Fuels from Crops

HOW IS A GROWING WORLD POPULATION that demands a higher standard of living going to be provided with the energy to meet its needs? This challenge is made more difficult as we face the eventual depletion of fossil fuels. One possible solution is to grow our own fuels.

Objective:

Explain the production of fuels from crops.

Key Terms:

aerobic
alcoholic fermentation
anaerobic
biodiesel
bioenergy
biomass
by-product
carbohydrates
carbon cycle
carbon dioxide
carbon monoxide
cellular respiration
disaccharides
distillation
ethanol
fermentation
fossil fuels
glycolysis
greenhouse effect
lactic acid fermentation
methane gas
methanol
monosaccharides
MTBE
nonrenewable resources
photosynthesis
polysaccharides
renewable resources
sinks
yeasts

Plant-Based Fuels

The **carbon cycle** is a biogeochemical cycle in which all the carbon atoms on Earth circulate. Carbon dioxide (CO_2) is a key molecule in the carbon cycle. It is present in the atmosphere. Plants absorb carbon dioxide from the atmosphere and, through photosynthesis, incorporate carbon atoms into carbohydrates, proteins, lipids, and nucleic acids. Carbon atoms return to the atmosphere in the form of CO_2 as a product of respiration. However, much of

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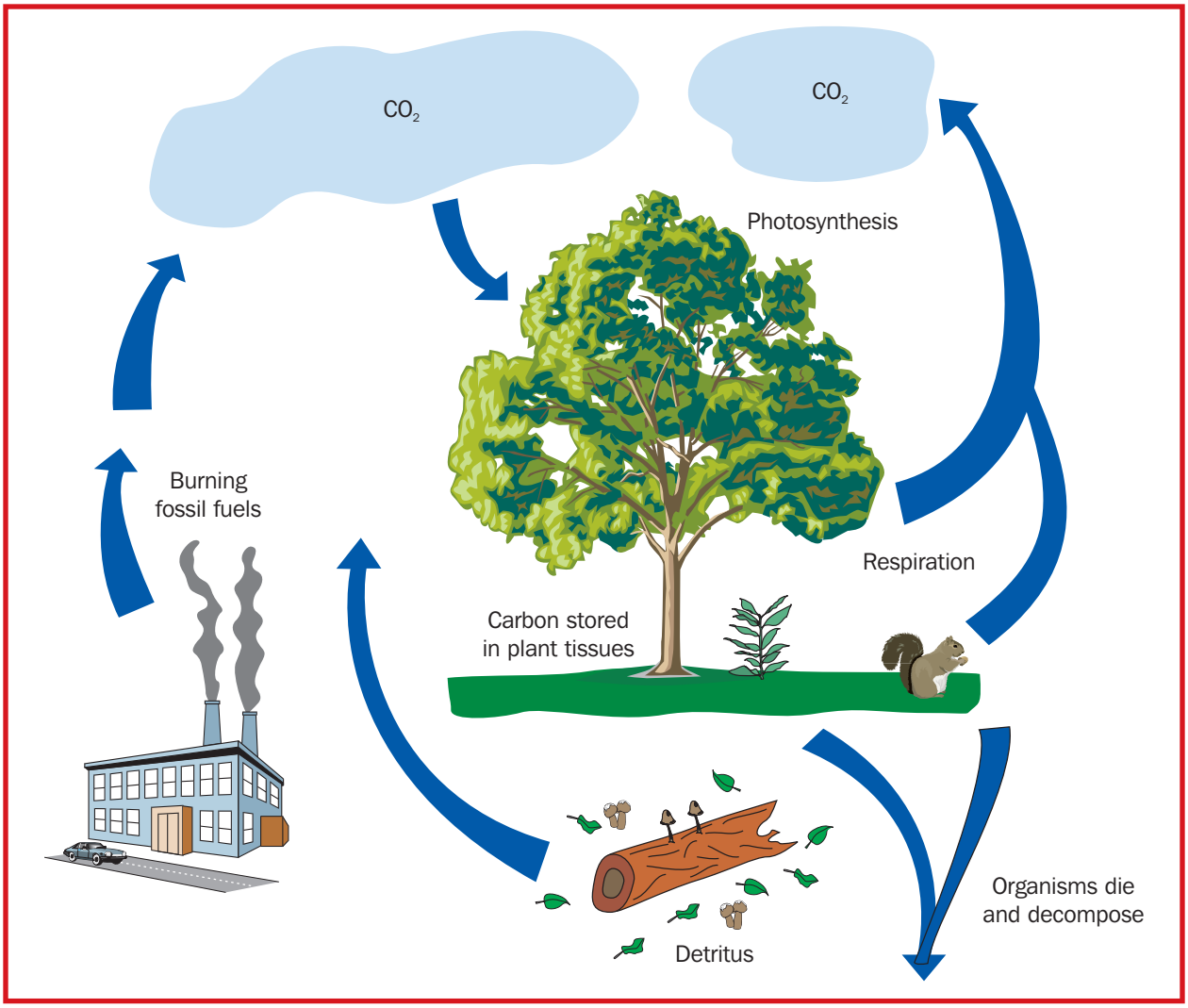

FIGURE 1. The carbon cycle.

the carbon absorbed remains "locked up" in the plants' biomass until decomposition or fire releases it back to the atmosphere.

Carbon is found in the biotic and abiotic reservoirs called **sinks**. Carbon is released from sinks in a number of ways. Natural cycling of carbon dioxide is nearly balanced between sinks and the atmosphere.

Terrestrial vegetation contains about 610 gigatons of carbon stored mostly as cellulose in the stems and branches of trees. It is estimated that soils hold 1,580 gigatons in the form of dead organic matter, or humus. The oceans contain some 39,000 gigatons, but the greatest part of these vast stores is tied up in the form of dissolved bicarbonate in the intermediate and deep ocean. Fossil fuels hold one of the largest reserves of carbon at 5,000 gigatons. **Fossil fuels** are fuels formed from the remains of animals and plants deposited in the geologic past.

Carbon is released naturally from sinks through the weathering of limestone rocks, the respiration of living organisms, volcanic activity, and forest fires.

The burning of fossil fuels and other organic matter by humans has released great quantities of carbon. Much more carbon is stored in fossil fuels than in the air. This is important because

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burning of the fossil-fuel reserves releases carbon directly into the air in the form of carbon dioxide. The result is very large changes in atmospheric CO_2. Additional carbon released from sinks by human activity has caused the rise in atmospheric carbon dioxide concentration over the last 150 years.

The cause of global warming today is attributed to an increased level of carbon dioxide, methane, and nitrous oxide in the atmosphere. Sunlight passes through these gases and strikes the earth. However, the same gases hold heat energy from the sunlight within the earth's atmosphere. This phenomenon is called the **greenhouse effect**.

Trees, in particular, hold large amounts of carbon in the form of cellulose. The clearing of forests and other native vegetation for agricultural production releases carbon dioxide into the atmosphere. The rate at which this is happening is estimated to be roughly 1.6 gigatons per year. This equals about 20 to 25 percent of the total annual human-induced CO_2 emissions.

With significant portions of global emissions coming from deforestation, forest protection must be included as a key component of any overall strategy to stabilize atmospheric CO_2 concentrations. Reforestation results in the removal of carbon from the atmosphere and storage in the biomass of trees through the process of photosynthesis.

THE ADVANTAGES OF USING FUELS MADE FROM CROPS

About 90 percent of the energy needs of the United States and other industrialized countries come from fossil fuels. Large quantities of nonrenewable resources, such as coal, natural gas, and oil, are used daily. Two-thirds of the oil consumed in the United States is used by the nation's more than 185 million vehicles.

Nonrenewable resources, such as fossil fuels, are resources that cannot be reused or replaced. However, alternative sources of energy are available: wind, solar, hydroelectric, geothermal, nuclear, biomass, and tidal energy. Many of these are replaced naturally and are classified as **renewable resources**.

Several things need to be considered when using nonrenewable sources of energy. Carbon dioxide is produced when fossil fuels, such as coal, oil, gasoline, and natural gas, are used. **Carbon dioxide** is a colorless, heavy, and odorless gas found in the atmosphere. **Carbon monoxide** is a gas formed when carbon-containing fuels are burned with an insufficient supply of air; it is colorless, odorless, and poisonous. Fossil fuels also create pollution, adding to smog and acid rain. Using renewable resources for energy can help to prevent or slow global warming and can reduce the incidence of pollution. Nuclear energy is one form of renewable energy, but radioactive waste is created by nuclear power plants, and it must be stored in safe locations.

Legislation's Impact on How Pollution Is Managed

In 1967 the United States enacted the Clean Air Act. The purpose of this act was to give the government power to reduce emissions of pollution from automobiles, chemical plants, refineries, power plants, and other sources. The Clean Air Act is overseen by the Environmental

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Protection Agency. This act placed guidelines on how automobiles were manufactured. Today's cars emit about 70 to 90 percent less pollution than cars 30 years ago.

The 1990 Clean Air Act Amendment dealt with a variety of issues, but instead of focusing on the automobile, it focused on the fuel used in the automobile.

In 1995 the EPA adopted the Federal Reformulated Gasoline (FRG) program, which required the worst urban areas in the United States to use oxygenated fuels. Oxygenated fuels displace the compounds that form smog by reducing the volatile organic compounds and toxic air emissions. **MTBE** (methyl tertiary butyl ether) was used extensively and is created from petroleum. MTBE is non-biodegradable, smells like turpentine, and is insoluble in water. As a result, MTBE has been found to contaminate water supplies and has resulted in the loss of usable drinking water in a number of places in the United States. Some have called for the elimination of the oxygenate requirements for gasoline and not just for MTBE.

Biofuels

The use of biomass for energy has regained new interest in recent years with the push to decrease our dependence on foreign oil supplies. **Biomass** is any organic plant or animal matter that can be used to produce energy. Grains, animal waste, plant waste, wood, algae, and many others may be used to produce energy.

Bioenergy is energy created from biomass. Although biomass can create many of the same pollutants that fossil fuels create, it is made from a renewable rather than nonrenewable resource. Biomass can be used to create fuels such as ethanol, methanol, and methane.

Many areas in the United States use **ethanol** (ethyl alcohol)–blended gasoline or biodiesel. Ethanol is increasingly used as a fuel for automobiles. Biomass fuels can be used in their pure form, or they can be blended with petroleum fuels. An E10 ethanol-blended gasoline contains 10 percent ethanol and 90 percent petroleum-based fuel. Ethanol is produced through the fermentation of grains, such as corn and sugar cane.

Methanol is colorless, odorless, and made from wood; it can be used as fuel for automobiles. Wood alcohol blends in excess of 5 percent have been shown to clog fuel injectors or carburetors.

Methane gas is a flammable gas that is made from waste and is also odorless.

Biodiesel is usually made from soybeans through a process called transesterification and is used in tractors, buses, and other diesel-burning vehicles. Biodiesel can also be used in its pure form or be blended with petroleum fuels. A B20 biodiesel blend contains 20 percent biodiesel and 80 percent petroleum. No major modifications are needed for

Figure 2. Biodiesel is used to fuel these pieces of equipment. (Courtesy, Agricultural Research Service, USDA)

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biodiesel to be used in compression-ignition (diesel) engines. Pure biodiesel contains no petroleum. It has been designated by the U.S. Environmental Protection Agency, U.S. Department of Energy, and U.S. Department of Transportation as a fuel or fuel additive. As compared with petroleum-based diesel, biodiesel has lower amounts of unburned hydrocarbons, particulate matter, and carbon monoxide. Additionally, sulfur oxides and sulfates, which are major components of acid rain, are basically eliminated from biodiesel emissions. Biodiesel can result in 50 percent less hydrocarbon emissions that create ozone, thus helping alleviate the greenhouse effect. When a switch is made to biodiesel, the fuel acts as a solvent and can release deposits from the inside of storage tanks and pipes, causing filters to initially become clogged.

Biofuels are cleaner burning and help to reduce our reliance on oil or nonrenewable resources.

Biofuels are considered renewable resources because they are made from fermented grains, such as corn and soybeans.

TABLE 1. Fuel Comparison Chart

Fuel	Chemical Structure	Main Fuel Source	Environmental Impacts of Burning Fuel
Gasoline	C_4 to C_{12}	Crude oil	Produces harmful emissions; however, gasoline and gasoline vehicles are rapidly improving, and emissions are being reduced.
No. 2 diesel	C_{10} to C_{20}	Crude oil	Produces harmful emissions; however, diesel and diesel vehicles are rapidly improving, and emissions are being reduced, especially with after-treatment devices.
Biodiesel (B20)	Methyl esters of C_{16} to C_{18} fatty acids	Soybean oil, waste cooking oil, animal fats, and rapeseed oil	Reduces particulate matter and global-warming gas emissions compared to conventional diesel; however, NO_x emissions may be increased.
Compressed natural gas (CNG)	CH_4	Underground reserves	CNG vehicles can demonstrate a reduction in ozone-forming emissions compared to vehicles using some conventional fuels; however, hydrocarbon emissions may be increased.
Ethanol (E85)	CH_3CH_2OH	Corn, grains, or agricultural waste	E85 vehicles can demonstrate a 25% reduction in ozone-forming emissions compared to vehicles using reformulated gasoline.
Hydrogen	H_2	Natural gas, methanol, and other energy sources	Zero regulated emissions for fuel-cell–powered vehicles, and only NOx emissions possible for internal combustion engines operating on hydrogen.
Liquified natural gas (LNG)	CH_4	Underground reserves	LNG vehicles can demonstrate a reduction in ozone-forming emissions compared to vehicles using some conventional fuels; however, hydrocarbon emissions may be increased.
Liquified petroleum gas (LPG)	C_3H_8	A by-product of petroleum refining or natural gas processing	LPG vehicles can demonstrate a 60% reduction in ozone-forming emissions compared to vehicles using reformulated gasoline.
Methanol (M85)	CH_3OH	Natural gas, coal, or woody biomass	M85 vehicles can demonstrate a 40% reduction in ozone-forming emissions compared to vehicles using reformulated gasoline.

Source: U.S. Department of Energy

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Advantages of Biofuels

Among the other advantages of using biofuels are the following.

- Increased use of domestic resources decreases the United States' dependence on foreign oil.
- Ethanol biodegrades quickly and is unlikely to contaminate water supplies.
- Farmers benefit from the increased demand and the increased price of crops.
- Better prices for farmers means less reliance on government subsidy programs.
- Carbon monoxide emissions are reduced.
- Carcinogens (cancer-causing substances) and lead are replaced by ethanol.
- Ethanol increases the octane level, reducing engine knock and creating cleaner engines.
- Ethanol is a water-free additive. Thus, it absorbs moisture and helps prevent gas lines from freezing.
- Fermented corn produces more than just ethanol. One bushel of corn (56 pounds) also produces 1.6 pounds of corn oil, 3.0 pounds of corn gluten meal, 13.0 pounds of gluten feed, and 12.5 pounds of carbon dioxide. The corn oil, corn gluten meal, and corn gluten feed are used in foods for humans and in high-protein livestock feeds. The carbon dioxide is used in carbonated beverages, as a refrigerant, in greenhouses to make vegetable crops grow faster, and to flush oil wells.
- For each 100 million bushels of corn used to make ethanol, an estimated 2,250 rural jobs are needed.

Disadvantages of Biofuels

As with almost all substances, there are disadvantages to using biofuels. Opponents to the use of biofuels state some of the following reasons for their position.

- Food grains should be used for food rather than for fuel.
- Ethanol should compete with other fuels equally.
- Ethanol can cause damage to fuel systems and can cause vapor lock in hot summer weather.
- Ethanol does not impact or reduce the importation of foreign oil.
- Ethanol should not have a portion of the motor fuel tax waived because that reduces the amount of money available for construction and repair of our highways.

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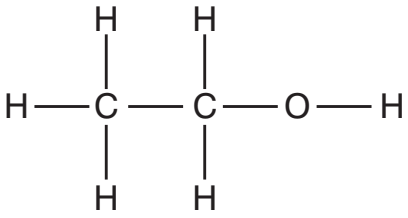
THE CHEMICAL NATURE OF ETHANOL

Currently, corn is considered the best source of biofuel. Ethanol is an example of an alcohol. The chemical formula for ethanol is C_2H_5OH, and the chemical structure of ethanol is shown below.



Ethanol is colorless and water-like in its pure form. It has a mild odor and boils at 172°F (78°C). It freezes at –170°F (–112°C). A pale blue flame is created with no soot when it burns; this makes it an ideal fuel. Ethanol mixes easily with water, is used as a solvent, and is used in hundreds of other chemicals. It has a pH of 7.0.

FIGURE 3. Currently, corn is considered the best source of biofuel.

RENEWABLE RESOURCES USED TO CREATE BIOFUELS

Grains, such as corn and soybeans; sugar cane; animal waste; plant waste; wood; algae; and many other sources may be used to produce biofuels. Ethanol is produced through the process of fermentation. Biodiesel is produced through the process of transesterification.

The starch in corn is made primarily of amylose and amylopectin and is the component used to make ethanol. Starch is an example of a carbohydrate. **Carbohydrates** are organic compounds that are the main source of energy for organisms. Carbohydrates are composed of carbon, hydrogen, and oxygen. The number of carbon atoms will vary, but the hydrogen and oxygen atoms will be found in a ratio of 2:1. Water is also found to have a 2:1 ratio. There are three types of carbohydrates.

Monosaccharides are simple sugars, or single-molecule sugars. They contain carbon, hydrogen, and oxygen in a 1:2:1 ratio. The most common monosaccharides are glucose, fructose, and galactose; all have a chemical formula of $C_6H_{12}O_6$. Molecules that have the same molecular composition but different structures are called isomers. Glucose is the main source of energy for plants and animals and is created during photosynthesis.

Disaccharides are double sugars. Lactose is formed from glucose and galactose and is found in milk. Sucrose is created from fructose and glucose and is found in sugar cane and sugar beets. Sugar cane is commonly used to produce ethanol. Maltose is formed from two glucose molecules.

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Polysaccharides are complex molecules containing three or more monosaccharides. Glycogen is the form in which animals store glucose. Starch is the form in which plants store glucose. Starch is found in potatoes, bread, vegetables, and rice. Cellulose is found in plants and is indigestible by humans.

The storage form of carbohydrates found in tubers, bulbs, and roots is starch. Two forms of starch are known: amylose and amylopectin. Carbohydrates in the form of starch are not used by plants because starch is insoluble in water. However, plants manufacture the enzyme amylase, which breaks starch down into soluble sugars for use by plants. Amylase is an enzyme important in germination because it breaks down the starch present in seed to provide energy for growing seedlings. Starch is easily digested by animals and an important source of energy.

FERMENTATION

Living things require energy. Organisms are classified by how they obtain their energy. Autotrophs are organisms, such as plants, that use the sun's energy to create energy. Autotrophs use **photosynthesis**, the process by which carbon dioxide and water are transformed, in the presence of light, into carbon-containing and energy-rich organic compounds. The basic equation for photosynthesis is:

$$\underset{\text{carbon dioxide}}{6CO_2} + \underset{\text{water}}{6H_2O} \xrightarrow[\text{(in the presence of sunlight)}]{\text{sunlight}} \underset{\text{sugar}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2}$$

Heterotrophs are organisms that consume other organisms to obtain their energy. Animals, including humans, are heterotrophs.

All organisms benefit either directly or indirectly from photosynthesis, since this is the lowest level of energy production for organisms. However, all organisms must use the process of cellular respiration to turn food into usable energy. **Cellular respiration** is the process of breaking down molecules of food (i.e., glucose) to release energy.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2} \rightarrow \underset{\text{carbon dioxide}}{6CO_2} + \underset{\text{water}}{6H_2O} + \underset{\text{energy}}{ATP}$$

The first step of cellular respiration is the process of glycolysis. **Glycolysis** is the first in a series of reactions during respiration in which a sugar molecule is degraded to pyruvic acid. Glycolysis means "breaking glucose." The glucose molecule is broken down into two pyruvic acid molecules (glucose → 2 pyruvic acid).

Fermentation is one process that occurs after glycolysis. **Fermentation** is a reaction in which complex organic substances are broken down into simpler ones. This causes energy to be released from molecules of food to furnish energy for metabolism and growth of microorganisms. Fermentation can occur in the presence of air or in the absence of air. **Aerobic** means that oxygen is present. **Anaerobic** means that oxygen is absent.

Fermentation changes the chemical environment of a food. Before humans knew much about fermentation, they simply used a small portion of food to add to new batches. This

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ensured that the microorganisms that are needed were included in the recipe. Fermentation is an important process in the preparation of many foods for human consumption and nonfood products such as ethanol. Many plant products undergo a fermentation process in order to produce the final products for the grocery shelf. Alcoholic fermentation and lactic acid fermentation are the two main types of fermentation.

Alcoholic Fermentation

Alcoholic fermentation is used by microorganisms, including yeast. The formula for alcoholic fermentation is:

$$\text{Pyruvic acid} + \text{NADH} \rightarrow \text{alcohol} + CO_2 + NAD^+$$

NAD^+ (nicotinamide adenine dinucleotide) is converted to NADH (NAD^+ + 2 high-energy electrons), which holds the electrons until they are moved to other parts of a cell to be used as energy.

Alcoholic fermentation is used to make bread. Yeast begins the process by using oxygen. After the oxygen is used up, carbon dioxide is produced, creating small air sacs in the dough. This causes the bread to rise. The alcohol that is produced evaporates.

Lactic Acid Fermentation

Lactic acid fermentation occurs in many cells, including muscle cells, and is used to make yogurt. Glycolysis produces pyruvic acid, which can then be converted to lactic acid and NAD^+ via fermentation. NAD^+ allows glycolysis to continue so that energy can continue to be produced. The equation for lactic acid fermentation is:

$$\text{Pyruvic acid} + \text{NADH} \rightarrow \text{lactic acid} + NAD^+$$

Oxygen is needed for the production of ATP. During intense exercise, the body produces a large amount of lactic acid because the body cannot take in enough oxygen. Lactic acid can build up in the muscle tissue and cause a burning and sometimes painful feeling. Continued intake of oxygen and "cooling down" will help use up the lactic acid.

Products of Fermentation

The primary purpose of fermentation is to furnish energy for metabolism and growth to microorganisms, including bacteria, yeast, and mold. By-products of fermentation are carbon dioxide, water, alcohol, and lactic acid. A **by-product** is anything produced in the course of making another thing—a secondary or incidental product or result. Fermentation creates a variety of substances used by humans.

Foods that undergo fermentation include yogurt, cheese, wine, cider, bread, sauerkraut, flavorings, candy, fruit juice, silage, and beer. Pickling involves fermentation. Foods that are frequently pickled include beans, onions, cauliflower, cucumbers, tomatoes, and cabbage.

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Nonfood items that undergo fermentation include ethanol, biodiesel, antibiotics, laundry detergent, insulin, growth hormone, cellulose, monoclonal antibodies, compost, Snomax (makes snow), Ice-minus (keeps ice off plants), medicine to dissolve tumors, and medicine to clot blood. Fermentation is a critical part of our well-being that supplies us with necessities beyond food.

ETHANOL PRODUCTION

To produce ethanol, the manufacturer must have adequate knowledge of microbiology, chemistry, and engineering. A variety of techniques have been developed over time.

A simplified procedure for ethanol production is provided here.

1. Corn is finely ground.
2. Water and enzymes are added to produce a slurry. Sodium hydroxide or sulfuric acid may be added to maintain a pH of 7.0.
3. The corn is cooked, and the enzymes alpha amylase and gluco amylase are added. Enzymes serve as a catalyst to help chemical reactions take place by decreasing the activation energy needed. For fermentation to occur, the starch must be broken down into monosaccharides. The addition of the enzymes and the use of heat cause the starch to be broken down into complex sugars called dextrins.
4. Through cooling and the addition of different enzymes, these complex sugars are broken down into simple sugars, or monosaccharides, such as glucose.

BROADENING AWARENESS...

AMAZING ASPECTS: Ethanol Production Trends

In the United States, ethanol has been mixed with gasoline since the late 1970s. Production and use of ethanol slowly increased, but in the first 10 years of the twenty-first century, ethanol became established as an important portion of the gasoline pool. By 2011, ethanol made up 10 percent of gasoline volume used for domestic consumption. More than 99 percent of ethanol is consumed as E10, a blend of 10 percent ethanol and 90 percent gasoline by volume. Gasoline blends with more than 51 percent ethanol by volume (E85) account for less than 1 percent of the total ethanol produced for motor fuels.

Production of ethanol for fuels reached an all-time high in 2011. However, expansion has stopped because of a saturation of the U.S. gasoline market with 10 percent ethanol blends. Trade with Brazil has also been a factor. That country is the world's other major producer of biofuels. As the United States became a net exporter of fuel ethanol in 2010, it began importing lower-carbon Brazilian sugar-cane ethanol to meet the California low-carbon fuel standard (LCFS).

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5. After the starch has been broken down, yeasts are added. **Yeasts** are any of various unicellular (single-celled) fungi in which little or no mycelium develops and that ordinarily reproduce by budding; they live on sugary solutions. The dry granules of yeast that are bought at the store become active when they become moist. *Saccharomyes* sp. (a type of yeast) grow and cause fermentation to occur.
6. The mash is then distilled, and the ethanol is collected through evaporation. **Distillation** is the process of heating a substance and then condensing the vapor or gas that is created to purify or concentrate it. Gasoline is created through the distillation of crude oil. Ethanol boils at 172°F (78°C); thus, the mash is heated to slightly higher temperatures, making collection relatively easy. The gas is captured and allowed to cool.
7. The ethanol is further purified.

Ethanol retains most of the energy produced through fermentation. This is not efficient for the yeast, but it makes ethanol an excellent fuel source.

Researchers are working on ways to decrease the fermentation process from a few days to hours. Geneticists and plant scientists are working on creating better varieties of corn. They hope to make the process more efficient by increasing the amount of starch in the corn.

FIGURE 4. Large facilities are used in the ethanol fermentation process.

Summary:

Plants incorporate carbon atoms into carbohydrates, proteins, lipids, and nucleic acids. Much of the carbon absorbed remains "locked up" in the plants' biomass until decomposition or fire releases it back to the atmosphere. Fossil fuels are fuels formed from the remains of animals and plants deposited in the geologic past.

Biomass is any organic plant or animal matter that can be used to produce energy, such as ethanol, methanol, and methane gas. Grains, such as corn and soybeans; sugar cane; animal waste; plant waste; wood; algae; and many other sources may be used to produce biofuels. Ethanol is produced through the process of fermentation. Biodiesel is produced through the process of transesterification.

Fermentation causes energy to be released from molecules of food to furnish energy for metabolism and growth of microorganisms. Alcoholic fermentation and

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lactic acid fermentation are the two main types of fermentation. Ethanol retains most of the energy that is produced through fermentation.

Checking Your Knowledge:

1. How does the carbon cycle relate to energy?
2. What forms of biomass are used for bioenergy?
3. How is bioenergy produced from biomass?
4. What are advantages and disadvantages associated with biofuels?
5. What is the process of fermentation?

Expanding Your Knowledge:

The use of corn as biomass for the production of ethanol has been somewhat controversial. Research the topic, and outline the arguments for and against the use of corn for bioenergy.

Web Links:

The Carbon Cycle
http://earthobservatory.nasa.gov/Features/CarbonCycle/

U.S. Energy Information Administration
http://www.eia.doe.gov/

U.S. Department of Energy
http://www.energy.gov/

How Biomass Energy Works
http://www.ucsusa.org/clean_energy/technology_and_impacts/energy_technologies/how-biomass-energy-works.html

Renewable Biomass
http://tonto.eia.doe.gov/kids/energy.cfm?page=biomass_home-basics

Agricultural Career Profiles
http://www.mycaert.com/career-profiles

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