NEW DEVELOPMENTS IN BIOFUELS
By Gary Antonides

Ethanol in Gasoline.

A few years ago, almost all the ethanol in gasoline was produced from edible corn, but there was an expectation that cellulosic ethanol would become a major source as production techniques improved. This was eagerly anticipated by conservationists because producing ethanol from corn has many problems. It uses a lot of land that could be used for other food production. Corn uses a lot of water and fertilizer to produce, depleting aquifers and polluting streams and rivers. It uses almost as much energy to produce as it yields in combustion. However, in 2005 and 2007, Congress mandated that we use certain amounts of ethanol in our gasoline, increasing year by year, in order to decrease our dependence on foreign oil and reduce tailpipe emissions. Congress also recognized that cellulosic ethanol was environmentally friendlier and mandated that an increasing share of the required amounts be cellulosic.

Now the situation is quite different than what was anticipated. The U.S. is producing lots of oil domestically, but consumers are using less. The lesser amount of gasoline used requires less ethanol if we continue to use the 10% blend (E10) that is common today. But the mandated amounts, which were expressed as definitive quantities rather than percentages, are greater than we can use in E10. As a result, E15 (15% ethanol) has been approved for cars built after 2000. The ethanol industry, which has some of its more than 200 plants idle is, of course, all for that. The oil industry, understandably, is against it. But almost everybody acknowledges there are problems with E15. It can't be used in ATVs, lawn mowers, other small engines, boats, etc., and there are claims that only cars built after 2012 can use it. Some say that auto manufacturers will not honor warranties if E15 is used. Gas stations must install new pumps if both E10 and E15 are sold. Blending pumps could be used instead, but the hose would hold about 1/3 of a gallon of whatever the previous customer bought. It has been proposed that cars be required to buy at least 4 gallons of gas to dilute what may be in the hose. Labeling is apparently up to the states, and not all require labeling ethanol content. To solve some of these problems, the EPA requires "Misfueling Mitigation Plans." The EPA apparently has some flexibility in setting ethanol quotas lower than the original law requires. The regulatory details and nuances are complex, but the EPA does seem to be setting quotas that are favorable to ethanol proponents. Obviously, the land use, water use, and fertilizer use problems are exacerbated by producing more corn ethanol.

At present, we are still dealing primarily with corn ethanol because production techniques for cellulosic ethanol, which can be produced from corn stalks, switchgrass, and many other plants, and which does not use nearly as much water or fertilizer, have not improved as much as anticipated. But there are some new promising developments as reported below.

Cellulosic Ethanol.

http://www.nature.com/news/cellulosic-ethanol-fights-for-life-1.14856**,** March 2014, reports that pioneering cellulosic biofuel producers feel they need US government aid to break into today's tough market. As an example, when this report was written, Abengoa Bioenergy's cellulosic ethanol plant near Hugoton, Kansas, was about to start production, and its owners expected it to join a fermented-fuel revolution. Unlike conventional ethanol factories, in which yeast feeds on sugars in foodstuffs such as corn kernels, the Hugoton facility will make use of what is largely agricultural waste – the cellulose in thousands of tons of corn stover (the leaves, stalks and husks left over after the corn harvest) which is much less controversial than conventional corn ethanol. Ethanol made from corn stover produces at least 60% less greenhouse-gas emissions than gasoline, and making it does not require any extra farmland.

Abengoa is a multinational company from Spain, and its plant is one of three US facilities that were to start commercial production of cellulosic ethanol in 2014. (The others are both in Iowa). Yet just as the fuel is on the cusp of making it big, a glut in the market and government policies could choke its progress, in addition to the fact that producing cellulosic ethanol is difficult.

Producers must dismember large, indigestible molecules such as cellulose and hemicellulose to yield fermentable sugars. This requires the biomass to be ground up and pretreated with acids. A cocktail of enzymes must then be applied to chop up the tough biological polymers inside, and then yeast is added to the resulting sugars.

Corn ethanol is now slightly cheaper than gasoline, but cellulosic ethanol is more expensive than both. A cellulosic-ethanol plant's capital costs are roughly twice those of a corn-ethanol plant. Unable to undercut its rivals, cellulosic ethanol will be heavily dependent on the Renewable Fuel Standard (RFS). Yet the problems with cellulosic and its delayed production has prompted the EPA to reduce the amount of cellulosic ethanol that refiners are required to blend into their gasoline. The RFS plan for 2014 originally called for 100 times what the EPA eventually proposed. Groups working on renewable fuel say that producers will easily make more than that once they get going, and the expensive excess ethanol might have to be sold at a loss on the open market, potentially crippling the fledgling cellulosic industry.

Cellulosic ethanol could get cheaper with more efficient stover harvesting, beefier enzymes and cheaper pretreatments. The industry has already cut costs from as much as $9 per gallon five or six years ago to close to $2 today, says Thomas Foust, director of the National Bioenergy Center, part of the National Renewable Energy Laboratory in Golden, Colorado.

In 2014, there were 6 cellulosic ethanol plants in North America, designed to produce 30 to 114 million liters each:

Biological Process

Location	Product	Feedstock
Emmetsburg, Iowa	Ethanol	Corn Stover
Nevada, Iowa	Ethanol	Agricultural Residues
Hugoton, Kansas	Ethanol	Corn stover/Ag Residues

Thermochemical Process

Location	Product	Feedstock
Edmonton, Alberta	Methanol	Municipal Solid Waste
Columbus, Miss.	Gas/Diesel	Woody Biomass
Vero Beach, Florida	Ethanol	Ag/Municipal Solid Waste

Thermochemical Processes

The costs mentioned above apply to the "Biological" process in the above list. But some see more promise in a different approach to breaking up cellulose, the "Thermochemical" process mentioned in the above list. This process is a brute-force combination of temperature, pressure and chemistry. It can produce either a crude bio-oil (by means of pyrolysis) or a stream of carbon monoxide and hydrogen known as syngas (by means of gasification). After further treatment and refining with the help of chemical catalysts, both can be turned into hydrocarbons such as gasoline, diesel and jet fuel. Crucially, these can replace normal fuels with no adjustments to engines, and don't contribute to the oversupply of ethanol.

Thermochemical processes can also use lower-quality feedstocks, anything from wood chips to municipal solid waste. For example, the plant in Edmonton will be able to transform syngas into methanol, then methanol into ethanol, and it will hopefully be cheaper than corn ethanol. This is mostly because the feedstock is cheap, if they are not actually paid to take it. If there's too much ethanol on the market, producing syngas also gives the company a lot of flexibility. If there are changes to policy mandates or to the market, the system could be switched to making hydrocarbon fuels or higher-value chemical products.

Research funding is shifting to thermochemical methods. In 2013, an energy-department project to supply the US Navy with advanced biofuels provided funding for four facilities that will all use thermochemical methods to make drop-in fuels. Thermochemical processes are also used in the first two commercial cellulosic plants in the United States, in Columbus, Mississippi and near Vero Beach, Florida.

In spite of these advantages, the biological approach may still be able to compete by using ever-cheaper feedstocks, and a new generation of enzymes that can turn municipal waste into ethanol. A pilot plant in Spain was built to demonstrate this approach, which may be eventually be used in the US.

In http://www.nature.com/news/renewable-energy-biofuels-heat-up-1.15074, April 2014, Kim Krieger describes some of the specifics of this new generation of thermochemical plants. After biomass is heated to 900 °C, it gives off hydrogen and carbon monoxide (gasification). These gases can be turned into liquid fuels by Fischer–Tropsch reactors, such as the one in the figure, which was built by Velocys in Plain City, Ohio.

One of the efforts (unfortunately unsuccessful) to use the thermochemical process was in London. By the end of 2015, all British Airways flights out of London City Airport were to be fueled by the rubbish discarded by the city's residents. The rubbish was to be processed at a biofuels plant to be constructed on the eastern side of the city. Each year it was to turn some 500,000 tons of the city's waste into 60,000 tons of jet fuel, a similar quantity of diesel fuel and 40 megawatts of power. This level of output would hardly be noticed at conventional petroleum refineries, which typically generate as much product in a week, but gathering enough biomass to run a petroleum-scale refinery is impractical. For this reason, many new biofuel reactors that take agricultural or other waste are small. The idea is that they can cut transportation costs by locating the reactors close to the feedstock. But it was reported in Sept. 2015 that the company contracted for this went bankrupt.

Thermochemical process proponents argue that novel catalytic techniques and compact designs will make these second-generation biofuel plants not just environmentally friendly, but also profitable enough to compete with petroleum-based fuels without subsidies. Commercial units have begun to spring up from Finland to Mississippi to Alaska. If these second-generation plants do succeed, they will have an advantage over their predecessors in that they create fuels in a low-carbon way that suits existing vehicles. Although fuel prices are low now, several years of historically high oil prices has spurred vigorous research into thermochemical reactors.

Gasification.

The most common thermochemical approach is gasification, in which carbon-rich materials such as coal, wood chips or municipal waste are heated to high temperatures (>700 C) in a controlled environment to produce synthesis gas or 'syngas', a mixture of mainly hydrogen and carbon monoxide. Usually, a limited amount of oxygen or steam is injected into the reaction chamber. The key is that combustion does not occur.

Some gasifier units vaporize the waste with jets of ionized plasma that heat the material to some 3,500 °C. Such torches are more energy intensive than other methods of gasification, but the plasma torches are better for municipal waste, whose contents can vary markedly, because the composition of the syngas can be kept consistent by adjusting the temperature of the torches. Consistency is important for optimizing the second step of the process, in which the syngas is sent into a chemical reactor where it undergoes the Fischer–Tropsch reaction, which fuses hydrogen and carbon monoxide into long-chain hydrocarbons.

The BioMax gasifier, developed by the Community Power Corporation in Englewood, Colorado, is small enough that four can fit into a standard shipping container, and can run on almost any kind of shredded biomass, from food scraps to cardboard to wood chips. The resulting syngas can then be used in place of natural gas for heating, cooling or electricity generation. A typical unit generates about 150 kilowatts, enough to power between 25 and 50 homes. And in the near future, BioMax units should be able to plug in a Fischer–Tropsch reactor and produce biodiesel as well. They hope to sell the units throughout Alaska and northern Canada, where electricity and transportation fuels are expensive.

Among the strongest selling points of the two-step gasification approach to biofuels is the fact that almost all the syngas gets turned into hydrocarbons of the kind that produce fuels that burn cleanly and completely. But that advantage has not kept researchers from exploring a single-step alternative. In the pyrolysis approach, the biomass is heated in the absence of oxygen to some 500 °C and converted into organic liquids directly. These liquids can then be refined into fuels using standard technology. Several companies are already testing the commercial viability of the technology. For example, Ensyn Technologies in Ottawa is marketing units which they would install next to lumber mills, where each one would be capable of turning waste wood into some 76 million liters of pyrolysis oil a year. That would be enough to warm 31,000 homes or to fuel about 35,000 automobiles. Green Fuel Nordic, from Finland, is planning to install at least one such unit in a Finnish town where it will process waste from the country's forestry industry.

The financial viability of any of the second-generation biofuel technologies is still an open question. For example, one of the world's most advanced pyrolysis biorefineries in Columbus, Mississippi. demonstrated its technical viability by producing some 3.5 million liters of gasoline and diesel fuel from wood waste in 2013. This is about as much as a conventional petroleum refinery produces in a day. Unfortunately, they expected to run out of operating funds last August.

https://www.wm.com/about/press-room/2010/20100303-energy-solutions-announces-plasma-gasification.jsp reports on a recent breakthrough in the gasification process. While this process has historically resulted in low yields, the

University of Minnesota has recently developed a metal catalyst, which reduces the reaction time for biomass by up to a factor of 100.

It also points out that, in industrial settings such as steel milling and petroleum refining, large amounts of waste gas are produced. Rather than vent these toxic gases into the atmosphere, they are captured and used to produce syngas. Doing so not only benefits the environment, but the products derived can be sold or used in cogeneration facilities.

Syngas can be used for the production of Hydrogen, Nitrogen, Ammonia, Carbon Monoxide, Carbon Dioxide, Steam, Minerals and Solids, and Sulfur, depending on the original feedstock. Though synthesis gas need only contain hydrogen and carbon monoxide, it frequently contains other components as well. Microbial fermentation of syngas can be used to develop, among other things, Ethanol, Butanol, Acetic Acid, Butyric Acid, and Methane.

The benefit of fermentation is that it is simpler and takes place at lower temperatures than chemical conversion. Biologic fermentation can also tolerate high levels of sulfur, making it ideal for use in steel factories and power plants that burn coal. In general, the biologic process is simpler because it does not require careful control of reaction conditions. The biggest disadvantage is its low throughput. It takes days to produce what a thermochemical process can produce in minutes. Another advantage of gasification is that it is able to extract more energy (about twice as much) from the biomass as biological processes.

It is estimated that as much as 1.2 billion dry tons of biomass could be available for conversion to syngas in the U.S. by 2050. This would result in about 21 quadrillion BTU/year of energy, which is well above the 16 quadrillion BTU/year used in transport and roughly 21% of the total 98 billion BTU of energy used each year in the United States.