

Biofuels

Biofuels have been used since the dawn of human civilization



Biofuels were used for cooking,...



**... for heating human dwellings,
e.g., caves...**



...or for making light.



**Oil lamp (olive oil, or
whale oil)**



Bee wax



Wooden torches

In the XX-th century simple biofuels like firewood were “running out of favor” – they were used mostly in leisure activities, e.g., for barbecuing, in “family time” at a fireplace, etc.

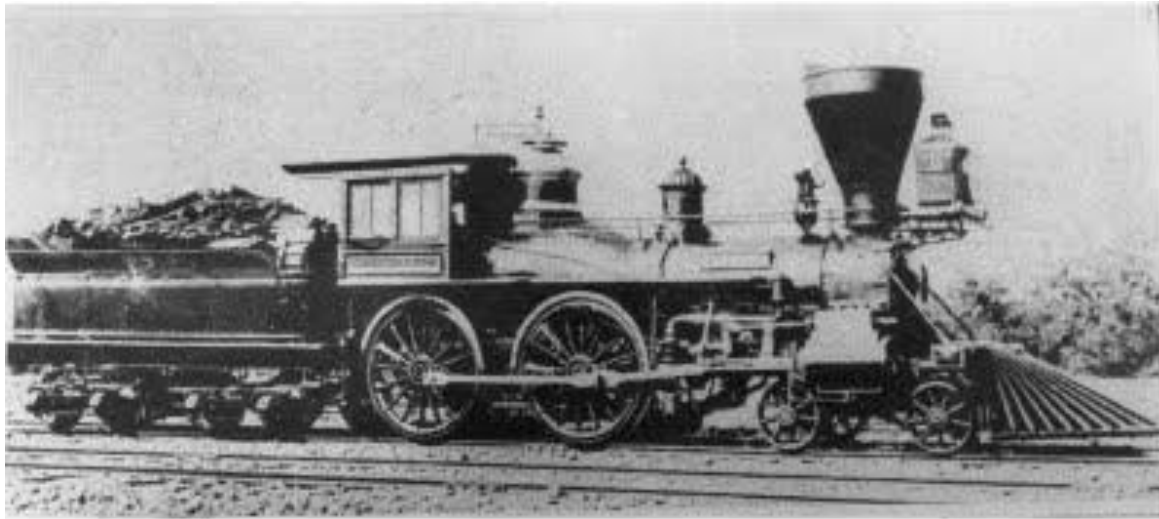


However, firewood is now “returning with vengeance”, as *wood pellets*.

Single-home heating installations using firewood in such form are fully automatic and require little maintenance.

The wood-pellet industry in the US is growing fast. Advantages: it’s a non-polluting fuel, does not add “new” CO₂ to the atmosphere (rather, it “recycles” the natural CO₂), and there is much wood available for making pellets.

However, today we most often talk about biofuels as of potential alternatives to fossil fuels used in transportation.



It's not a new concept – in the XIX Century many American trains were running on firewood.

**Yet, today we need “bio-alternatives”
to liquid petroleum-based fuels,
such as gasoline, diesel,
and jet fuel.**

A promising alternative to gasoline is bio-ethanol.

Bio-ethanol has been used by humans since ancient times, but rather for “fueling” people (by drinking beer, wine, whisky...), not cars.



Essentially, almost all ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) ever made by humans was “bio”, because it was obtained from natural sugars made by plants, through a fermentation process involving yeast (single-cell living microorganisms).



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Gasoline engines can run on ethanol or ethanol-gasoline mixtures after a small modification of the fuel-injection system (up to 15% of ethanol, no modification is even needed).

The energy content of ethanol is only ~2/3 of that of gasoline.

**Still, not a major problem.
We can make the fuel
tanks larger!**

A real “bio-ethanol paradise” is Brazil. About 50% of their cars run on ethanol, not on gasoline.

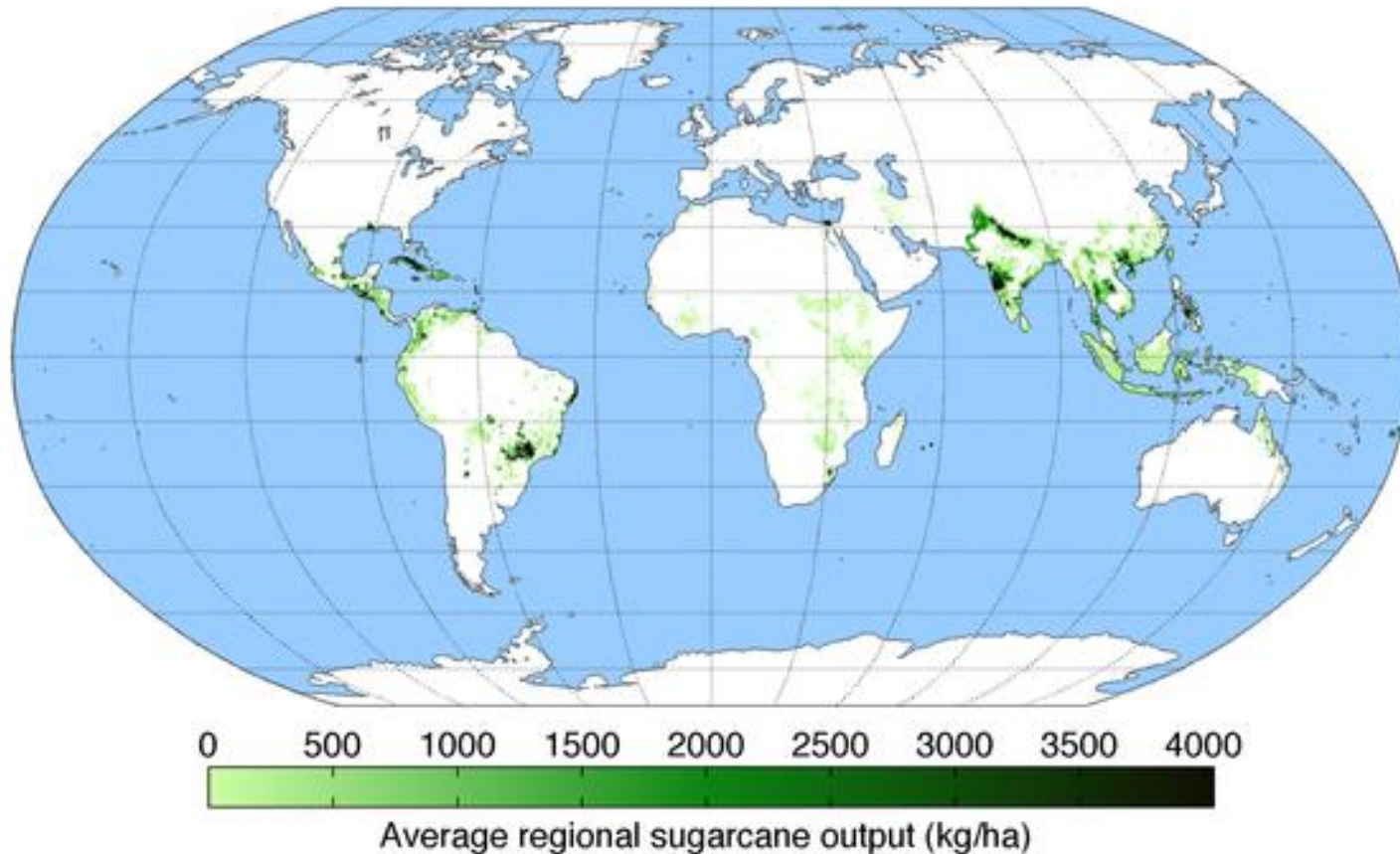




Brazilians make their ethanol from sugar cane – a plant that grows very well in their hot climate. The process is pretty straightforward: the “syrup” extracted from the canes is fermented by yeast. The product contains ~15% of $\text{CH}_3\text{CH}_2\text{OH}$. Then, pure ethanol is extracted from it by distillation.

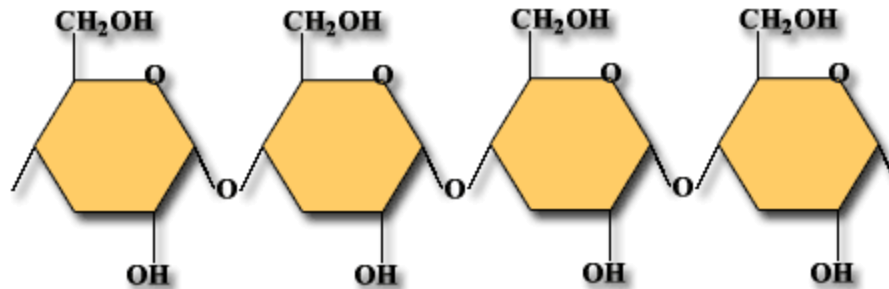
Brazilian biofuel: $\frac{\text{Energy content}}{\text{Total energy input}} \approx 6$

Unfortunately, sugar cane does not grow well in most of the territory of the United States...



However, ethanol can also be obtained from starch. Starch molecules are made up of many sugar molecules, linked into a long “chain”.

However, ethanol can also be obtained from starch. Starch molecules are made up of many (several hundred) sugar molecules, linked into a long “chain”.

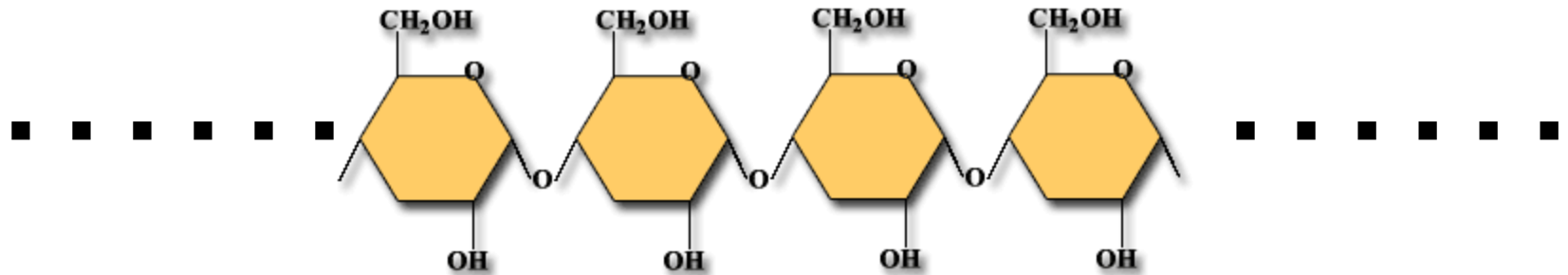


There are many starch-producing plants that grow well in the US: wheat, barley, potato, corn (a.k.a. maize). The latter is the best “starch-producer” of all of them.



But yeast cannot convert starch to ethanol directly. Therefore, a two-step process is needed:

Amylose (starch) molecule: 500 or more sugar molecules are linked to form a long chain:



The two-step process:

(a) First, the amylose chain has to be broken down into individual sugar molecules by special enzymes .

Fortunately, the enzyme is easy to obtain – there is plenty of it in sprouting barley seeds. The recipe has been known for centuries, and widely used, e.g., by whisky distillers (whisky is made from starch!)

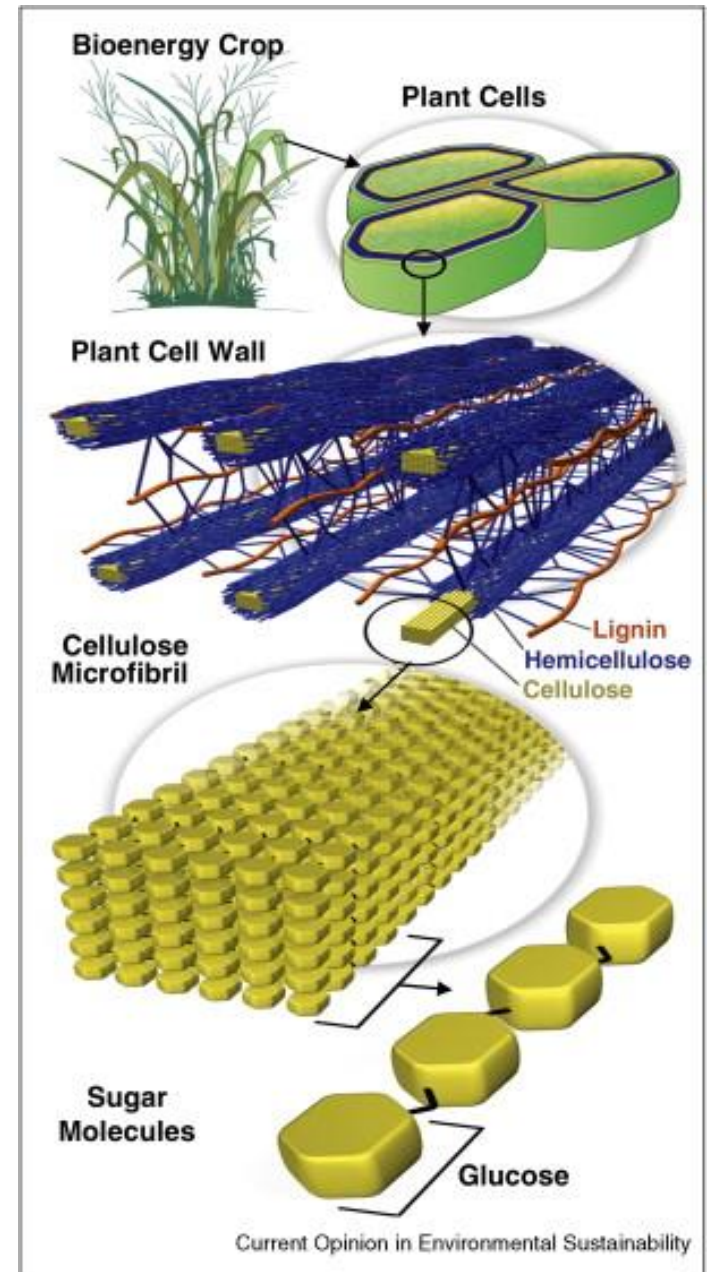
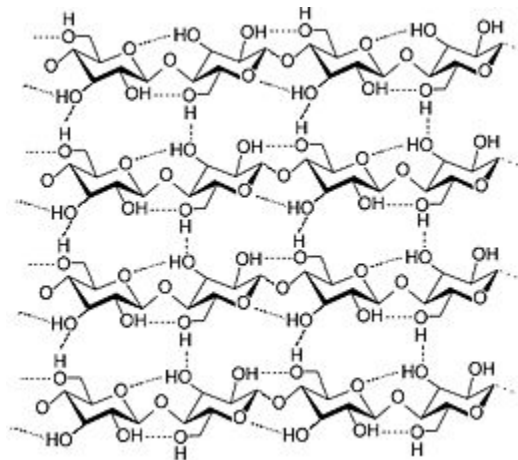
(b) Then, the sugars are fermented by yeast, the same way as in the Brazilian process.

However, the entire process is much more energy-consuming than that used in Brazil. The energy content of US bioethanol is only about **two times higher than the net energy input. Some critics claim that the ratio is **even less than two**.**

One highly interesting possible solution of the bioethanol problem, namely:

Cellulosic ethanol!

In plants, cellulose is the compound that gives rigidity to the cells. The bonds between each cellulose molecule are very strong, which makes cellulose very hard to break down.

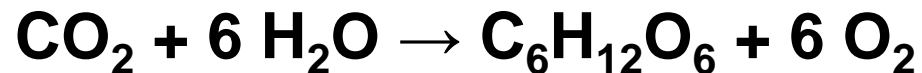


The “scaffoldings” that makes the plant rigid and allows them to “stand up”, overcoming gravity – are made up of three major compounds:

- (a) Cellulose**, with crystalline-like structure, built exclusively of interconnected glucose chains with very strong bonds between them;
- (b) Hemicellulose**, a close cousin of cellulose, but with shorter chains made of many different sugar molecules, including such with **five carbon atoms**;
- (c) Lignin** – a compound of a complex chemical structure, **not** made up of sugar molecules.

The “elementary building blocs” used by the plant for making its body and for performing all vital functions are **sugars**, created in the process of photosynthesis:

The formula for photosynthesis is:



In other words:

Carbon dioxide + Water + Light energy → **Glucose** + Oxygen

But most of the sugar produced by photosynthesis in plants is converted into “scaffolding” compounds, not left in the sugar form, or converted to starch.

Even in maize (corn) about 85% of sugar is used for making fibers, leaves, the stem....

In the existing technology of making corn bioethanol, the cellulose is simply wasted.

If we were able to decompose cellulose back into sugars, we could “employ” yeast to do the fermentation, and from one maize plant we would obtain **six times as much bioethanol** as from the starch-based process!

Actually, corn wouldn't even be needed any longer – there are other plants that yield much more cellulose per acre than corn, and are much less “demanding” – one such plant is switchgrass that can be grown almost everywhere in the US.



Rosy Future?



From Grow to Go!

How Biomass Can Work for Tennessee

The state needs clean, alternative fuels. Grain-based ethanol and biodiesel are important, known commodities, but a plentiful and untapped fuel source, biomass, offers Tennessee the opportunity to create a sustainable biobased economy with cellulosic ethanol.

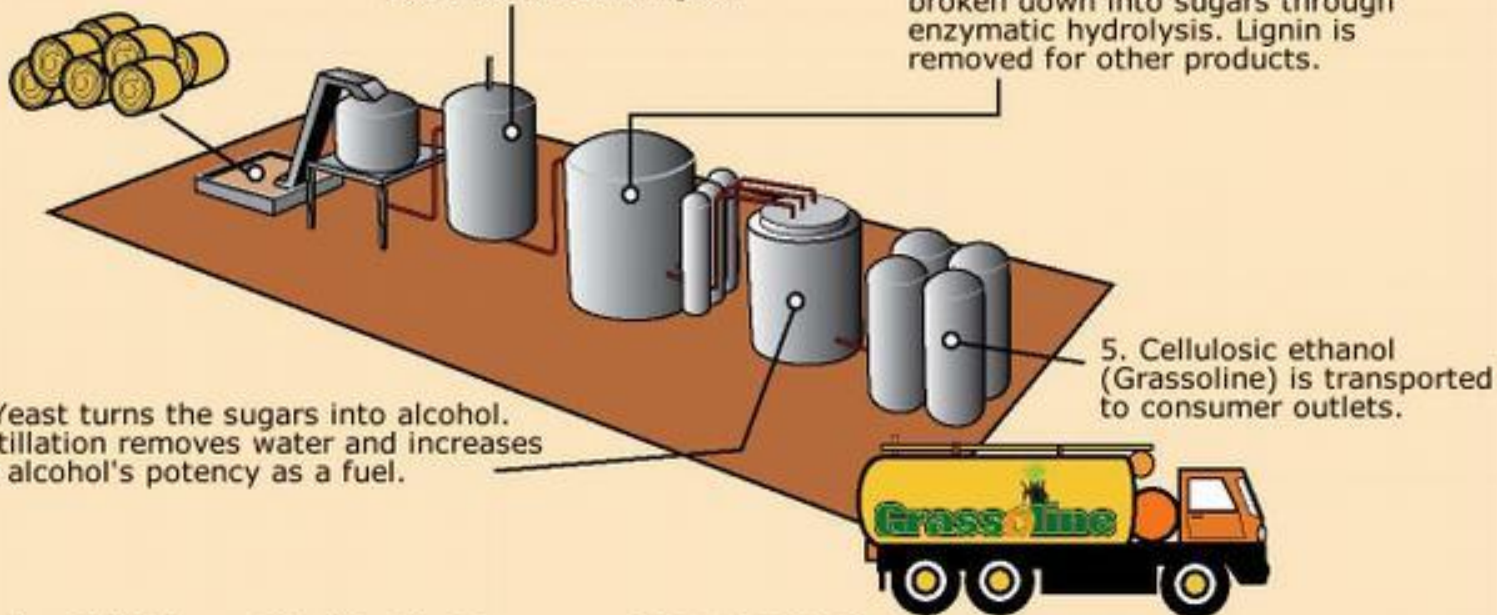
1. Switchgrass, wood chips and other biomass arrive at the biorefinery.

2. Steam and acid separate shredded biomass into cellulose, hemicellulose and lignin

3. Cellulose and hemicellulose are broken down into sugars through enzymatic hydrolysis. Lignin is removed for other products.

4. Yeast turns the sugars into alcohol. Distillation removes water and increases the alcohol's potency as a fuel.

5. Cellulosic ethanol (Grassoline) is transported to consumer outlets.



For the full vision outlined by the Tennessee Biofuels Initiative see www.UTbioenergy.org

Unfortunately, ...



In the case of “cellulosic bioethanol”, the bottleneck is...



**Termites do it... Mushrooms do it...
Even cows do it! (well, with the help
of some microorganisms, but they do it!)**

Enzymatic cellulose hydrolysis:

- Industrial-scale technologies do exist;
- Several pilot installations are operating;
- But a big challenge still is to make them **cost – competitive!!!**

For details, please look at the Websites listed [here](#).

Hydrolysis + fermentation is not the only possible way of obtaining biofuels from “biomass”:

Another method which is currently the subject of vigorous research is **“gasification”** -- through reacting the biomass with steam and air at high temperatures.

The gas mixture generated may be further processed to obtain **liquid biofuels.**

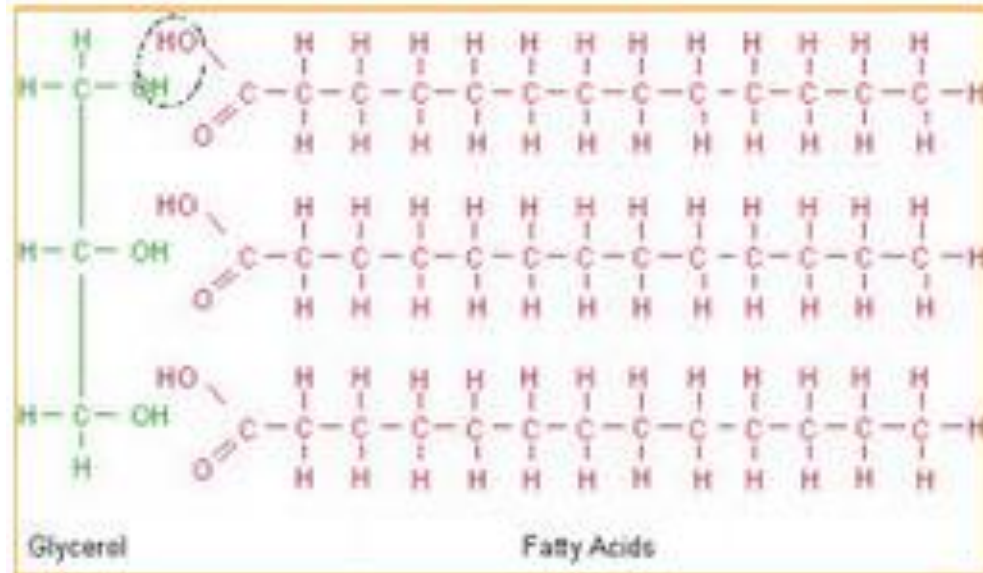
Yet another method may be by simple burning of the biomass in conventional-type thermal power plants.

Please read the article from “SCIENCE” magazine, in which the “pros” and “cons” of different methods of biomass processing are discussed.

Another liquid biofuel that currently receives strong interest is “biodiesel”.

“Normal” diesel fuel consists of hydrocarbon molecules (general chemical formula: C_nH_{2n+2}) with $n = 12-16$.

Almost all fats produced by plants or animals have the same general structure: namely, three “fatty acid molecules” are attached to a single glycerol molecule.



A single “fatty acid chain” contains a similar number of carbon atoms as an average hydrocarbon molecule in diesel fuel.

The viscosity of some vegetable oils is low enough for using them directly as a fuel for a Diesel engine.

In fact, in the first public demonstration of the engine – at the Paris World Exhibition in the year of 1900 – Dr. Rudolf Diesel used peanut oil as a fuel.



Dr. Rudolf Diesel

However, the viscosity is still “a bit too high”. In cold weather, the oil “thickens”, and the engine cannot be started.

Some ingenious “biodiesel fans” install special heaters that heat the oil up to about 180 F. Then they can run, e.g., on leftover oil they can buy for cents from restaurants.



The first engine prototype

However, a better solution is to de-attach the fatty acid chains from the glycerol molecule. Single chains are chemically quite similar to the diesel fuel hydrocarbon chains – except that they are acids, meaning that they are pretty corrosive substances.

Fortunately, their acidity can be easily neutralized by combining each chain with a molecule of methyl alcohol CH_3OH , in a process called “esterification”. The physical properties and the energy content of the “fatty acid methyl esters” obtained in that way are very similar to those of a “normal” diesel fuel.

This is how biodiesel is being made at industrial scale – but the esterification apparatus is so simple that one can install such a device in a garage. Many such “esterifiers” have been built by OSU student.