogenandfuelcells/education/h2iq.html>)
2. Students could research and report (individually or in teams) on single alternate types of fuel cell, comparing and contrasting them to hydrogen fuel cells and to combustion.
3. You might have students research the Apollo 13 NASA space mission and report on the role fuel cells played in that moon travel/rescue mission.
4. Students can research and report on non-automotive uses for hydrogen (or other types of) fuel cells. They are used for stationary power, portable electronic devices, aerospace applications, etc.

References (non-Web-based information sources)

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site: <http://www.acs.org/chemmatters>. (At the bottom of the Website screen, click on the *ChemMatters* CD image like the one at the right.)



Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

Michalovic, M. Beyond Hydrogen: The New Chemistry of Fuel Cells. *ChemMatters*, December, **2007**, 25 (4), pp 17-19. Dr. Michalovic provides the same basic information as Baxter's article, but he also includes some of the other sources of hydrogen, such as methane, ethanol and methanol. His laid-back style is easy for students to follow and understand, especially in the section where he explains the oxidation-reduction reaction and the process inside the fuel cell that produces the electricity.

Scott, D. Lost in Space: Apollo 13's Flight for Survival. *ChemMatters*, February, **1994**, 12 (2), pp 4-8. Author Scott focuses on the problems encountered in the explosion of one of the outside oxygen tanks on the Apollo 13 mission, but he includes a sidebar that discusses hydrogen fuel cells and their uses aboard the spacecraft. It's useful for students to see that fuel cells are used in settings other than the automobile. (Besides, this is a very interesting story for students—and a very teachable moment for us.)

Jones, D. Hydrogen Fuel Cells for Future Cars. *ChemMatters*, December, **2000**, 18 (4), pp 4-6. Dr. Jones writes about the Ford P2000, a hydrogen fuel car on the road in 2000. The car got about 65 miles per gallon with no pollution. He also mentions the SOFC, the solid oxide fuel cell, as a possible alternative to the hydrogen fuel cell. He discusses the benefits and pitfalls to development of the hydrogen fuel cell car, which are very similar to those described in Baxter's article.

Shirkhazadeh, M., Maynard, J. Thin-Layer Fuel Cell for Teaching and Classroom Demonstrations. *Journal of Chemical Education*, March, **2009**, 86 (3), pp 324-329. The authors show how to construct a simple hydrogen fuel cell (requires platinum wire). They use a DC power source to generate hydrogen gas, then remove the power source and use the produced hydrogen to fuel the cell to produce electricity. Subscribers to *JCE* can search for the article on the *JCE* website at <http://jchemed.chem.wisc.edu/>.

Lawrence, R., Bowman, W., Space Resources for Teachers: Life-Support Systems for Manned Space Flights. *Journal of Chemical Education*, April, **1971**, 48 (4), pp 260-262. The article describes the need and the methods used to remove CO₂ from the atmosphere inside space capsules, sources of oxygen aboard the craft, food and water supplies, and the need to produce water for survival. Methods include extraction of water from organic waste and the

hydrogen fuel cell. The material is dated, but it provides a glimpse into the space program in its early days.

Lawrence, R., Bowman, W., Space Resources for Teachers: Electrochemical Cells for Space Power. *Journal of Chemical Education*, June, **1971**, *48* (6), pp 359-361. The article describes the role that batteries and the hydrogen fuel cell play in the space program. The material is dated, but it provides a glimpse into the space program in its early days.

Dinga, G. Hydrogen: The Ultimate Fuel and Energy Carrier. *Journal of Chemical Education*, August, **1988**, *65* (8), pp 688-691. The author provides a question-and-answer format to address many of the questions that students may have about a hydrogen economy. He includes many equations describing the reactions involved in producing hydrogen from varied fuel and non-fuel sources.

Web sites for Additional Information (Web-based information sources)

More sites on hydrogen fuel cell vehicles

This is the site for the illustration of a fuel cell car used in the ChemMatters article:
<http://fueleconomy.gov/feg/fuelcell.shtml>.

The hyperphysics web site has a good article on the thermodynamics of electrolysis and the hydrogen fuel cell. It shows how the efficiency of the hydrogen fuel cell (83%) is calculated. (<http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/electrol.html#c2>)

For a very good 13-minute Public Broadcasting System (PBS) NOVA video about the hydrogen fuel cell, see <http://www.pbs.org/wgbh/nova/tech/fuel-cells.html>. It includes a good (tennis court) analogy for the chemical reaction inside the hydrogen fuel cell.

The US Department of Energy (DOE) hosts several videos that test various cars powered by hydrogen fuel cells. You can see several of these at http://www.fueleconomy.gov/feg/fcv_whatnews.jsp. As you view these videos, more will appear on the YouTube site.

General Motors has a page on their website devoted to the Chevy Equinox Fuel Cell car. The page shows an animated sequence of slides depicting what happens in a fuel cell. View it at <http://www.gm.com/vehicles/innovation/fuel-cells/>.

The FuelCellStore sells a model demonstrator hydrogen fuel cell car (\$200 as of 2/15/11) at <http://www.fuelcellstore.com/en/pc/viewPrd.asp?idproduct=434&IDCategory=137>. Carolina Scientific sells one, too, for \$215: <http://www.carolina.com/product/759932.do>.

GM's website has an Interactive Tour that takes you step-by-step through the parts of a hydrogen fuel cell vehicle. It can help to explain the parts seen in the automobile diagram included in the *ChemMatters* article. Go to Hydrogen Basics, at http://www.gm.com/corporate/responsibility/education/9-12/fuels_energy/hydrogen_basics.jsp and click under the "Interactive tour" icon at the bottom left of the screen. This tour continues with a description of how the fuel cell actually works, complete with an animated sequence showing the motion of particles in the fuel cell.

The 2010 annual DOE Hydrogen Report was “hot off the presses” as this Teacher’s Guide was being prepared. You can view it at http://www.hydrogen.energy.gov/annual_progress10.html.

To see where hydrogen filling stations are presently located, and where new stations are planned to be located—both in the US and internationally—see the multi-page chart from FuelCells2000 at <http://www.fuelcells.org/info/charts/h2fuelingstations.pdf>.

The “Hydrogen Fuel Cars Now” website has a relatively complete list of links to more than 50 hydrogen fuel cell cars now on the road or in development by almost 30 car manufacturing companies. View the list at <http://www.hydrogencarsnow.com/hydrogenfuelcellcars.htm>. The site also contains a historical timeline of fuel cell vehicle development.

NOVA has a nice illustration of a fuel cell vehicle that, when clicked to enlarge, has each part of the car (motor, fuel stack, etc.) clickable for more information. View it at <http://www.pbs.org/wgbh/nova/tech/fuel-cell-car.html>.

More sites on hydrogen fuel cells

The US Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) division shows a simple animation of a typical hydrogen fuel cell with explanations for what is happening at <http://fueleconomy.gov/feg/animation/swfs/fuelcellframe.html>. Students can replay sections as often as necessary for understanding.

The DOE has a general website devoted to hydrogen technology: <http://www.hydrogen.energy.gov/>.

The University of Cambridge, UK, hosts a “Teaching and Learning Package” about fuel cells at <http://www.doitpoms.ac.uk/tlplib/fuel-cells/index.php>.

How Stuff Works presents “How Fuel Cells Work” at <http://auto.howstuffworks.com/fuel-efficiency/alternative-fuels/fuel-cell.htm>. The site contains several videos showing how fuel cells work, as well as 8 other “chapters” containing information about fuel cells, all but one of which focus on PEM fuel cells.

The Smithsonian National Museum of American History web site, “Collecting the History of Fuel Cells”, has a page of source materials related to fuel cells at <http://americanhistory.si.edu/fuelcells/sources.htm#webpages>.

The Lawrence Hall of Science has a nice animated sequence of the workings of the hydrogen fuel cell at its SEPUP web site: <http://www.sepuplhs.org/hytec/hydrogensim.swf>. Each part of the cell can be seen close-up, with a description of what’s happening at that part of the cell.

A PBS video, featuring Tom & Ray of “Car Talk” radio, focuses on the hydrogen fuel cell car. It includes an analogy using players on a tennis court to help explain the chemical reaction inside a hydrogen fuel cell. The 13-minute video contains a few errors, which you could direct students to try to find as they watch the video. (<http://video.pbs.org/video/980048834/?starttime=623000>)

More sites on Iceland's hydrogen economy

A 2008 PBS NOVA video, "Car of the Future", features Tom & Ray Magliozzi ("Click" & "Clack"), the NPR radio car-talk guys, as they travel to various sites to investigate alternative fuels for cars. The first 16 minutes of the 53-minute video focuses on the need for reducing fuel consumption and how we're doing that. Part of the video (10:20-16:35) focuses on the hydrogen shift in Iceland and that country's fuel cell-powered transit buses. (Other parts of the video feature corn-ethanol fuel, friction-reduction inside the internal combustion engine, the hyper-car—more aerodynamic, higher efficiency car, hybrid cars, and electric cars.) (<http://video.pbs.org/video/980048834/?starttime=623000>)

A brief excerpt from a PBS show, starring Alan Alda: <http://www.youtube.com/watch?v=bgGIE97rJl4> (3 minutes)

An interview with the president of Iceland and scientists researching hydrogen fuel in Iceland: <http://www.youtube.com/watch?v=U79CWDtdZOA&NR=1> (18 minutes)

"Hydrogen Hopes", the complete PBS show from which the 3-minute excerpt above was taken: <http://www.youtube.com/watch?v=THGarJkZJgk&feature=related> (26 minutes)

More sites on hydrogen storage

A paper that describes many of the materials currently being researched for hydrogen storage can be found here: http://nano-ram.org/files/NANOMATERIALS_FOR_HYDROGEN_STORAGE_-_REVISED.pdf

See the PBS video "Hydrogen Hopes" <http://www.youtube.com/watch?v=THGarJkZJgk&feature=related> for more information on hydrogen storage.

One of PBS's NOVA 53-minute-long videos in the "Making Stuff" series, "Making Stuff: Cleaner", focuses on alternate sources of energy. One piece (at 15:40) discusses hydrogen fuel cell cars and then (at 17:55) talks about the need to store hydrogen and discusses research using chicken feathers as a means to store hydrogen. (<http://video.pbs.org/video/1768954299>.)

More sites on alternate energy source fuel cells

The DOE hosts a web page listing and briefly describing 6 different types of fuel cells. The page includes drawings of most of the fuel cells. View the page at http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc_types.html. At the bottom of this page is a tab to click that takes you to a one-page comparison of the different cells, including output, applications and advantages of each.

Ben Wiens, a Canadian inventor who won the 2010 non-European award of the European Invention Awards, has a very informative website that details the six primary fuel cell types, including the PEFC, the Polymer Electrolyte Fuel Cell (the cell described in this *ChemMatters* article). His thorough coverage includes the pros and cons of each fuel cell type and gives his view of the future of each. You can find his material at www.benwiens.com/energy4.html.

If you are interested in learning how microbial fuel cells work, The Ohio State University has a “Microbial Fuel Cell Learning Center in the Classroom” at <http://digitalunion.osu.edu/r2/summer07/nskrinak/class.html>. It contains both student and teacher materials. You can build your own classroom microbial fuel cell that uses cow rumen as the fuel source. The schematic is provided, as are the part numbers, which you can purchase from an outside company (recommended).

Here is another site, Science in School, that provides material for classroom use of a microbial fuel cell, but it requires purchase of the fuel cell: <http://www.scienceinschool.org/2010/issue14/fuelcell>.

Here’s a set of directions for building a microbial fuel cell—this one from Jell-O, dry yeast and carbon paper. It’s from the “Instructables” web site, so it may be a little less scientific than the one above from Ohio State, but you don’t have to buy the fuel cell, either. Check it out at <http://www.instructables.com/id/Lime-Jello-Yeast-and-Carbon-Paper-Fuel-Cell/>.

About.com provides diagrams explaining how each of 5 different types of fuel cells work. The cells include PEM (proton exchange membrane), MCFC (molten carbonate fuel cell), PAFC (phosphoric acid fuel cell), SOFC, (solid oxide fuel cell), and AFC (alkaline fuel cell). View them at <http://alternativefuels.about.com/od/researchdevelopment/iq/Fuel-Cell-Diagrams/PEM-Fuel-Cell.htm>.

The English!Info website provides a page on fuel cells that shows a table of the many fuel cell types and specific information about each one, including the status of development of each, and myriad other links to information about fuel cells. (<http://english.turkcebilgi.com/Fuel+cells>)

More sites on other uses for fuel cells

Submarines can be powered by fuel cells. See a short article in *Gizmag* about these German subs at <http://www.gizmag.com/go/3434/>

For a closer, detailed look at how hydrogen fuel cells are used by NASA, see “Fuel Cell Power Plants on the Space Shuttle Orbiter” at About.com, http://inventors.about.com/od/fstartinventions/a/fuel_cell_plant.htm.

General Web References (Web information not solely related to article topic)

The “Related Sites” page of the Schatz Energy Research Center (SERC) web page from Humboldt State University at http://www.schatzlab.org/related_sites.html contains many links to other sites for information on topics including “Renewable Energy Education Resources”, “Hydrogen Education Resources”, “Energy Efficiency”, “Clean Energy News” and “Other Resources”.

More Web sites on Teacher Information and Lesson Plans (sites geared specifically to teachers)

The National Energy Education Development Project, Project NEED, has an extensive booklet of activities focusing on hydrogen, the hydrogen economy and the hydrogen fuel cell, called "H₂ Educate". The booklet involves multi-disciplinary activities. Both student and teacher versions of the booklet are available. The student version (28 pages) contains an electrolysis experiment, a fuel cell simulation, reproducible handouts and background material for the student. The teacher version (32 pages) contains correlations to National Science Education Standards (grades 5-8 and 9-12), materials, preparation, how-to instructions for activities, a game, assessments, rubrics and reproducible handouts to provide students. One of the activities involves a fuel cell car kit, which would need to be purchased. This activity could be skipped, or replaced with other materials about the fuel cell car. This is a very complete package.

"Student Guide": <http://www.need.org/needpdf/H2%20Educate%20Student%20Guide.pdf>.

"Teacher Guide": <http://www.need.org/needpdf/H2%20Educate%20Teacher%20Guide.pdf>.

Check out the "Fuel Cells 2000" website education web page at <http://www.fuelcells.org/ced/education.html#stud> for a long list of links to student activities and teacher materials.

If you need more general information about major energy sources, consumption, efficiency, conservation, transportation and emerging technologies, see the 2010 "Secondary Energy Infobook", an 80-page booklet produced by NEED, the National Energy Education Development Project. It contains a series of 4-page fact sheets on ten different energy sources. The 14 MB file downloads slowly. Get a copy at <http://www.need.org/needpdf/Secondary%20Energy%20Infobook.pdf>.

NEED also has a series of activities that accompany the Infobook: <http://www.need.org/needpdf/Secondary%20Infobook%20Activities.pdf>. These consist of reproducible games, puzzles and worksheets to reinforce vocabulary, concepts and information contained in the fact sheets. Answers are provided for all student sheets.

A Single Ignition: A Cautionary Tale

Background Information (teacher information)

More on crude oil

Approximately 72 million barrels of crude oil were produced in the world each day in 2010, with about 5.3 million barrels produced daily in the United States. Another 8.4 million barrels were imported daily to the United States. In 2010, there were 137 operating refineries in the United States. Getting the crude oil to these refineries from the well where it has been drilled or from the port receiving imported oil requires hundreds of miles of pipelines throughout the country. And at each refinery (and other key locations throughout the petroleum distribution system) there are storage tanks like the one in the article. These storage tanks are located on tanks farms adjacent to refineries and key pipeline intersections throughout the U.S. In late 2010, approximately 245 million barrels of crude oil were flowing through pipelines in the U.S. or being stored in tanks.

The *Teacher's Guide* to the April, 2007 *ChemMatters* issue contains information about crude oil. The *Teacher's Guide* is available [on line](#).

“A barrel of crude oil contains 42 gallons. The origin of this volume goes back to the early days of crude oil discovery, extraction, and transport in Pennsylvania. Oil drillers used old wine barrels to carry the crude to market, either by wagon or boat. Those barrels originally held 48 gallons of wine, but when the oil men transported the crude by wagon or boat, some oil inevitably leaked out in transport, so the dealers who received the oil at the end of the trip only paid for 42 gallons of oil, to allow for some spillage during the trip. Eventually, oil men only put 42 gallons in the barrel in the first place, hence the 42-gallon barrel.”

More on the chemistry of crude oil

The *Teacher's Guide* to the April, 2007 *ChemMatters* issue (above) also contains this information about crude oil.

Crude oil differs greatly in composition dependent on its place of origin. “Light”, “heavy”, “sweet”, and “sour” are all terms applied to crude oil. Light crude has low viscosity, while heavy crude is very viscous. Sweet crude has low sulfur content, while sour crude contains more sulfur. Colors range from yellow to orange to green to black.

Light, sweet crude is usually the petroleum of choice because it contains larger percentages of the more desirable lower molecular weight hydrocarbons, so it requires less processing (cracking), and because it contains less sulfur, so distilling this crude ejects less pollution into the atmosphere.

Geologic conditions in the past help to determine the content of crude. In the Middle East, crude contains more straight chain hydrocarbons, while crude from Nigeria is mainly aromatics and cyclic hydrocarbons. Mexican crude can contain up to 5% sulfur, while Pennsylvania crude contains less than 0.1% sulfur.

As the article states, crude oil is a mixture of dozens of chemical compounds that are made up primarily of carbon and hydrogen. In these compounds, called hydrocarbons, the carbon-hydrogen bonding is covalent in nature. You can preview or review bonding types as students read this article. Each carbon atom has four valence electrons and each hydrogen atom has one. The simplest of the hydrocarbons, therefore, is methane, CH₄. Since carbon atoms can combine with other carbon atoms, a series of possible hydrocarbons can be formed. If we combine two carbon atoms and then add the remaining required hydrogen atoms, the compound will contain two carbons and six hydrogens, C₂H₆. Adding a third carbon and the necessary hydrogens to this molecule yields C₃H₈. If we continue this process of adding a carbon and the required hydrogens we can produce a series of compounds with the general formula C_nH_{2n+2}.

Formula	Name
C ₂ H ₆	ethane
C ₃ H ₈	propane
C ₄ H ₁₀	n-butane
	iso-butane
C ₅ H ₁₂	n-pentane
	iso-pentane
•	
•	
•	
C _n H _{2n+2}	

Note that beginning with butane, each of the hydrocarbons exists in more than one isomeric form. You can review isomers with your students here too. Isomers have very similar but not identical properties. The reason that is important in this context is that the boiling point is an important property for each of the components of crude oil, and isomers have slightly different boiling points. For example, n-butane boils at -0.5°C, and isobutane boils at -11.7°C.

There are two reasons that boiling points are important for the purposes of this article. First, crude oil is refined by fractional distillation, as the article says. In this process the crude oil is heated so that each component boils out of the mixture. Since each liquid in the mixture has its own unique boiling point, each liquid boils at a different temperature. In the fractionating towers in which the process takes place, each liquid component can be recovered by cooling. The components are then re-mixed or further processed to produce commercial products like gasoline, heating oil, lubricating oil, jet fuel, etc. Even though the hydrocarbon compounds listed above are the components of crude oil, they are usually thought of in boiling point “bands” or ranges in the crude oil refining process (see table below).

Fraction	No. Carbons	b.p. (°C)	% of Crude
Gases	1-4	< 0	2
Light naphtha	5-7	27-93	34
Heavy naphtha	6-10	93-177	
Kerosene	10-15	177-293	11
Light gas oil	13-18	204-343	21
Heavy gas oil	16-40	343-565	31
Residue	>40	565	

The second reason that boiling points are important in an article about an explosion in a crude oil storage tank is that the boiling behavior of liquids is related to a number of other properties of liquids that are important in understanding their explosive behavior—vapor pressure, volatility, flash point and ignition temperature. These properties will be discussed in the next section.

More on combustion of crude oil

There were approximately 480 storage tank fire incidents world-wide between 1951 and 2003. Most incidents occurred at refineries. Most were caused by lightning but other causes include corrosion, human intervention and improper maintenance.

The article reminds us that in order for combustion to occur, there must be fuel (in our case the hydrocarbons in the tank), oxygen (air) and a temperature high enough to ignite the fuel (a static spark, a cigarette, etc). So inside the storage tank in Mississippi, some of the component liquids vaporized, mixed with the air in the tank, and when a match or cigarette was dropped into the tank, the vapors burned rapidly leading to an explosion. In this section we will describe the factors that lead to the crude oil burning and in the next section we will discuss explosions.

So, what are the properties of the crude oil in the tank that contributed to combustion? As noted in the article, crude oil itself does not burn readily. In fact, liquids do not burn. Many of the hydrocarbons that make up the crude oil mixture are volatile liquids which means they vaporize easily. It is the vapor form of the liquid that is flammable. The property of liquids that determines volatility is vapor pressure, and vapor pressure is linked to boiling point. This relationship, described in more detail below, is the reason the article emphasizes the boiling points of the hydrocarbons in crude oil. Vapor pressure and boiling point help us understand the paragraph in the article that emphasizes that it was the vapors in the tank, not the crude oil liquid that was ignited.

As the article notes, boiling point is an important property, especially for liquids like the hydrocarbons in crude oil. Like all matter, the molecules in a liquid are in constant random motion. Some molecules move faster, others slower. When faster moving molecules overcome the intermolecular forces in the liquid phase, these molecules become part of a vapor above the liquid. The liquid is vaporizing, that is, molecules are leaving the surface of the liquid and becoming a vapor. The vapor forming above a liquid exerts pressure on the liquid and this is called the vapor pressure of the liquid. The higher the vapor pressure of a liquid, the easier it vaporizes. And the easier a liquid becomes a vapor, the lower its boiling point. A liquid boils when its vapor pressure equals the pressure of the atmosphere above it. At the boiling point, the molecules in a liquid are able to overcome the intermolecular forces holding them together and vapor forms within the liquid. So liquids with lower boiling points evaporate easily. Consider the boiling points of some crude oil hydrocarbons:

Name	Formula	Boiling Point (°C)
pentane	C ₅ H ₁₂	36
hexane	C ₆ H ₁₄	69
heptane	C ₇ H ₁₆	98
octane	C ₈ H ₁₈	125
nonane	C ₉ H ₂₀	151
decane	C ₁₀ H ₂₂	174
undecane	C ₁₁ H ₂₄	196

Temperature affects vapor pressure and the rate of evaporation; the higher the temperature, the higher the rate of evaporation, and the higher the temperature, the higher the vapor pressure (because more evaporation takes place, more molecules are in the vapor phase, causing more collisions and more pressure). So, inside that storage tank in Mississippi in late October where the daily high temperature is about 80°F, at least pentane and hexane would evaporate easily, forming a mixture with the air in the tank.

A word or two about intermolecular attractions here: you might wish to delve a bit deeper into these attractions as a way to help students understand the forces at work during evaporation of the hydrocarbons in the storage tank. Molecules in liquids—like those in the storage tank—are held together by relatively weak intermolecular forces. Collectively these forces are known as van der Waals forces, but there are three different types of forces here—London dispersion forces, dipole-dipole interactions and hydrogen bonding. It is these forces that must be overcome in order for a liquid to vaporize.

London dispersion forces are the result of temporary charges that arise in non-polar molecules as a result of the shifting shape of the electron cloud in the molecules. These forces are at work in both polar and nonpolar molecules. London forces increase with increasing number of electrons in a molecule and so London forces increase with molar mass. So heptane molecules have stronger London forces than, say, pentane molecules. That would suggest that pentane would vaporize more easily than heptane and would also boil at a lower temperature. (See data, above, to confirm.) London dispersion forces are the major intermolecular attractions in alkane molecules. It is worth noting that in the branched chain alkane isomers, the London dispersion forces are slightly less than in the straight chain form because branched chain molecules cannot come as close to each other as the straight chain forms. The dispersion forces, therefore, have less effect. So, for example, n-pentane has a lower vapor pressure than its isomer 2,2-dimethylpropane (and so a higher boiling point)

Dipole-dipole interactions are electrostatic forces created by the partial positive and negative charges within neighboring molecules that exhibit some degree of polarity. When added to the effect of London forces, dipole interactions increase the attraction between molecules of a liquid and make them less easily vaporized. These are of minimal importance when discussing crude oil components because these molecules are essentially nonpolar.

Hydrogen bonds are attractions between a polar covalently bonded hydrogen atom in one molecule and an electronegative atom with one (or more) nonbonding pair(s) of valence electrons in a neighboring molecule. Hydrogen bonding occurs most often in covalently bonded molecules involving nitrogen, oxygen, fluorine and chlorine. Since the components of crude oil are composed almost exclusively of hydrogen and carbon, hydrogen bonding is not an issue.

So, in the storage tank at the time of the explosion were residual liquid petroleum, several hydrocarbons (in vapor form) and the air that got into the tank, as the article suggests, by means of a fractured seam or a hole created by rusting of the tank. What, then, are the factors that must exist in order for the mixture to burn?

As mentioned in the article, it is not the liquid hydrocarbon that burns, but the vapor produced by the liquid. So were the conditions in the tank conducive to producing vapor from the crude oil components? Here we need to consider a property called flashpoint. Flashpoint is the lowest temperature at which a liquid produces a sufficient concentration of vapor above it so

that it forms an ignitable mixture with air. The lower the flashpoint, the easier it is for vapor to form above the liquid. Flashpoints of six hydrocarbons that would have been in the Mississippi tank are shown here:

Substance	Flash Point (°C)
n-pentane	-49
n-hexane	-23
n-heptane	-3
n-octane	14
n-nonane	31
n-decane	46

As mentioned above, the average daily high temperature in that part of Mississippi in late October is 80°F (about 27°C) so at least pentane, hexane, heptane and octane would have reached their flash point during the day.

The next question, as the article states, is whether there would have been *enough* flammable vapor in the tank to sustain combustion. The property that measures sufficient flammable vapor above a liquid is called its flammable range. This is the range of concentrations of vapor in air of a flammable substance necessary for combustion to occur. Also, there must be an ignition source available for combustion to occur. Consider the flammable range of the six hydrocarbons from above:

Substance	Flammable Range (% at 25°C)
n-pentane	1.4-7.8
n-hexane	1.2-7.4
n-heptane	1.1-6.7
n-octane	0.95-6.5
n-nonane	0.85-6.1
n-decane	0.75-5.6

Because the tank exploded we can be sure that the hydrocarbons evaporated in sufficient quantities to reach their flammable ranges.

Flashpoint and flammable range must be combined with knowledge of ignition temperatures in order to understand the mechanism of combustion. Listed below are the same hydrocarbon's ignition temperatures and the temperatures of some common sources of ignition (plus the Bunsen burner for classroom reference).

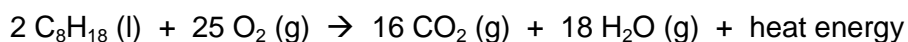
Ignition Temperatures		Common Ignition Sources	
<u>Substance</u>	<u>Ign. Temp. (°C)</u>	<u>Substance</u>	<u>Ign. Temp. (°C)</u>
n-pentane	260	Lighted cigarette	288
n-hexane	225	Lighted match	800
n-heptane	225	Candle flame	600
n-octane	220	Electric stove	550
n-nonane	205	Fluorescent light	80
n-decane	210	Incandescent light	100
		Electric arc	1093
		Bunsen burner	1570
		Lightning	30000

So, if a lighted cigarette was dropped into the tank at 288 °C, that temperature would have been sufficient to ignite all of the listed hydrocarbons. Combustion would have occurred. In the next section we will consider why the tank exploded.

More on the chemistry of explosions

During its investigation of the Carnes explosion described in the article, the Chemical Safety Board found that "...similar accidents have occurred at rural oil and gas sites in states across the country, killing and injuring children, teenagers, and young adults. The CSB found 26 similar accidents at such sites resulting in 44 fatalities among teenagers and young adults between 1983 and 2010. The Board found that since 2003 alone, oil and gas site explosions caused 16 deaths to members of the public, all of whom were under 25 years of age. As a result of these findings the CSB convened a task force to look into state and federal rules and regulations governing the safety and security of oil and gas production sites. The task force will release its final case study in early 2011."

It might be helpful to explain the difference between rapid combustion and an explosion. The article illustrates the combustion process by showing the reaction for the combustion of octane:



Combustion involves the combination of a fuel (octane in this example) with oxygen (from air) to produce, in the case of complete combustion, carbon dioxide and water. Energy in the form of heat and perhaps light is also produced. If the process takes place in an open system, the gaseous products and the heat energy simply dissipate into the environment. It is when combustion takes place in a closed system that an explosion is possible.

In general an explosion is the result of a gas being produced at a high pressure. The gas may be produced by combustion taking place in a confined volume, like the storage tank, or within a firecracker, for example. Or the gas may be produced by physical or mechanical means, as in heating water in a closed container like a steam boiler or heating an aerosol can in a fire. Regardless of the cause it is the production of gas and the resulting increase in pressure inside the container that distinguish an explosion from standard combustion.

The article says that there are two factors that contribute to combustion becoming explosive—the production of gases in the combustion process and their expansion due to the heat produced. As an example of combustion producing a greater volume of gases refer to the equation for the combustion of octane, above. In this reaction there are 25 moles of gaseous particles on the reactant side of the equation and 34 moles of gas on the products side. The resulting increase in moles will, in fact, cause an increase in pressure in a closed system like the storage tank. The pressure ratio is 1.36:1 (34:25) in the above example.

The other explosion factor is the increase in pressure as a result of heating gases in a closed container. All combustion reactions are exothermic. The heat produced as the hydrocarbons burned in the tank raised the temperature of the gases. Ordinarily we would expect the volume of the gases to increase, but the tank has a fixed volume. As a result, the pressure inside the tank increases instead, since the increased molecular motion results in greater numbers and force of collisions. This pressure increase might be as much as eight times the ambient pressure, according to explosion experts. We should note that an 8:1 pressure increase as a result of hydrocarbons burning is a much greater effect than the increase in

pressure due to the increase in the number of molecules (only 1.36:1). And if we note that many storage tanks are designed for pressure increases of only about 4:1, there is no doubt that an explosion will result.

The *Teacher's Guide* to the December, 2010 *ChemMatters* issue contained additional information about explosions. (The *Teacher's Guide* is available from ACS at http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_SUPERARTICLE&node_id=354&use_sec=false&sec_url_var=region1&uuid=c5ec7b43-f469-4c96-8a42-fddc13460d2b.)

Most rapid chemical reactions, like combustion and explosions, involve solids and gases (e.g., dust explosions with solid dust and air), liquids and gases (e.g., liquid fuels burning in air), or gases and gases (e.g., methane, ethane or propane burning in air). Gases are involved in all explosions, since gases are individual atoms or molecules and can react upon impact with other molecules. Solids and liquids involved in explosions must, of necessity, exist as extremely tiny particles—dust or powder in the case of solids, and very tiny droplets or even vapor for liquids. These very tiny particles can then react quickly with gas particles to form new compounds, usually gases, with the subsequent release of large amounts of energy. All combustion or explosive reactions are exothermic.

Typically, molecules of gaseous products, like CO₂ and H₂O, are very stable molecules, while the reactant molecules (the fuel) contain much more stored chemical energy. As the bonds of the fuel molecules are broken and new bonds form in the production of the more stable gaseous products, energy is released from the reacting system. It is this energy that drives molecules to higher and higher velocities, producing greater pressures that eventually result in the explosion. (TG, page 32)

It is not only the large increase in the number of particles of gas (as new gases are produced in combustion) that creates the pressure inside the [tank] necessary for an explosion; the gases are also exposed to extreme heat inside the [tank] as the combustion reaction occurs. This huge increase in temperature causes the gas molecules to increase their speed, increasing the pressure inside the [tank] even more. This “double whammy” results in the explosion of the [tank]. This is a great example of Amontons' Law (sometimes mistakenly referred to as Gay-Lussac's Law), which states that as temperature increases, gas pressure increases directly, providing amount and volume are constant. The volume remains constant inside the [tank] until the explosion occurs, at which time the volume increases explosively. (Now we can apply Charles' Law of temperature and volume varying directly; since the temperature increased and the pressure can now be “let out”—to atmospheric pressure, the volume will increase proportionally to the temperature increase. (TG, page 34)

So, to summarize, two things have to happen for an explosion to occur, remembering that the explosion in the article is the result of combustion. Also remember that an explosion is the result of combustion taking place in a confined space, a container with a fixed volume. First, there is an increase in the number of gas molecules as a result of the combustion and this serves to increase the pressure inside the container. Second, the combustion produces heat which raises the temperature of the molecules in the container, which, in turn, increases

the pressure. The explosion is the result of the pressure in the container rupturing the container instantaneously.

More on oil tanks

Above ground oil storage tanks can be found at multiple locations along the supply chain. There are about 500,000 of these tanks in the U.S. with capacities ranging from 1000 barrels to 120,000 barrels. In 2010, the total volume of stored oil in any given month was about 240 million barrels of crude. By far the greatest storage capacity is along the Gulf Coast states, the setting for this article.

Tanks are usually made of steel with welded construction. Tanks like the one in the article are typically found at the ends and at key points along crude oil pipelines, at marine loading and unloading terminals and at refinery sites. A site with many tanks is often referred to as a tank farm. At any of these locations there might be hundreds of thousands of barrels of oil in storage at any time, and a fire at one of these locations could prove disastrous.

The underlying principle in all tank design is safety. There are several ways in which oil tanks like the one in the article are designed. Some tanks are pressurized and other are not (these are called “atmospheric tanks”). Most of the tanks in the U.S. are not pressurized. There are hundreds of federal, state, industry and company regulations governing oil storage tanks and their design.

The vertical tanks like the one in the article have several features aimed at preventing fires and explosions. Some have cone shaped roofs that allows vapors from the crude oil to collect. The only gases in the head space are crude oil vapors. There is no air so combustion cannot take place. The problem with this design is when the tanks are being drained. As the crude is drained out a partial vacuum is created in the sealed tank, and if there are any air leaks there is a danger of fire. In some tanks of this design a flexible membrane floats on the oil and covers the surface, preventing vapors from forming. These cone roof tanks also usually have a vapor recovery system built in that systematically removes crude oil vapors. These tanks often have double wall bottoms to prevent leakage and also have corrosion protection systems installed to prevent rusting.

Other vertical tanks have floating roofs to minimize vapor formation. If any head space does form it is vapor-rich and well outside the flammable range. The edge of the floating roof has a double seal to keep vapors from escaping into the atmosphere while at the same time allowing the roof to rise and fall with the crude oil levels in the tank.

In many cases individual tanks are clustered together in tanks farms. Individual tanks are required to be surrounded by berms, or walls made of earth or clay or concrete. These are designed to prevent both spills and fire from traveling from one tank in the farm to others.

Fires in tank farms are fought by the usual methods: the fuel can be removed by closing off the system of valves that control the flow of oil in these installations or by covering the liquid with foam to prevent vapors from forming; foam can also cover the crude so as to prevent exposure to air and the oxygen the combustion requires; nitrogen is also sometimes pumped into tanks to replace air; water (with its high heat capacity) might be used to lower the temperature of the liquid below the ignition temperature.

More on the Chemical Safety Board

According to its web site, the Chemical Safety Board “is an independent federal agency charged with investigating industrial chemical accidents. Headquartered in Washington, DC, the agency's board members are appointed by the President and confirmed by the Senate.

“The CSB conducts root cause investigations of chemical accidents at fixed industrial facilities. Root causes are usually deficiencies in safety management systems, but can be any factor that would have prevented the accident if that factor had not occurred. Other accident causes often involve equipment failures, human errors, unforeseen chemical reactions or other hazards. The agency does not issue fines or citations, but does make recommendations to plants, regulatory agencies such as the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA), industry organizations, and labor groups. Congress designed the CSB to be non-regulatory and independent of other agencies so that its investigations might, where appropriate, review the effectiveness of regulations and regulatory enforcement.

“The CSB investigative staff includes chemical and mechanical engineers, industrial safety experts, and other specialists with experience in the private and public sectors. Many investigators have years of chemical industry experience.”

Further, the web site says that “The U.S. Chemical Safety Board is authorized by the Clean Air Act Amendments of 1990 and became operational in January 1998. The Senate legislative history states: “The principal role of the new chemical safety board is to investigate accidents to determine the conditions and circumstances which led up to the event and to identify the cause or causes so that similar events might be prevented.” Congress gave the CSB a unique statutory mission and provided in law that no other agency or executive branch official may direct the activities of the Board. Following the successful model of the National Transportation Safety Board and the Department of Transportation, Congress directed that the CSB's investigative function be completely independent of the rulemaking, inspection, and enforcement authorities of EPA and OSHA. Congress recognized that Board investigations would identify chemical hazards that were not addressed by those agencies.”

Connections to Chemistry Concepts (for correlation to course curriculum)

1. **Combustion**—The chemical reaction that leads to the explosion in this article is combustion. This presents a chance to review this type of reaction as well as the other basic types of reactions covered in most chemistry texts.
2. **Organic chemistry**—The compounds that make up crude oil are organic compounds. You may or may not cover these in your courses, but if you do, the article provides a nice application to a very important topic.
3. **Isomers**—Although not mentioned in the article, the crude oil components do exist in isomeric forms and you can, if you wish, use them as examples to discuss isomers in general.
4. **Safety**—This article represents an EXCELLENT chance for you to review safety concerns and to show students that safety is NOT something confined to your high school classroom. It is a major issue in the chemical industry.
5. **Gas Laws**—The gas laws are very important in understanding the way in which explosions occur. This article can give students a preview or review of the gas laws.

6. **Change of phase**—An important factor in the explosion of the tank was the fact that the components in the liquid crude evaporated in sufficient quantity to burn. You can review the relationships between vapor pressure, evaporation and boiling point using this article.
7. **Intermolecular Forces**—Although not a point of emphasis in the article, knowledge of intermolecular forces will help students understand the evaporation of crude oil.

Possible Student Misconceptions (to aid teacher in addressing misconceptions)

1. **“Liquids are flammable.”** *The article notes that liquid are not flammable. In order for a liquid to burn the reaction would have to occur at the liquid surface, which exposes a very small number of the liquid molecules to needed oxygen. However, when the liquid vaporizes all of the gas molecules are exposed to oxygen molecules, allowing the reaction to proceed easily. See “More on combustion of crude oil” for details.*
2. **“Petroleum is a single, pure substance.”** *Petroleum is a mixture of many different carbon-containing compounds which are separated out from each other using fractional distillation.*
3. **“Combustion and explosions are the same thing.”** *Maybe, but not necessarily. The explosion described in the article is the result of combustion, but combustion can take place in an open atmosphere without an explosion occurring. In fact, most combustion reactions do not involve an explosion. On the other hand it is possible for an explosion to occur without combustion occurring. For example, a steam boiler (in which only a physical change is taking place) can explode.*

Anticipating Student Questions (answers to questions students might ask in class)

1. **“The article discusses boiling, vaporizing and distilling. Are they the same thing?”** *No, they are not the same, but they are related. The terms “vaporizing” and “boiling” are names for the liquid-to-gas change of phase. When a liquid vaporizes it goes from the liquid phase to the gas phase. This can happen in one of two ways—evaporation or boiling. A liquid evaporates when molecules of the liquid are moving rapidly enough to overcome the forces of attraction in the liquid. In evaporation molecules escape the liquid from its surface, and the process can take place at any temperature. If we heat the liquid (raise its temperature) it will eventually reach its boiling point and the liquid will change phase to a gas. The boiling point of a liquid is the temperature at which its vapor pressure equals atmospheric pressure. Distilling is a term used to denote a process in which a mixture with a liquid component is heated to boiling in order to separate the components. In the case of crude oil, all the components are liquids, so the process is called fractional distillation.*
2. **“The article says that gasoline is one component of crude oil. Then it says that gasoline is a mixture. Please explain.”** *Perhaps the article should have said that the hydrocarbons that eventually make up gasoline are components of crude oil. Crude oil is refined by heating it so that each liquid in the mixture boils off separately. These liquids are collected and then remixed to produce products we buy—like gasoline. See “More on the chemistry of crude oil” for additional details.*
3. **“In an explosion, is it mostly the production of gas products in the reaction or the increase in temperature that creates the explosion?”** *The increase in temperature has the greater effect. If you compare the number of moles of reactant gases and the number of*

moles of produced gases in a combustion equation, the ratio is less than 1:2. However, the pressure increase as a result of the temperature change during combustion might be as high as 1:8 because the pressure increase is directly proportional to the temperature according to Amontons' Law.

In-class Activities (lesson ideas, including labs & demonstrations)

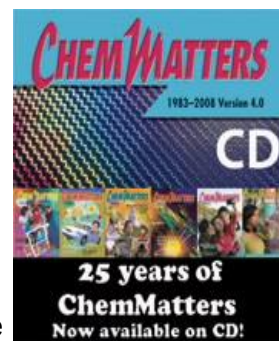
1. SciNetLinks from AAAS has a series of lessons on the chemistry of crude oil and lists other resources too. <http://www.sciencenetlinks.com/lessons.php?BenchmarkID=4&DocID=469>
2. This site has detailed background and procedure for performing a distillation of Cherry Coke®: <http://assets.chemheritage.org/EducationalServices/pharm/chemo/activity/sep.htm>. Here is another site that provides a very complete fractional distillation experiment for students. You might want to check out the safety of the organic liquids used in the distillation before you do the experiment with students. (<http://swc2.hccs.edu/pahlavan/2423L7.pdf>)
3. Students can make hydrocarbon models using commercially available model kits if you have them or you can make molecular models using gum drops and toothpicks or work with them on line here: <http://www.nyu.edu/pages/mathmol/library/hydrocarbons/>.
4. To demonstrate the idea that the rate of combustion depends on mixing the fuel and oxygen in predictable proportions you can do this series of demonstrations with hydrogen balloons. <http://www.practicalchemistry.org/experiments/exploding-balloons,47,EX.html> or this experiment <http://www.scribd.com/doc/18946589/Blast-Off-Demo-for-Chemistry>
5. Here's a micro-scale version of fractional distillation <http://chemmovies.unl.edu/chemistry/beckerdemos/BD049.html>
6. Do a heat of combustion lab using several hydrocarbon fuels, instead of just measuring the heat of combustion of a burning candle. For example, use propane, butane, and kerosene as fuels. Have students measure heats, calculate heats of combustion and compare them as fuels – on a heat per gram basis and a heat per mole basis
7. Observing the necessary safety precautions, you can perform the “hydrogen rocket” Pringles can demonstration to illustrate the concept of flammable limits. This video uses methane gas in place of hydrogen, but explains the process well. This version of the video provides a brief written explanation: <http://www.stevespanglerscience.com/experiment/exploding-pringles-can> . If you have not been trained to do this demonstration, do not attempt it. Rely on the video.

Out-of-class Activities and Projects (student research, class projects)

1. Students can research oil tank explosions listed on this web site and prepare a report: http://www.google.com/search?source=ig&hl=en&rlz=1G1TSNB_ENUS387&=&q=history+oil+tank+explosions&btnG=Google+Search&aq=f&oq=#q=history+oil+tank+explosion&hl=en&sa=G&rlz=1G1TSNB_ENUS387&tbs=tl:1,tl_num:50&prmd=ivns&ei=EYhFTa3tKYSs8AbMhKydAg&ved=0ClOBEMsBKAM&fp=767f3a0459a2a284.
2. Students can research the various components of crude oil to determine molecular formulas of these hydrocarbons. It would be a good introduction to organic chemistry for those students who have had none
3. Students can watch videos of oil tank fires on the web and make observations of each. They can then write a brief paragraph comparing the explosions. (See “More sites on other fires and explosions,” below.)

References (non-Web-based information sources)

The reference below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site: <http://www.acs.org/chemmatters>. (Part way down the website screen, click on the *ChemMatters* CD icon like the one shown here at the right.)



Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

Baxter, R., Gold in Your Tank. *ChemMatters*, April, 2007, pp 8-10. The author explains the extraction, refining and enhancement of crude oil.

Web sites for Additional Information (Web-based information sources)

More sites the Carnes, MS, explosion

For a video of the Carnes, MS, story described in the article see http://www.csb.gov/videoroom/detail.aspx?vid=43&F=0&CID=1&pg=1&F_All=y. The DVD can be ordered from the Chemical Safety Board at <http://www.csb.gov/videoroom/videorequest.aspx>.

You can read the *New York Times* article on the incident here: http://www.nytimes.com/2010/04/13/us/13tank.html?_r=2. (You must first register.)

More sites on other fires and explosions

The web has many videos of fires and explosions in oil tanks. A sampling:

Texas City, TX, 2009 <http://www.youtube.com/watch?v=TN0Nx92dplc>

Woodward, OK, 2008 <http://www.youtube.com/watch?v=b5c7va7G6tl&feature=related>

Fredonia, KS, 2009 <http://www.youtube.com/watch?v=QVU2r7dR8LU&feature=related>

George, TX, <http://www.youtube.com/watch?v=L5clQA8qeJM&feature=related>

Emerson, AK, 2010 http://www.youtube.com/watch?v=QtT_RRhvmLg&feature=related

Greensboro, NC, <http://www.youtube.com/watch?v=oAsBscxpKks&feature=related>

Lamesa, TX, 2009 <http://www.youtube.com/watch?v=6qcrwNM74sg&feature=related>

This video is shot in slow motion.

More sites on organic chemistry (including hydrocarbons and isomers)

For an online summary of organic chemistry with an emphasis on hydrocarbons, see <http://www.krysstal.com/organic.html>.

More sites on oil production

More on the basics of crude oil production and refining can be found here: http://tonto.eia.doe.gov/kids/energy.cfm?page=oil_home#tab2.

For a document that provides detailed information about the composition of crude oil, see http://www.epa.gov/region6/6en/xp/longhorn_nepa_documents/lppapp6a.pdf.

More sites on oil storage tank safety

This site provides many industry standards for tank safety: [http://www.ifc.org/ifcext/enviro.nsf/AttachmentsByTitle/gui_EHSGuidelines2007_CrudeOil/\\$FILE/Final+-+Crude+Oil+and+Petroleum+Product+Terminals.pdf](http://www.ifc.org/ifcext/enviro.nsf/AttachmentsByTitle/gui_EHSGuidelines2007_CrudeOil/$FILE/Final+-+Crude+Oil+and+Petroleum+Product+Terminals.pdf).

For a detailed study of tank storage fires and explosions see <http://www.firedirect.net/Technical/StorageTankFiresStudy.pdf>.

This online book provides extensive details on fighting oil storage tank fires: http://books.google.com/books?id=MWjcgamm2QC&pg=PA194&lpg=PA194&dq=%22crude+oil+storage+tanks%22+explosion&source=bl&ots=By713u4nH0&sig=jFht6fJb8euFlhvSdijs6OzZMSk&hl=en&ei=ODsVTdHJFsKB8qaW4_HZDQ&sa=X&oi=book_result&ct=result&resnum=8&ved=0CEwQ6AEwBw#v=onepage&q=%22crude%20oil%20storage%20tanks%22%20explosion&f=false.

Sweet but Good For You?

Background Information (teacher information)

More on field corn

Three major types of corn are grown in the United States: field corn (also called grain corn), sweet corn, and popcorn. When students think of corn, sweet corn and popcorn probably come to mind first rather than field corn, the type discussed in the Brownlee article. Less than 1 percent of the U.S. corn crop is sweet corn, which finds its way to our plates as canned and frozen corn, and fresh corn on the cob. The majority of the U.S. corn crop is field corn, even though it is not primarily grown for humans to eat directly as kernels. The USDA's National Agricultural Statistics Service reports that in 2010, U.S. corn production was 12.4 billion bushels. ([http://www.nass.usda.gov/Charts and Maps/graphics/cornprod.pdf](http://www.nass.usda.gov/Charts_and_Maps/graphics/cornprod.pdf)) The National Corn Growers Association shows a breakdown of the uses of the field corn supply (http://www.ncga.com/files/pdf/TaleofTwoCorns_1.2011.pdf):

37% is used as feed for livestock such as beef, pork or poultry

34% is used for ethanol production. Besides the ethanol this produces, this corn also will result in approximately 1.5 billion bushels of distiller's grains to be used as livestock feed.

13% is exported to other countries. The top five countries to which the United States exports corn are Japan, Mexico, South Korea, Taiwan and Egypt.

10% of the corn goes to other food, seed and industrial uses. Field corn is a source of corn cereal, corn starch, corn oil and corn syrup. Hundreds of other products are also derived from corn, such as certain plastic packaging and even fabrics.

6% of the total corn supply is carried over as a surplus for the next year.

There are also variations among types of corn. The National Corn Handbook (<http://corn.agronomy.wisc.edu/Management/pdfs/NCH10.pdf>) states: "Corn variation may be artificially defined according to kernel type as follows: dent, flint, flour, sweet, pop and pod corn. Except for pod corn, these divisions are based on the quality, quantity and pattern of endosperm composition in the kernel and are not indicative of natural relationships." As the Brownlee article states, the endosperm of the corn kernel contains starch as its key ingredient. The different endosperm compositions of the major types are described in the Handbook as follows: Dent corn is characterized by the presence of corneous, horny endosperm at the sides and back of the kernels, while the central core is a soft, floury endosperm extending to the crown of the endosperm where, upon drying, it collapses to produce a distinct indentation. (This gives it the name "dent".) Flint corns mostly have a thick, hard, glassy or corneous endosperm layer surrounding a small, soft granular center. Very little flint corn is produced and utilized in the U.S. today. Flour corn is one of the oldest types; American Indians ground the soft kernels for flour. Flour corn has soft starch throughout, with practically no hard, vitreous endosperm.

More on carbohydrates

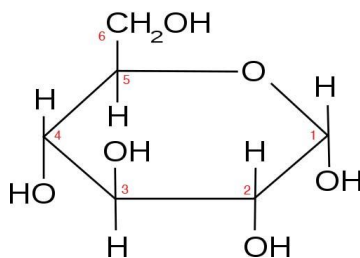
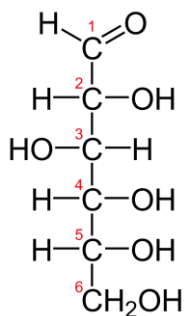
The production of high fructose corn syrup (HFCS) presented in the Brownlee article touches on several carbohydrates as the process used to make HFCS makes its way from the

starch found in field corn, to the glucose that makes up corn syrup, to the fructose that is needed to give HFCS its sweetness. The article also compares the sweetness of HFCS with table sugar, or sucrose. Starch, glucose, fructose, and sucrose are all compounds that are known as carbohydrates. A carbohydrate is made up of the elements carbon, hydrogen, and water. For example, glucose, the body's main fuel source, has the molecular formula $C_6H_{12}O_6$. The history of the use of the name carbohydrate is briefly described in the textbook *Chemistry in the Community* (5th ed.). "When such formulas were first established, chemists noted a 2:1 ratio of hydrogen atoms to oxygen atoms in carbohydrates, the same as in water. They were tempted to write the glucose formula as $C(H_2O)_6$, implying a chemical combination of carbon with six water molecules. Chemists even invented the term 'carbohydrates' (water-containing carbon substances) for glucose and related compounds. Although chemists later determined that carbohydrates contained no water molecules, the name persisted. However, like water, carbohydrate molecules *do* contain O–H bonds in their structures." (p 583)

Rather than being hydrates of carbon, as the name suggests, carbohydrates are polyhydroxy aldehydes or ketones.

Carbohydrates, including those discussed in the article, can be arranged into three main groups:

- Monosaccharides.** The prefix *mono-* suggests that one unit of a saccharide, or sugar, is present. Monosaccharides are referred to as simple sugars. Examples presented in the article are glucose and fructose; several others are galactose, xylose, mannose, and ribose. Monosaccharides may exist in linear structures, but more often are found as cyclic structures. For example, *Chemistry: The Central Science* states about glucose: "Glucose, having both alcohol and aldehyde functional groups and having a reasonably long and flexible backbone, can react with itself to form a six-member-ring structure. Indeed, only a small percentage of the glucose molecules are in the open-chain form in aqueous solution" (p 962). The figures below show linear (left) and ring (right) structures of glucose. When the ring structure forms, the OH group located on the first carbon (labeled with red numbers in the figures below) can either be on the same side or the opposite side of the ring as the OH group located on the second carbon. If these two OH groups are on the same side, it is called α -glucose; if on opposite sides, it is called β -glucose. The α -ring structure of glucose is the one shown below. Fructose is also found in cyclic structures, forming either five- or six-carbon rings.



- Disaccharides** are formed through the linkage of two monosaccharides. Two common disaccharides are sucrose, which is formed from the linkage of the two monosaccharides glucose and fructose, and lactose (milk sugar), which links the monosaccharides galactose and glucose. The two monosaccharides are linked by a glycosidic bond. The condensation reaction between glucose and fructose to form the

products sucrose and water is shown in the article and also as an animation online at <http://nutrition.jbpub.com/resources/animations.cfm?id=6>.

- **Polysaccharides** are polymers made up of many smaller sugar units. Starch, present in corn as a place to store energy, is an example of a polysaccharide. Starch consists of glucose molecules linked together. As the article states, starch molecules come in two varieties: amylose, a long, linear chain of the glucose units, and amylopectin, which has a branched structure of glucose units. The linear chains in amylose are connected with α -1,4-glycosidic linkages. In order to make the branching chains present in amylopectin, there are also α -1,6-linkages present. The “1,4” and “1,6” notation describes which carbon atoms in each glucose participate in the bond; in “1,4” the glycosidic bond links carbon #1 of the first glucose molecule to carbon #4 of the second glucose molecule.

Another common polysaccharide is cellulose, which is also found in plants as a place to store energy. Cellulose is also made up of repeating units of glucose. However, in cellulose, the glucose units are instead connected with β -1,4-glycosidic linkages. α -1,4-glycosidic linkages, such as those found in starch, are able to be digested by animals, including humans, while β -1,4-glycosidic linkages found in cellulose are not, making the starch present in plants, rather than the cellulose, the portion used for human consumption. Herbivores that consume cellulose as the main part of their diet use cellulase, an enzyme that breaks down cellulose into other saccharides that can be digested. Cellulase is produced by grazing animals such as cows, with the aid of the beneficial bacteria that reside in the animal’s digestive tract (http://www.naturalhealthschool.com/6_5.html).

More on corn refining

The corn refining industry has evolved over the years to encompass the production of an ever-growing number of products, including high fructose corn syrup. The Corn Refiners Association offers the webpage “A Brief History of the Corn Refining Industry” (<http://www.corn.org/about-2/history/>). Highlights from that page include:

- Corn refining began in the United States around the time of the civil war with the development of the process for corn starch hydrolysis. Prior to this time, the main sources for starch had been wheat and potatoes. In the mid-1850s, starch was the only product of the corn refining industry, with its largest customer the laundry business.
- The next major event in the history of corn refining was the production of dextrose from corn starch in 1866.
- Other product developments in corn sweeteners took place with the first manufacture of refined corn sugar or anhydrous sugar in 1882.
- The industry also began to realize the value of the non-starch parts of corn. Fiber, germ, and protein from the corn had simply been discarded until manufacturers discovered they could turn them into valuable feed ingredients. The industry then discovered that corn oil could be extracted from the germ. In 1893, the industry began to recover the steepwater used to release the starch in the refining process and condense it to use in feed products.
- The first commercial shipment of high fructose corn syrup took place in 1967.
- The production of ethanol by corn refiners began after World War II, but major quantities were not manufactured until the 1970’s.

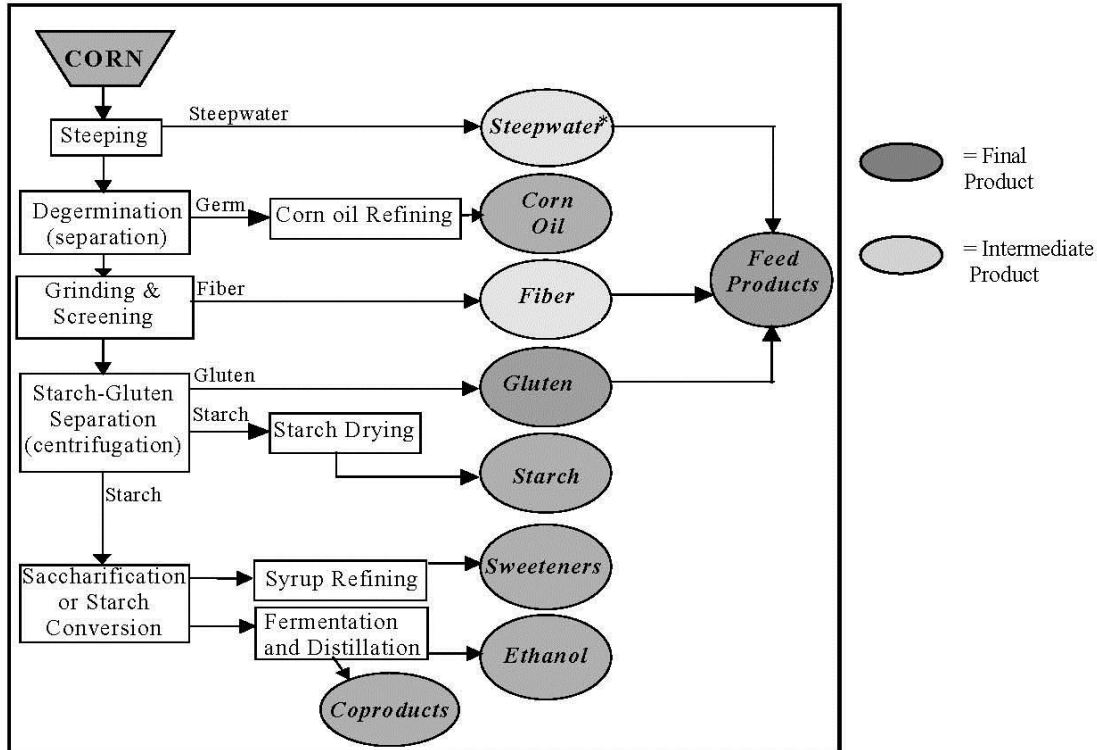
It is interesting to note that originally, the only product of corn refining was starch, and that the remaining parts of the corn were discarded. The refining industry has come to use all parts of the corn since then, even materials that are used in the corn refining process, such as the water that is used to first soak the corn kernels (steepwater). More recent product developments include the use of corn in bioplastics, which was described in the *ChemMatters* article “Plastics Go Green” (Apr. 2010, pp 10–12):

http://portal.acs.org:80/portal/PublicWebSite/education/resources/highschool/chemmatters/archive/CNBP_024548.

There are two main processes involved in corn processing: dry milling and wet milling. The “wet” in wet milling refers to the use of water to soak the corn at the start of the process in order to soften it before separating out its various components. Wet milling is used in the majority of corn processing. The basic steps of wet milling as described by the Corn Refiners Association (<http://www.corn.org/process/>) are:

- **Inspection and cleaning**
This step removes pieces of corn, dust, chaff, and foreign materials. Corn is then conveyed to storage silos until ready for steeping.
- **Steeping**
Kernels are soaked for 30–40 hours in water that is 50 °C. The addition of 0.1 % sulfur dioxide prevents excessive bacterial growth in the warm environment. The mild acidity of the steepwater begins to loosen the gluten bonds within the corn and release the starch. The corn is then coarsely ground to break the germ loose from other components. The water is condensed to capture nutrients in the water for later use.
- **Separation of the germ**
Cyclone separators spin the low density corn germ out of the slurry. The germs are washed to remove any starch left in the mixture. Other processes are used to extract the oil from the germ, with the germ residue saved for an animal feed component.
- **Fine Grinding and Screening**
The corn and water slurry undergoes a second, more thorough, grinding to release the starch and gluten from the fiber in the kernel. The suspension of starch, gluten, and fiber is screened; the screens catch fiber but allow starch and gluten to pass through. The fiber is used for animal feeds.
- **Starch Separation**
Gluten has a low density compared to starch. By passing mill starch (the starch–gluten suspension) through a centrifuge, the gluten is spun out for use in animal feeds. The starch goes through several dilution and washing stages to remove any traces of protein. Some of the starch is dried and marketed as unmodified corn starch, some is modified into specialty starches, but most is converted into corn syrups and glucose.

The flowchart below illustrates various stages in wet milling and the intermediate and final products obtained from each stage. The table below the flowchart shows the rough yields of products that are obtained from a single bushel (56 pounds) of corn that begins this wet milling process.



*Certain grades of steepwater may also be a final product

(from <http://www.energystar.gov/ia/business/industry/LBNL-52307.pdf>, “Energy Efficiency Improvement and Cost Saving Opportunities for the Corn Wet Milling Industry”, figure 4)

Product	Yield (pounds or gallons)
Starch	31-32 pounds
Ethanol ²	(2-3 gallons)
Sweeteners ²	(33 pounds)
Corn gluten feed	11-14 pounds
Corn gluten meal	2-3 pounds
Corn oil	1-2 pounds

¹ 1 bushel = 56 pounds (25.4 kg)

² Ethanol and sweeteners are produced from final starch product

Sources: Shapouri et al., 1995; NCGA, 2002; CRA, 2002.

(from <http://www.energystar.gov/ia/business/industry/LBNL-52307.pdf>, “Energy Efficiency Improvement and Cost Saving Opportunities for the Corn Wet Milling Industry”, table 3)

At the end of the wet milling process, starch can be converted to syrup through treatment with various enzymes. Brownlee describes three enzymes and their action: 1) α -amylase to break the amylose form of starch into glucose; 2) glucoamylase to break up the branch points of the amylopectin form of starch into glucose; and 3) glucose isomerase to convert some of the glucose into fructose. α -amylase breaks down the amylose form of starch by hydrolysis, or the addition of water between glucose units, specifically at α -1,4-glucosidic linkages in the starch. This results in the formation of individual glucose units, along with maltose, which is a disaccharide formed from two units of glucose. Use of the amylase produces about 10–20% glucose; glucoamylase further breaks down the starch, yielding 93–

96% glucose.

(http://chemwiki.ucdavis.edu/Biological_Chemistry/Sweeteners/High_Fructose_Corn_Syrup) It was the development and large-scale use of glucose isomerase (for the final enzymatic step) in the 1950s and 1960s that led to the commercialization of high fructose corn syrups.

Students may have already heard the term amylase if they have previously tried an activity similar to the one found in the Brownlee article, where a cracker or piece of bread is chewed until it tastes sweet, due to the action of amylase in human saliva on starch in the cracker or bread. The amylase used in industry is produced using *Bacillus* spp., a type of bacteria, while the glucoamylase is produced from fungi such as *Aspergillus*. Both are made inexpensively and are added directly to the processing slurry and are used only once. (http://www.academicjournals.org/bmbr/PDF/Pdf2010/Dec/Parker_et_al.pdf) The glucose isomerase used is a synthetic enzyme. While amylase and glucoamylase are directly added to the starch slurry, glucose isomerase, being much more expensive than the other two, is not. "Instead, glucose-isomerase is packed tightly into specially designed columns, and the liquid slurry is passed over it. This allows the enzyme to be used again and again until it eventually loses its activity." (<http://www.thehfcs.com/hfcs-55/>)

Before the discovery of the three enzymes and their potential use in starch processing, starch was treated with acids at high temperatures and pressures. The move to the use of enzymes allowed for processing at lower temperatures and pressures. Since enzymes are specific in their action, it also reduces the occurrence of additional reactions that could produce undesired flavors and colors that would require additional treatment by processors.

The action of α -amylases helping to break down starch also leads to their use in laundry detergents. Starch is commonly found in foods that are likely to find their way onto our clothing as we eat. The book chapter "Enzymes for Technical Applications" (http://www.wiley-vch.de/books/biopoly/pdf_v07/vol07_04.pdf) lists several such foods as chocolate, baby food, barbeque sauce and gravy, and states "Removal of starch from surfaces is also important in providing a whiteness benefit, since it is known that starch can be an attractant for many types of particulate soils." (p 384)

More on high fructose corn syrup

As the Brownlee article states, there are different types of high fructose corn syrup depending on the amount of fructose present. The percentage of fructose in the syrup gives the different corn syrup varieties their name. For example, high fructose corn syrup with 42% fructose and 55% glucose is labeled as high fructose corn syrup 42, or HFCS 42. Other HFCS varieties in common use are HFCS 55 and HFCS 90. HFCS 90 can be used in specialty applications but is more often blended with glucose syrup to produce the other two varieties of HFCS. These two types of syrup (HFCS 42 and HFCS 55) find extensive use in different types of food products.

"Because of its higher fructose content, HFCS-55 is sweeter than sucrose and is thus used extensively as sweetener in soft, juice, and carbonated drinks. HFCS-42 has a mild sweetness and does not mask the natural flavors of food. Thus it is used extensively in canned fruits, sauces, soups, condiments, baked goods, and many other processed foods. It is also used heavily by the dairy industry in yogurt, eggnog, flavored milks, ice cream, and other frozen desserts." (http://www.academicjournals.org/bmbr/PDF/Pdf2010/Dec/Parker_et_al.pdf)

The use of HFCS rather than sucrose as a sweetener in beverages and other foods has certain benefits for manufacturers. HFCS has better stability, particularly in acidic soft drinks, and also has preservative qualities. It is less expensive than sucrose. Manufacturers can also depend on a stable supply of HFCS. Areas where sugar cane is grown can be subject to the chance occurrences of hurricanes, which can affect the eventual crop and its price. As a liquid, HFCS is easier to transport and has a better solubility than sucrose.

Recently the makers of Mountain Dew and Pepsi sodas released the sodas in new “Throwback” versions that use sugar instead of high fructose corn syrup. A bottling plant located in Dublin, Texas, produces Dr. Pepper soda that contains sugar. Many consumers seek out Coke that has been made in Mexico, which also uses sugar, and can often be found in local Hispanic-themed stores.

(http://www.associatedcontent.com/article/1737202/pepsi_throwback_not_the_only_soda_with.html?cat=22) A consumer culture writer for *The New York Times* commented on the cult following that such sodas can obtain. (<http://www.nytimes.com/2009/10/11/magazine/11fob-consumed-t.html>) Students may also be familiar with brands that are marketed as sodas “made with pure cane sugar”, such as Jones and Hansen’s.

Students may also be interested to find that HFCS is not just for human consumption; it also finds use by commercial beekeepers as bee feed during times when natural food is not available.

(http://portal.acs.org/portal/PublicWebSite/pressroom/podcasts/globalchallenges/safefood1/CNB_P_023783) However, its use with bees does have a potential problem linked to the formation of hydroxymethylfurfural (HMF), which is formed at high temperatures from dehydration of fructose present in HFCS (see section “More on high fructose corn syrup and health”). HMF is also a part of caramelization reactions during cooking.

More on high fructose corn syrup and health

Discussions of the positives and negatives of using high fructose corn syrup for food products meant for human consumption and other uses abound on the internet and can become highly charged. Those against its use may even go so far as to claim it’s “evil”, while an argument of supporters can be that it’s “essentially the same as sucrose”.

A 2010 *Biotechnology and Molecular Biology Review* article “High fructose corn syrup: Production, uses and public health concerns”

(http://www.academicjournals.org/bmbr/PDF/Pdf2010/Dec/Parker_et_al.pdf) summarizes: “There are three major concerns about the use of HFCS related to public health. The first is its possible role in obesity, cardiovascular disease, and other metabolic syndromes. The second is mercury contamination of HFCS samples during production and the third its toxicity to honey bees with possible contribution to colony collapse disorder (CCD) of honey bees.” The article succinctly describes the three problems:

Several studies published in the last 10 years present data that suggest a correlation between increased consumption of HFCS in the past three decades with increased incidence of obesity and cardiovascular diseases in the US. Others studies have been published in defense of HFCS and emphasizing the absence of strong evidence that HFCS and sucrose have differing metabolic effects; and suggesting no causal role for HFCS in obesity. ... There has been a reassessment of the overall intake of high caloric sweeteners by several scientific organizations such as the American medical association (AMA), the American dietetic

association (ADA) and the International life sciences institute (ILSI). The consensus is that HFCS should not be singled out from other sweeteners as the cause of increasing obesity in the US, and that the broader focus should be on combating the increase in consumption of high caloric diets coupled with increased inactivity in the general population. However, HFCS is a relatively recent addition to the US diet and studies to understand its functionality and possible adverse effects are warranted ...

A second concern related to HFCS consumption is the presence of trace amounts of mercury in HFCS manufactured in the US. Caustic soda used in HFCS production is typically made at chlor-alkali plants that use mercury cells. ... Dufault et al. (2009) collected and analyzed twenty HFCS samples from three different manufacturers and found that 11 of 20 samples contain levels of mercury that were below detectable limits of 0.005 μg of mercury/g of HFCS while 9 of 20 had levels that ranged between 0.065 to 0.570 μg of mercury/g of HFCS. Since the average daily consumption of HFCS is approximately 50 g/person, Dufault et al. (2009) stated that there was need to account for mercury from this source in the diet of sensitive populations such as children and others when examining total exposure to mercury. ...

It [HFCS] is used by commercial beekeepers as food for honey bees to promote brood production in the spring for commercial pollination. It is also used to feed honey bees when sources of pollen and nectar are scarce. Hydroxymethylfurfural (HMF) is formed at high temperatures from dehydration of fructose. ... Leblanc et al. (2009) found that at temperatures above 45 °C, HFCS begins to form HMF, a byproduct that is very toxic to bees.

The topic is a good opportunity for students and teachers to explore the various arguments surrounding the issue, to evaluate whether they are reasonable arguments and if they are currently supported by scientific data, and to be aware of which particular group is making an argument to consider any potential bias. Multiple websites are included in the “More sites on high fructose corn syrup and health” section below as a starting point.

Connections to Chemistry Concepts (for correlation to course curriculum)

1. **Polymers**—Starch is an example of a polymer formed of many glucose monomers. A related polymer to discuss is cellulose, which is also formed of many glucose monomers, but with different orientations of the monomers. Instructors could discuss the ability of different organisms to digest these polymers.
2. **Isomers**—The two monosaccharides presented in the article, glucose and fructose, both have a molecular formula of $\text{C}_6\text{H}_{12}\text{O}_6$. However, they each have a different arrangement of atoms, making them isomers.
3. **Enzymes**—Enzymes, including the three that are used to convert starch to high fructose corn syrup, are catalysts that speed or facilitate chemical reactions without undergoing changes themselves. A discussion of enzymes could include information about activation energy, the fact that enzymes are normally large protein molecules, the specificity of enzymes, and an enzyme’s active site.

4. **Carbohydrates**—Starch belongs to the family of molecules called carbohydrates, which help the body store and transport energy. Instructors could discuss other common carbohydrates that make up a part of our diet, along with other families of molecules such as proteins and fats.
5. **Molecular Structure**—The chemical structures used in this article can introduce students to common representations of organic molecules as well as the appearance of ring structures.
6. **Nutrition**—Students can learn about the caloric content of different types of molecules, such as carbohydrates, proteins, and fats, and could discuss interpreting food labels and making healthy and informed eating choices.

Possible Student Misconceptions (to aid teacher in addressing misconceptions)

1. **“When I drive by a corn field, it’s probably a crop of sweet corn.”** *Less than one percent of the U.S. corn crop is sweet corn that we eat as corn on the cob. The majority of the corn crop is field corn, which is used for livestock feed and other corn-based products, including high fructose corn syrup.*
2. **“Corn is only grown for humans and livestock to eat.”** *Much of the corn grown in the U.S. is used for livestock feed and a very small amount is eaten in kernel form by humans (canned and frozen, and fresh corn on the cob). However, corn is used in many other products, including ethanol production, bioplastics, fabrics, and industrial products. It is also present in many food products, such as corn cereal, corn starch, corn oil, and products that contain high fructose corn syrup.*
3. **“There is only one kind of high fructose corn syrup.”** *There are different types of high fructose corn syrup. They vary in the ratio of fructose to glucose that they contain. One type, high fructose corn syrup 42, has 42% fructose and 55% glucose, and is a bit less sweet than sugar. Another type, high fructose corn syrup 55, has 55% fructose and 42% glucose, and is a bit sweeter than sucrose.*
4. **“I should replace all the high fructose corn syrup in my diet with sucrose so I’ll be healthier.”** *Both high fructose corn syrup and sucrose are high in calories, with no other nutrients. Marion Nestle, a nutrition scientist quoted in the Brownlee article, recommends “It’s best to keep intake of any kind of added sugar to a minimum.”*

Anticipating Student Questions (answers to questions students might ask in class)

1. **“Is Karo® corn syrup from the store high fructose corn syrup?”** *Karo-brand corn syrup and store-brand corn syrup products are not high fructose corn syrup. It contains only glucose, rather than a combination of glucose and fructose, because it has not had an enzyme added to transform a portion of the syrup’s glucose to fructose. It is not as sweet as high fructose corn syrup, and is only about 60% as sweet as table sugar.*
2. **“Why are some sodas labeled as being made with natural cane sugar? Are they better for me?”** *The majority of sodas use high fructose corn syrup as a sweetener. Some sodas are made with cane sugar (sucrose made from sugar cane). However, neither type of soda is particularly healthy, in that both are mainly water, flavoring, and a large amount of sweetener that provides empty calories.*

In-class Activities (lesson ideas, including labs & demonstrations)

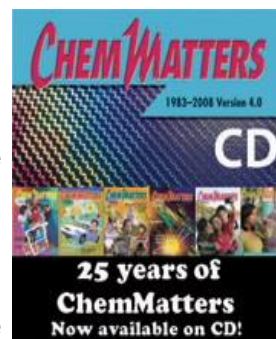
1. In a food-safe environment, students can experiment with making two candy products related to ideas in the article: peanut brittle and chocolate-covered cherries. Peanut brittle uses corn syrup (glucose solution) as an ingredient to help prevent crystals from forming in the candy. The *ChemMatters* article “Peanut Brittle” includes a recipe (*ChemMatters*, Dec. 1991, pp 4–7). Chocolate-covered cherries use the action of the enzyme invertase (available from candy-making suppliers) to create the liquid center. The enzyme catalyzes the breakdown of sucrose into fructose and glucose. Recipes are available online; one example is http://www.nydailynews.com/lifestyle/food/2010/02/10/2010-02-10_for_valentines_day_homemade_chocolates_that_are_guaranteed_to_melt_hearts.html.
2. Students could dissect corn kernels to see if they can locate each of the parts shown in the composition of a corn kernel figure from the Brownlee article. They could perform the dissection on two different kernels: one soaked in water, similar to the process it undergoes in the corn refining process, and one not soaked.
3. Students can use corn products (cornstarch and corn oil) to make a compostable bioplastic in the microwave using the activity “Make Your Own Compostable Bioplastic” from the April 2010 issue of *ChemMatters*, p 12. (http://portal.acs.org:80/portal/PublicWebSite/education/resources/highschool/chemmatters/archive/CNBP_024548)
4. Cornstarch is also used to make biodegradable packing peanuts. Activities that compare the properties of cornstarch packing peanuts and polystyrene packing peanuts, along with each type’s impact on the environment, are available online. One example is http://www.mrsec.psu.edu/ipse/activities/polymers/packingpeanuts_activity.pdf. An extension of this type of activity is to observe the action of amylase on cornstarch packing peanuts, including testing for starch with iodine solution and glucose with Benedict’s solution. (http://www.occc.edu/bbdiscovery/documents/Modules/Packing_peanuts.htm)
5. An experiment that uses an enzyme found in readily-available foods is the investigation of the action of catalase on the decomposition of hydrogen peroxide. A typical procedure is to add 3% hydrogen peroxide to pieces of potato or liver and observe if any bubbles form, and if so, to compare the rates. One such lab is in *Chemistry in the Community* (5th edition, pp 610–611).
6. Corn syrup is an optically active solution that can be used in a “Kaleidoscopic Sugar Rotation” demonstration performed on an overhead projector with polarized filters. See <http://dwb4.unl.edu/chemistry/beckerdemos/BD004.html>, which includes pictures and movies of the demonstration, and a less detailed example at <http://demolab.phys.virginia.edu/demos/demos.asp?Demos=H&Subject=6&Demo=6H30.40-subtopic>.
7. A taste test lab available online (http://www.auburn.wednet.edu/amhs/Science/ChemFiles/Unit_1/Lab_Taste_Test.pdf) describes blind taste tests performed between Coke and Pepsi soft drinks, and asks students to develop a hypothesis that can be tested about these products. The example given is testing Coke sweetened with sugar vs. Coke sweetened with high fructose corn syrup. Some soda brands are now produced using artificial sweeteners such as Splenda®, which could provide an additional sample option.
8. Many laboratory manuals include an experiment to determine the amount of calories in various foods. Often, a protein food item is compared to a carbohydrate food item, such as a nut and a marshmallow. One example is found online at <http://www.tutushouse.org/docs/CaloriesExperiment.pdf>. Another is available in *Chemistry in the Community* (5th ed): “Snack-Food Energy” (pp 570–571).

Out-of-class Activities and Projects (student research, class projects)

1. Students could compare various sweeteners, such as the several mentioned in the Brownlee article (sucrose, honey, corn syrup, high fructose corn syrup), along with artificial sweeteners. Investigations could include the relative sweetness of the products and how effective it can be to substitute one sweetener for another. For example, Consumer Reports tested how several lower-calorie and no-calorie sweeteners worked in drinks and in baking. (<http://www.consumerreports.org/cro/food/resource-center/sweeteners-10-07/overview/sweet-ov.htm>)
2. Students could discuss the effect that perception, rather than actual facts, can have on our beliefs about a particular product. The Corn Refiners Association has discussed changing the name of high fructose corn syrup to corn sugar. (<http://chemistry.about.com/b/2010/09/16/different-names-for-chemicals-high-fructose-corn-syrup-vs-corn-sugar.htm>) The author of the website brings up the question that most chemicals have multiple names, e.g. “Do you put baking soda in your cookies or do you use bicarbonate of soda?”
3. The topic of high fructose corn syrup is a good opportunity to explore and evaluate the various arguments surrounding its use. Multiple websites are included in the section below (“More sites on high fructose corn syrup and health”) as a starting point.
4. Students could investigate food ingredient labels in the home and local stores to learn how many of the products they commonly consume contain high fructose corn syrup, sucrose, and/or other sweeteners.

References (non-Web-based information sources)

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site: <http://www.acs.org/chemmatters>. (Part way down the Website screen, click on the *ChemMatters* CD icon shown at the right.)



Selected articles and the complete set of Teacher’s Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher’s Guides are available on the 25-year CD for all past issues, up to 2008.)

“Corn—The A’maz’ing Grain” (Haines, G. *ChemMatters*, **2006**, 24 (4), pp 4–7) focuses on the history of corn, including its use for ethanol, high fructose corn syrup, and popcorn, and describes the science and issues surrounding genetically modified corn.

“Carb Crazy” (Rohrig, B. *ChemMatters*, **2004**, 22 (3), pp 6–8) discusses carbohydrates commonly found in our diet, how our body uses them, and the topic of low-carb diets.

“Plastics Go Green” (Washam, C. *ChemMatters*, **2010**, 28 (2), pp 10–12) discusses the production of bioplastics by converting the sugar present in corn into plastic. The article includes the activity “Make Your Own Compostable Bioplastic”, which uses a mixture of cornstarch, corn oil, and water heated in the microwave. This article is also available in the online archives section of *ChemMatters* at

http://portal.acs.org:80/portal/PublicWebSite/education/resources/highschool/chemmatters/archive/CNBP_024548.

“Peanut Brittle” (Catelli, E. *ChemMatters*, 1991, 9 (4), pp 4–7) describes the chemistry involved in making crystalline vs. amorphous candies, information about sucrose, and the formation of hydroxymethylfurfural, which is involved in caramelization. A recipe for peanut brittle is included.

Chemistry textbooks commonly contain sections on several of the topics in the Brownlee article, including carbohydrates, enzymes, and polymers. One textbook quoted in this Teacher’s Guide is *Chemistry: The Central Science* (Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E., 7th ed.; Prentice Hall: Upper Saddle River, NJ, 1997.

Chemistry in the Community (5th ed.; American Chemical Society: Washington, DC, 2006) contains two laboratory investigations that could potentially be used in connection with the Brownlee article: “Enzymes” (pp 610–611) to test fresh and boiled food samples for the presence of catalase and “Snack-Food Energy” (pp 570–571) to determine the energy contained in samples of snack foods.

Web sites for Additional Information (Web-based information sources)

More Web sites on corn

The Illinois Corn website offers lesson plans on the physical differences between field corn and sweet corn, their different uses, and statistics using corn, along with downloadable videos to accompany each. (<http://www.ilcorn.org/high-school/1-a-tale-of-two-corns/>)

The National Corn Growers Association website includes an Educational Resource Center page that contains multiple links to corn- and farm-related primary and secondary educational resources for parents and teachers. (<http://www.ncga.com/educational-resource-center>)

Purdue University’s Department of Agronomy shares links to multiple sites that offer classroom resources for teaching about corn. (<http://www.agry.purdue.edu/ext/corn/culture/classroom.html>)

While not particularly science-related, students may have had up-close experience with corn by finding their way through a cornfield maze. This Purdue University site provides links to many mazes and maze designers. (<http://www.agry.purdue.edu/ext/corn/culture/maze.html>)

More Web sites on carbohydrates

A “ChemCard stack” focusing on carbohydrates is available online at <http://www.hcc.mnscu.edu/chem/V.25/index.html>. The stack of 58 cards is meant to be viewed sequentially, with each card providing a small chunk of information. The cards include many different carbohydrate structures, such as glucose, galactose, maltose, lactose, and sucrose.

This page focuses on monosaccharides and the cyclic and non-cyclic structures of sugars, including many molecular structure representations. (<http://chemistry2.csudh.edu/rpendarvis/monosacch.html>)

The basics of carbohydrates are presented at <http://staff.iccc.net/pdecell/biochemistry/carbohyd.html> - top.

More Web sites on corn refining

This page on the Corn Refiners Association website gives an overview of the corn refining process, with links to more detailed information on each part of the process, and a flow chart of the process and its resulting products. (<http://www.corn.org/process/>)

The bulk of this report sponsored by the U.S. Environmental Protection Agency focuses on how to improve the energy efficiency of processes in the corn wet milling industry, but the first part of the document provides detailed information on processes corn undergoes as it progresses from plant to sweeteners and other products. (<http://www.energystar.gov/ia/business/industry/LBNL-52307.pdf>)

This brochure by a Canadian company involved in the wet milling of corn has a second page with extensive tables that illustrate the brochure's phrase "Good things come from corn". It lists large numbers of common products and shows various corn products that are used in each. (http://www.casco.ca/eng/pdf/Good_things_come_from_Corn_ENG_FINAL.pdf)

More Web sites on high fructose corn syrup

The enzyme used in corn refining, alpha-amylase, was described in a "Molecule of the Month" feature on the RCSB Protein Data Bank website at http://www.pdb.org/pdb/static.do?p=education_discussion/molecule_of_the_month/pdb74_1.html. All three of the enzymes used in corn refining are also shown on another page of the website at http://www.pdb.org/pdb/static.do?p=education_discussion/molecule_of_the_month/pdb74_2.html.

Elmhurst College's "Virtual Chembook" contains a page on corn syrup, which includes molecular structures for starch hydrolysis, glucose, and fructose. The page also includes a link to the textbook's introduction to sweeteners. (<http://www.elmhurst.edu/~chm/vchembook/548HFSyrup.html>)

"Sweetose", an early "high-sugar-content" corn syrup patented in 1938, is described in this blog post and briefly discussed in connection with high fructose corn syrup. (<http://candyprofessor.com/2009/10/05/corn-syrup-history-sweetose/>)

The paper "High fructose corn syrup: Production, uses and public health concerns", published in December 2010 in *Biotechnology and Molecular Biology Review* provides a readable summary of the basics of high fructose corn syrup production along with a discussion of three major public health concerns related to HFCS. (http://www.academicjournals.org/bmbr/PDF/Pdf2010/Dec/Parker_et_al.pdf)

More Web sites on high fructose corn syrup and health

The TIME magazine article “Ad Wars: Is High-Fructose Corn Syrup Really Good for You?” discusses an ad campaign by the Corn Refiners Association to improve the image of HFCS and the response of others to the campaign.

(<http://www.time.com/time/health/article/0,8599,1841910,00.html>)

A piece from *The New York Times* discusses the petition by the Corn Refiners Association to start calling high fructose corn syrup “corn sugar”.

(<http://well.blogs.nytimes.com/2010/09/14/a-new-name-for-high-fructose-corn-syrup/>)

A 2008 article from the *American Journal of Clinical Nutrition* “Straight talk about high-fructose corn syrup: what it is and what it ain’t” briefly discusses the history of HFCS and evaluates “the strength of the popular hypothesis that HFCS is uniquely responsible for obesity.”

(<http://www.ajcn.org/content/88/6/1716S.full>)

The Princeton University website describes a recent Princeton study that has generated a lot of discussion. The site states that the study demonstrates that all sweeteners are not equal when it comes to weight gain. (<http://www.princeton.edu/main/news/archive/S26/91/22K07/>)

A CNN health article responds to the Princeton study described above.

(http://articles.cnn.com/2010-03-25/health/corn.syrup.sugar_1_high-fructose-corn-syrup-corn-refiners-association-audrae-erickson?s=PM:HEALTH)

A 2009 *Environmental Health* article “Mercury from chlor-alkali plants: measured concentrations in food product sugar” describes the results of an analysis of high fructose corn syrup samples for mercury content. (<http://www.ehjournal.net/content/8/1/2>)

The Global Development and Environment Institute, Tufts University, presents a 2009 policy brief that discusses a possible connection between farm subsidies and the U.S. obesity epidemic. (<http://www.ase.tufts.edu/gdae/Pubs/rp/PB09-01SweeteningPotFeb09.pdf>)

The Corn Refiners Association website lists multiple studies from 2005 to 2010 regarding research on high fructose corn syrup. (<http://www.cornnaturally.com/sweeteners-science/sweetener-research/>)

“Soda Warning? High-Fructose Corn Syrup Linked To Diabetes, New Study Suggests” describes research reported at a 2007 American Chemical Society meeting.

(<http://www.sciencedaily.com/releases/2007/08/070823094819.htm>)

A USA Today article “Nutrition experts battle industry groups over sugar” discusses two sides to the argument. (http://www.usatoday.com/news/health/2010-03-02-sugarwars02_ST_N.htm)

More Websites on Teacher Information and Lesson Plans (sites geared specifically to teachers)

Iowa State University’s Office of Biotechnology offers several biorenewable curriculum modules that include a corn kernel module with a corn kernel dissection lab, and a

fermentation/ethanol module.

(<http://www.biotech.iastate.edu/publications/BiorenewablesCurriculum/>)

The Nebraska Corn Board offers nine units of “corn curriculum” with teacher’s keys. The units cover all subject areas, including science, language arts, art, social studies, math, etc., and are connected to Nebraska education standards. (http://www.nebraskacorn.org/wp-content/uploads/2010/07/unit9_TeachersKey.pdf)

Authentic or Not? Chemistry Solves the Mystery

Background Information (teacher information)

More on chemistry and art

There are many methods of detecting an art forgery. The article describes several high-tech methods of detection, but there are dozens of other methods. You can point out to your students that art forgeries are one specialized area of criminal forensics, which many students find especially interesting.

In some cases, detection depends on the expert opinions of art historians, artists, conservators and curators, any of whom might be able to see a difference between the style or technique of the original artist and that of a forger. But modern science brings methods of analysis to the art world that can provide indisputable evidence regarding the authenticity of a painting. Chemical analysis of the materials used is one general approach, and the other is the kind of instrumental analysis described in the article.

The examples of forgeries used in the article are oil paintings so it might be helpful to provide a little background on this type of art. An oil painting is composed of four layers: support, ground layer, paint layer, and varnish. The support is traditionally made of wood. X-rays can be used to penetrate to the wood layer to reveal certain characteristics. For example, prior to the 1800's and the Industrial Revolution hand saws were used to cut wood panels. Hand saws produce uneven characteristic marks on wood whereas mechanical or power saws leave even markings.

The fabric used in the support layer is most often canvas. Canvas is a plain weave fabric. The fabric is produced by aligning threads on the vertical (known as the warp) and then interweaving horizontal threads called the weft. Generally in canvas the warp threads have a more regular pattern while the threads of the weft are often a bit more irregular due to the way they are compacted on the loom at intervals in the weaving process. Linen is often the thread used due to its strength and because it is less hygroscopic than other fibers. So when scientists analyze the canvas layer they look for the thread count. Generally the warp thread count is higher. But when artists cut canvas from the roll they may orient the warp on the vertical with respect to the support or they may orient the weft on the vertical. Art historians and scientists know that specific artists had their preferences and so look for these when investigating art forgeries. X-ray and CT scanning are often the technologies of choice when attempting to examine the underlayers of a painting. CT scans produce a kind of 3-D image of the painting and X-radiation is used to examine each individual layer, including the canvas and thread count.

Historically, a coating called the ground surface, was applied to the wood or canvas. On canvas the ground was usually a white oil primer. On wood a mixture of chalk or gypsum and animal glue, called gesso, was applied as the ground. Gypsum is a very soft mineral composed of calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It was used by artists in southern Europe. Artists in northern Europe used calcium carbonate, CaCO_3 , in a glue binder. The glue, primarily a protein, was prepared by boiling the hooves and skins of animals, especially rabbits, making a glue that is flexible. Today a white acrylic polymer is often used.

The varnish layer helps to preserve the painting. Varnishes were usually made up of a resin, a drying oil and a solvent. Natural resins are viscous liquid terpenes secreted by plants. Drying oils include linseed oil, tung oil, and walnut oil. These oils “dry” not by evaporation but by reacting chemically with oxygen to form a hard polymer on the surface of the painting. The varnish solvent was often turpentine.

The paint layer is of most interest to chemists. Paint pigments are simply chemical compounds or mixtures of compounds suspended in a medium like oil or tempera. Prehistoric cave paintings reveal pigments that were mostly minerals like limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$), hematite (Fe_2O_3) and calcite (CaCO_3) or elements like carbon black. In artists terms limonite is yellow ochre, hematite is red ochre and calcite is lime white. Historians believe that the desire for these kind of mineral pigments provided the impetus for mining the earth. Records indicate that painters traveled long distances to obtain, for example, hematite ore. Often the mineral was found in clay deposits and the clay was often mixed with the hematite to form a pigment that had a consistency conducive to painting. Another advantage of using minerals like hematite as a pigment was that the compound is chemically stable, meaning that the painting retained its colors over time.

Further historic development of pigments is attributed to the Egyptians, Greeks and Romans. The Egyptians continued to use natural pigments like red ochre, yellow ochre, umber (a tan to brown mixture of three oxides— Fe_2O_3 , MnO_2 and Al_2O_3), orpiment (arsenic sulfide, a yellow pigment) and the green malachite (copper(II) carbonate). They added to the pigment palette dyes that were converted to pigments in a process called laking. The dye molecule is reacted chemically with a metal salt to precipitate the pigment molecule. Principal among these converted dyes were madder and indigo. For example, the root of the madder plant was dried and crushed into powder. The powder was dissolved in water to make a red dye. In order to produce a pigment, the dye was then reacted with crushed bones, chalk or white clay. Today alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), aluminum oxide, barium sulfate or calcium sulfate are used. The Egyptians pioneered this process. The two colorants in the madder root are alizarin (1,2-dihydroxyanthraquinone) and purpurin (1,2,4-trihydroxyanthraquinone). In the early 1800s alizarin was synthesized in the lab for the first time, and red pigments based on alizarin have been synthesized since then. The Egyptians also used an “Egyptian blue” pigment that was made from finely ground glass in which copper ions imparted the blue color.

The Greeks’ contribution to pigments was lead white, which is lead(II) carbonate. The solid is derived from the naturally-occurring mineral cerusite. The Romans added vermilion, a reddish pigment made from cinnabar. The compound is actually mercury(II) sulfide, HgS .

In the Medieval period pigments were mixed with water and egg to form tempera, and this mixture was used for the paint layer. Tempera paint dries rather quickly, but if applied in thicker layers it tends to crack. So tempera paints were applied in multiple thin layers. Medieval artists used many of the same mineral pigments used by the Egyptians. A newer popular pigment was Verona green or green earth, which was composed of hydrosilicates of iron, magnesium, aluminum and potassium. A blue pigment called ultramarine came into use during the Middle Ages. This pigment comes from the expensive mineral lapis lazuli, which is a complex sodium calcium aluminum silicate sulfate. Azurite was also added to the painter’s palette in the Middle Ages. Azurite is a basic copper(II) carbonate and produces a blue pigment. It was the dominant blue pigment throughout the Middle Ages and the Renaissance.

The Renaissance period (1400-1600) saw a number of changes in paints and pigments. Tempera was replaced by linseed or walnut oil as a paint medium. Pigments used in previous times remained in use, but three new pigments were added—Naples yellow, smalt and carmine lake or cochineal. Naples yellow is lead(II) antimonate, $Pb_3(SbO_4)_2$. Smalt is potassium glass powder which has been made with cobalt ions added for the blue color. The pigment is produced by adding cobalt oxide to molten potassium carbonate glass. The resulting glass is ground into a coarse powder for use as a pigment. The third new pigment in this period is carmine lake or cochineal. Recall from above that a lake is an insoluble solid produced from a water-soluble dye. Cochineal is an insect (*Dactylopius coccus*) from which carmine dye, actually carminic acid, can be extracted. The dye is then converted to a lake which is used as a pigment. Cochineal is an example of a pigment produced not from a mineral but from organic matter.

In the 1700s the pigments in use were much the same as in the past, with two new pigments added. They were Prussian blue and cobalt green. Both of these pigments were made of compounds synthesized chemically. These were early synthetic pigments that scientists were beginning to develop during the eighteenth century. Prussian blue is a compound called iron-hexacyanoferrate, $Fe_7(CN)_{18} \cdot 14H_2O$. Cobalt green is a cobalt-oxide-zinc-oxide combination. The pigment was made possible in the late 1700s due to the synthesis of zinc oxide.

The 1800s saw a great many new pigments become available, primarily because of developments in the preparation of synthetic dyes for the growing textile industry. In 1856, William Henry Perkin, an English chemist, was attempting to make quinine but made instead a substance that could dye silk a rich purple color. Perkin called the substance Mauveine and found that aniline was one of the primary ingredients. His discovery ignited a wave of research into synthetic dyes, which had great commercial value. New pigments for paints were by-products of this interest in synthetic dyes.

As a result, new pigments like synthetic red ochre, chrome orange, chrome yellow, cobalt blue, viridian, cadmium yellow, cerulean blue, French ultramarine, zinc white, cobalt violet and emerald green were made available. The chemical makeup of each is listed below:

synthetic red ochre – Fe_2O_3
chrome orange – $PbCrO_4$
chrome yellow – $PbCrO_4$
cobalt blue – $CoO \cdot Al_2O_3$
viridian – $Cr_2O_3 \cdot H_2O$
cadmium yellow – CdS with Se added
cerulean blue – Co_2SnO_4
French ultramarine – $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$
zinc white – ZnO
cobalt violet – $Co_3(PO_4)_2$
emerald green – $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$

The invention of synthetic pigments continued into the 20th century. The most important change in paint pigments in the 20th century was the advent of acrylics. Acrylic resins were invented by German chemist Otto Rohm in the early 1900s. Plexiglas was the first application. Just after World War II acrylics were marketed for artists by Bocour Artists Colors, Inc. Acrylic paints are made chemically from an acrylic monomer in aqueous solution. A bond is broken in the monomer, producing a polymerization reaction in which as many as 10,000 monomer units are bonded together. As the reaction proceeds, the chains take the shape of extremely small spheres. These spheres disperse in the water to produce the paint. Today acrylic paints are the medium of choice for many artists.

The point of describing these changes is that the compounds used to produce colors in paintings have changed over the centuries. Some of the compounds used for pigments in ancient times are not readily available today. So a person attempting to forge an older painting might use a pigment not known in ancient times. For example, if there was a painting that someone claimed was done in medieval times and the painting was found to have cobalt blue as one of its pigments, it would be judged a forgery because cobalt blue did not come into use as a pigment until the nineteenth century. Another similar example is the case of the Jackson Pollock “Ferrari red,” which is described in the article.

The way a specific pigment compound changes chemically while it is part of a painting is also a subject for artists and scientists to understand. Components of the painting might react chemically with oxygen in the air, chemical pollutants and light. Temperature and humidity also may affect the chemical makeup. It is interesting to note that since most pigments are suspended in an oil medium, there is only a remote chance that pigments will react with each other chemically. Your students will likely understand that many chemical reactions between compounds take place only in aqueous solution. Compounds must be water soluble in order to form a solution, and most, if not all, pigment compounds are not water soluble. Suspending pigment compounds in an oil medium usually prevents chemical reactions from occurring. Water solubility is also important in distinguishing *pigments* from *dyes*. Chemical compounds used as dyes are all water soluble. Pigments are insoluble. Converting a dye to a pigment using the “laking” method is described earlier in this section.

More on X-rays, other technologies and art

The article describes three radiation methods of detecting forgeries—X-rays, X-ray fluorescence and Raman spectroscopy. These are several methods in an increasing battery of high-tech methods of examining art work without destroying the art. Such nondestructive methods are important not only to forensic scientists but to art curators and conservators as well. The three technologies mentioned in the article are described further below, followed by other technologies that are currently used to detect art forgeries.

X-rays – X-rays can penetrate the surface layer(s) of the painting to reveal what, if anything, lies underneath. As the radiation passes through, it is absorbed to a greater or lesser degree depending on the density (atomic mass) of the substance it encounters. Denser substances appear white on the radiograph and less dense substances appear in shades of gray or black. Most pigment layers are transparent to x-rays with the exception of those containing lead and mercury. X-rays can show how the original painting evolved and how, if at all, the painting was changed by forgers. Many artists reused their canvasses and in this case there would be another drawing or painting under the one visible. If the sketch or painting revealed by x-rays does not match the style or content or time period of the visible painting, the work might be a forgery. As the article mentions, x-rays can also be used to analyze the supports for the painting by revealing construction markings, ground layer or fastening devices.

X-ray fluorescence – When a painting is exposed to high-energy x-rays (or gamma rays) the radiation is sufficiently energetic to ionize atoms of exposed substances. Atoms are ionized (in this case) because the incoming photons remove one or more electrons from an atom’s inner orbitals, making its electron configuration unstable. Electrons in higher orbitals lose energy and “fall” into the lower energy orbitals, and in doing so emit energy. In x-ray fluorescence the emitted energy photon is also in the form of x-radiation but of lower energy

than the incident radiation. Different chemical elements have known x-ray fluorescence emission spectra, and by matching the re-emitted energy with known spectra, scientists are able to identify the elements present in the exposed sample. In this way scientists can determine if the chemical elements in the paint pigments match the composition of pigments at the time the real painting was created. If elements are present that were only used in pigments in more recent times, the painting can be labeled a forgery.

Raman spectroscopy – Raman spectroscopy relies on the idea that when incident light of a known frequency (typically laser light) is scattered by the atoms or molecules of a substance, most of the scattered light is of the same frequency as the incident light, but a small amount—about 0.001%—is of a higher or lower frequency. This scattering of light with higher or lower frequency is called the Raman effect. The Raman effect is due to the fact that a few collisions between exposed molecules and the incident photons of light are inelastic. That is, instead of the scattered light emerging with the same frequency as the incident light (the result of an elastic collision), a very small per cent is scattered with a different frequency. Each different molecule has a known range of Raman frequencies and so the Raman spectra can be used to identify, for example, the composition of the paint pigments in a work of art. This technique can detect inorganic and organic pigments as well as binding media and varnishes.

Infrared Reflectography – This nondestructive method of analysis uses infrared radiation with wavelengths slightly longer than visible light (called near infrared). The method is useful in detecting and artist's underdrawings—preliminary sketches, sometimes in great detail, that an artist makes prior to actually laying down paint. Near infrared radiation is able to pass through the paint layer—it is transparent to IR—and to visualize the underdrawing if it was made with substances like charcoal or graphite which absorb infrared radiation. The ground layer of the painting reflects infrared and an infrared camera can capture the contrast between absorbed and reflected regions of the preliminary sketch. To see infrared photographs of a painting see <http://www.artsmia.org/restoration-online/quercino/if-uv.cfm>.

Fourier-Transform Infrared Microspectroscopy – This technique is useful for identifying both organic and inorganic substances, making it a good choice for identifying paint pigments, which can be either. It can be applied to the analysis of solids, liquids, and gases. In this method infrared light is passed through a sample of an unknown substance, like a small chip of paint. Some of the light is absorbed and some transmitted. In practice the IR radiation is sent in two separate beams through an interferometer which employs two mirrors that reflect the light in such a way that when the two beams reunite, they interfere with each other. So the light that passes through the sample has information about every wave length represented in the original IR radiation. The article describes the behavior of electrons in this analysis. What emerges is data that describes the way the wavelengths interfere with each other. In order to produce an absorption spectrum from this data a computer applies a mathematical formula called a Fourier transformation. An IR absorption spectrum is the result. This series of peaks and valleys, described in the article, corresponds to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum.

Ultra-violet analysis – UV radiation is a standard tool used to study the varnishes or shellacs used to seal paintings. It can also detect differences within the painting that might indicate a forgery. The usual method of analysis is to look at the fluorescence produced under UV radiation.

More on the van Gogh case

As the article states, Otto Wacker was a German art dealer whose brother, Leonhard, was a painter and restorer. It is believed that Leonhard created the fake van Goghs. In 1928, Otto Wacker convinced no less than four van Gogh experts that he had come upon 33 van Goghs that were available for sale. One of those experts was Jacob Baart-de la Faille, who compiled the first complete catalogue of van Gogh's work. The book was to be released in 1928, and the exhibit of the Wacker paintings in four different Berlin galleries was to coincide with the publication.

The general managers of the exhibition, Grete Ring and Walter Feilchenfeldt, suspected the paintings were fakes, despite de la Faille's opinion. When one of the galleries sued Wacker, de la Faille changed his opinion and agreed that the paintings were fakes. However, when called to testify at the trial, which began in 1932, he changed his opinion again, saying that five of the paintings were authentic. In the end, despite conflicting testimony on the part of art experts, the paintings were declared fakes and Wacker was convicted of fraud and sentenced to nineteen months in jail. Important testimony in the trial was given by a Dutch art restorer who was able to show that the pigments used in the fakes were different from those van Gogh used.



To the right is a photograph of the fake van Gogh work in "the Wacker case" described in the article. The number assigned to it—F 614--was the number of the painting in the 1928 catalogue, called a *catalogue raisonné* book produced by de la Faille. Even after Wacker's conviction doubt remained about the authenticity of this painting.

In the summer of 2000, the then current owners of the painting took the painting to the Canadian Conservation Institute in Ottawa, Canada, as the article describes. In a 2001 CCI newsletter, senior conservation scientists Marie-Claude Corbeil and Elizabeth Moffatt, along with conservation scientist Geneviève Sansoucy and senior scientific documentation technologist, Jeremy Powell, reported their testing results.

Once in the CCI laboratory F 614 was carefully examined first with the unaided eye and then with a stereo-microscope. It was radiographed and documented using various photographic techniques, and microscopic paint samples were removed for chemical analysis to determine the nature of the binder and pigments. The painting was then sent to the van Gogh Museum in Amsterdam.

Several observations suggested the painting was not by van Gogh, and test results brought to light various anomalies in the materials used to produce the painting, two of which were very significant.

First, the painting had been executed on a symmetrical, plain weave canvas, (the number of threads being the same in the warp and weft directions), instead of the asymmetrical canvas typically used by van Gogh toward the end of his life. The original appearance of the canvas, which had been obscured by the painting's lining, was revealed by X-radiography.

Second, the paint's binding medium contained resin in addition to oil. The presence of a mixture of oil and resin was not, per se, anomalous; however, at the time of the scandal about a third of the paintings had been submitted to chemical analysis and resin had been found in the Wacker paintings but not in original van Goghs. Also, although very few binding medium analyses of van Gogh paintings have been reported in the modern conservation literature, those results have never shown the presence of resin.

The experts at the van Gogh Museum noted the anomaly regarding the canvas as soon as they saw the X-radiographs. With their vast knowledge of van Gogh's technique, they also discerned other aspects of the painting that indicated it was not his work. (<http://www.cci-icc.gc.ca/about-apropos/nb/nb27/f614-eng.aspx>)

For much more on van Gogh and art forgery you can read an online book, titled "A Real van Gogh: How the Art World Struggles with the Truth", at <http://www.scribd.com/doc/37457450/A-Real-Van-Gogh-How-the-Art-World-Struggles-With-Truth-2010>.

More on the Pollock case

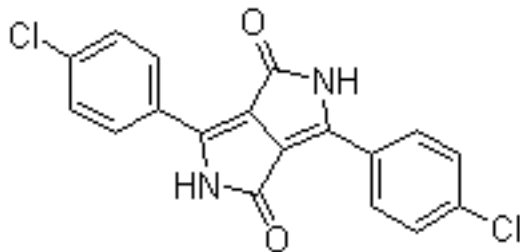
In 2003, Alex Matter claims to have found the 32 paintings described in the article as possible Jackson Pollock paintings. Alex Matter is the son of two artists, Herbert and Mercedes Matter, both of whom were friends with Jackson Pollock and his wife Lee Krasner. Alex Matter claimed that he found the paintings wrapped in brown paper and labeled as Pollock paintings in his father's handwriting. There is some evidence that the Matters had purchased paintings from Pollock before his death in 1956, and there are indications that Pollock may also have given paintings to the Matters.

Alex Matter took the 32 paintings to a gallery owned by Mark Borghi in New York City. The paintings were to be part of an exhibit of Pollock paintings in 2006, the 50th anniversary of his death. The announcement of the paintings' existence created a huge controversy in the art world. Leading experts disagreed on their authenticity. The case was immensely complicated with several galleries, universities and many individuals getting involved. Interestingly, it was Alex Matter himself who allowed James Martin to do the Raman analysis on his paintings. Experts at the Harvard University Art Museums in Boston, Massachusetts, examined the paintings and found pigments not available to Pollock during his lifetime. As the article describes, Martin did 323 Raman analyses on 23 of the disputed paintings and arrived at a similar conclusion regarding the Ferrari red pigment. (See "Raman Spectroscopy, above for more details.) In addition, in 2006, Robert Taylor, a University of Oregon physics professor, used fractal analysis to conclude that the paintings were not original Pollocks. Fractals are geometric patterns that repeat over and over in a system that may look chaotic and random. Taylor performed a computer analysis of 5 million separate drip patterns in the Pollock paintings and concluded they were fakes.

One of the participants in the controversy, Mark Gottsegen, who is affiliated with [Art Materials Information and Education Network](#) and who describes himself as an artist with a special interest in materials, tells the story [here](#).

As the ChemMatters article describes, the synthetic paint pigment identified as DPP, Pigment Red 254 or "Ferrari red" found in the Matter painting was invented in 1974, by a

University of Michigan chemistry professor named Donald G. Farnum. (Remember that Pollock died in 1956.) The discovery was a by-product of an experiment that had nothing to do with paint pigments. The compound, a diketopyrrolopyrrol (DPP), is an insoluble crystalline compound with a chemical name of 3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione and a formula of $C_{18}H_{10}Cl_2N_2O_2$. Its structure is:



Although he synthesized the molecule, Farnum did not patent the process. Ciba-Geigy, Ltd. did so in 1983.

In addition to the Pollock case described in the article, a second Pollock forgery involved a fingerprint found on an alleged Pollock painting, originally titled "Untitled 1948" and later nicknamed "Teri's Find," after Teri Horton, a retiree who bought the painting for \$5 at a thrift shop in California in 1992. The painting, if authentic, would bring \$50 million at auction. Horton hired one art forensic specialist, Paul Biro, who authenticated the painting as a genuine Pollock. However, it was later re-examined by a fingerprint expert named Pat Wertheim. Wertheim examined the painting in question and took photos and other evidence. He then went to Pollock's studio in East Hampton, Long Island, now an art center, and took plaster casts of known Pollock fingerprints left on a paint can. Wertheim's report concluded "My investigation and examination led to the conclusion that the fingerprints on the painting indeed match one on a paint can in Jackson Pollock's studio. However, I also concluded that the fingerprints on the painting were forged, placed there by means of an inked rubber stamp made from a cast taken from the print on the paint can in the Pollock studio." You can read Wertheim's complete report at http://www.fineartregistry.com/about_FAR/includes/PatWertheimReport.pdf and you can read the complete story of Teri Horton and her \$5 painting at http://www.cbsnews.com/stories/2007/05/03/60minutes/main2758110_page2.shtml?tag=contentMain;contentBody. As of July 2009, the painting had not been sold.

Connections to Chemistry Concepts (for correlation to course curriculum)

1. **Spectroscopy**—The article emphasizes spectrographic methods of analyzing paintings. You may not cover much in the way of spectroscopy in your course, but you can apply the basic concepts of electromagnetic radiation and the interaction between energy and molecules, using this article as an example.
2. **Atomic structure**—Because the article emphasizes spectroscopy, you can easily reinforce ideas that you have taught about the atom, atomic structure and sub-atomic particles.
3. **Compounds and their uses**—many students will never have thought about paint pigments being chemical compounds. The Teacher's Guide provides multiple compounds used as pigments. You might also note to students that as chemists became better able to synthesize more complex compounds, artists were able to make use of synthetic pigments.

Possible Student Misconceptions (to aid teacher in addressing misconceptions)

1. **“Aren’t dyes and pigments the same thing?”** *No they are not the same. Dyes are water soluble compounds that add color to fabric, for example, when the water evaporates. Pigments are water-insoluble compounds typically suspended in an oil medium. When the oil evaporates the solid pigment remains.*
2. **“Isn’t a painting just paint on canvas?”** *An oil painting is composed of four layers: support, ground layer, paint layer, and varnish. The support is traditionally made of wood. The fabric used in the support layer is most often canvas. Canvas is a plain weave fabric. Historically, a coating called the ground surface, was applied to the canvas, usually a white oil primer. On wood a mixture of chalk or gypsum and animal glue, called gesso, was applied as the ground. Paint pigments are simply chemical compounds or mixtures of compounds suspended in a medium like oil or tempera. Varnishes were usually made up of a resin, a drying oil and a solvent.*

Anticipating Student Questions (answers to questions students might ask in class)

1. **“In the article it says that the X-rays of the van Gogh F 614 canvas allowed scientists to see an image of the threads. How can this be?”** *The article explains that the canvas van Gogh used was often coated with a lead-based wash. This wash fills in between the threads of the canvas to a greater depth than it does on top of each thread. The lead in the thicker wash in between the threads absorbs X-rays more than the lead that just coats the top of the threads. So the X-ray image appears white in between the threads and gray to black where the threads are. Thus the pattern of white and dark is an image of the threads, which can be counted in the x-ray image.*
2. **“How does Fourier Transform Infrared Spectroscopy work?”** *In this method infrared light is passed through a sample of an unknown substance, like a small chip of paint. Some of the light is absorbed and some transmitted. In practice the IR radiation is sent in two separate beams through an interferometer which employs two mirrors that reflect the light in such a way that when the two beams reunite, they interfere with each other. So the light that passes through the sample has information about every wavelength represented in the original IR radiation. What emerges is data that describes the way the wave lengths interfere with each other. In order to produce an absorption spectrum from this data a computer applies a mathematical formula called a Fourier transformation. An IR absorption spectrum is the result. This series of peaks and valleys, described in the article, corresponds to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum.*

In-class Activities (lesson ideas, including labs & demonstrations)

1. Students can experiment with creating paints using several media in this activity: http://www.sewanee.edu/chem/chem&art/Detail_Pages/Laboratory/Pigments&Binders/Pigments-Dyes%20Lab%203-07.pdf. (If this URL doesn't respond when you 'control-click' it, cut and paste the URL into a search engine; it is live, as of 2/15/11.)
2. A paint and varnish are prepared in this lab activity: <http://www.terrificscience.org/lessonpdfs/SurfaceCoating.pdf>.
3. Here is a detailed lab activity about making paint with blue pigments: http://www.wellesley.edu/Chemistry/Chem&Art/Topics/Pigments_Painting/Painting_pdf_material/paint_labs2002.pdf.
4. A lesson plan on making tempera paint can be found here: http://www.renaissanceconnection.org/lesson_science_egg.html.
5. This lab activity makes paint using chalk as the pigment: <http://education.sdsc.edu/makingpaint.html>.
6. Invite the art teacher in your school to discuss art forgeries, art and chemistry, the composition of paint pigments or other topics relevant to this article.
7. Where on the periodic table do you find the metal ions that make up many of the traditional paint pigments? Here is a sampling:

Pigment	Composition	Metal
Naples yellow	antimony oxide	Sb
yellow orpiment	arsenic(III) sulfide	As
malachite	copper carbonate	Cu
azurite	copper carbonate	Cu
hematite	iron oxide	Fe
limonite	iron oxide	Fe
galena	lead sulfide	Pb
cerussite	lead carbonate	Pb
cinnabar	mercury sulfide	Hg
cassiterite	tin oxide	Sn
zincite	zinc oxide	Zn

You can add to this list other pigments listed in the Teacher's Guide and have students locate the metals on the periodic table and draw conclusions.

8. You can purchase a commercial art forgery student lab kit, which includes references to van Gogh and Pollock, on this site: http://www.carolina.com/product/212145.do?s_cid=ppc_gl_Products.
9. Labs on paint-making are included in the *ChemSource* series of chemistry modules. See the module titled "The Chemistry of Color." The modules are available for purchase at <http://www.chemsource.info/>.

Out-of-class Activities and Projects (student research, class projects)

1. This article in *The Science Teacher* by Arthur Eisenkraft describes a problem based unit on chemistry and art. (<http://www.cosmic.umb.edu/documents/tst-artistaschemist.pdf>.) Students can be assigned this article and pursue the topics it describes.

2. Students could be assigned to read this interesting case study of the restoration of a painting and compare the methods of study with those described in the *ChemMatters* article: <http://www.e-conservationline.com/content/view/747>.
3. If your school is located in the vicinity of a Native American Indian reservation, your students might talk directly with native artists about materials they use or have used as pigments.
4. There are many articles about art forgeries on the web. Students can be required to search for general or specific articles and report on them. In addition to the two cases described in the article, students can look for articles about Han van Meegeren, Elmyr de Hory, John Myatt, Eric Hebborn, Tom Keating, William Blundell, or Kenneth Walton. There are more.

References (non-Web-based information sources)

Orna, M.V. Chemistry of Color and Art. *Journal of Chemical Education*, **2001**, 78 (10), p 1305. The author discusses the extraction of pigments from naturally-occurring materials and the development of thousands of synthetic pigments.

Orna, M.V. *ChemSource*, The 2010 version of this set of 40 very complete chemistry teacher reference modules on CD, including a module of "The Chemistry of Color", is available for purchase at <http://www.chemsource.info/>.

Schmuckler, J. The Chemistry of Art. *Journal of Chemical Education*, **1981**, 58 (4), p 326. This article provides an overview of resources for chemistry instructors interested in describing the connections of chemistry to art.

Web sites for Additional Information (Web-based information sources)

More sites on scientific painting analysis

This online article describes modern art analysis techniques being used in museum laboratories today.

(<http://www.biotechniques.com/BiotechniquesJournal/2010/February/Museum-Laboratories-Where-Art-Meets-Science/biotechniques-187815.html>)

This web site focuses on the history and analysis of Bellini's "Feast of the Gods" painting. There is a series of pages here, the second half of which describes how a painting can be analyzed scientifically. (<http://www.webexhibits.org/feast/analysis/index.html>)

For more on Raman spectroscopy see http://www.rsc.org/images/Spectroscopy%20in%20Art_tcm18-170760.pdf.

This web site explains Raman scattering: http://content.piacton.com/Uploads/Princeton/Documents/Library/UpdatedLibrary/Raman_Spectroscopy_Basics.pdf.

The paper by Hughes, Graham and Rockmore as it appeared in the Proceedings of the National Academy of Sciences in 2010, focuses on sparse coding as an analytical method. (<http://www.pnas.org/content/early/2010/01/04/0910530107.full.pdf+html>)

This general article from *Forbes* magazine describes some analytic methods used in detecting forgeries: http://www.forbes.com/2008/12/03/collecting-forgery-art-forbeslife-cx_sf_1203fake.html.

An introduction (with diagrams) to Fourier Transform Infrared Spectroscopy can be found at <http://mmrc.caltech.edu/FTIR/FTIRintro.pdf>.

More sites on paint pigments

The web site “Pigments through the Ages” provides a comprehensive look at paint pigments and their evolution: <http://www.webexhibits.org/pigments/>.

This site gives background, history and direction for making paint pigments: <http://www.paintmaking.com/index.html>.

This extensive article from the American Chemical Society’s *Today’s Chemist at Work* describes synthetic pigments in “Pigments of Your Imagination” at: http://pubs.acs.org/subscribe/archive/tcaw/12/i06/pdf/603willis_neitzke.pdf.

This article describes the chemistry that causes paintings to change as a result of environmental influences: <http://chemeducator.org/bibs/0002001/00020101.htm>.

More sites on art forgeries

This page provides a history of art forgeries. (<http://mystudios.com/gallery/forgery/history/forgery-15.html>)

This is a brief but useful summary of how art forgeries can be detected: <http://www.enotes.com/forensic-science/art-forgery>.

From the Encyclopedia of Hoaxes: http://www.denisdutton.com/art_hoaxes.htm

For much more on van Gogh and art forgery you can read an online book, titled “A Real van Gogh: How the Art World Struggles with the Truth”, at <http://www.scribd.com/doc/37457450/A-Real-Van-Gogh-How-the-Art-World-Struggles-With-Truth-2010>. This is a 345-page book, so it loads slowly.

More sites on art conservation

This extensive article from *Chemical and Engineering News* describes the role of chemists in the art conservation: <http://pubs.acs.org/cen/coverstory/7931/7931art.html>.

More sites on canvas analysis

For a detailed and technical paper analyzing the canvas van Gogh used, see <http://people.ece.cornell.edu/johnson/ICASSP2010.pdf>.

More sites on Pollock forgery cases

To review all of the documentation on the “Teri’s Find” forgery case collected by Fine Art Registry, see <http://www.fineartforensics.com/articles/>.

This *New York Times* article is about a second Pollock forgery case: http://www.nytimes.com/2005/05/29/arts/design/29kenn.html?_r=2. You must register and log in to access the article.

New Yorker magazine published this extensive article on Paul Biro, the supposed expert who first authenticated the Pollock paintings, and whose results were overturned by James Martin, as described in the *ChemMatters* article: http://www.newyorker.com/reporting/2010/07/12/100712fa_fact_grann.

One of the people involved in the Pollock case tells his story at <http://www.amien.org/forums/showthread.php?2282-Science-Connoisseurship-and-Art-Authentication-September-2010>.