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INDUSTRIAL DEVELOPMENT ORGANIZATION

**GREEN  
CHEMISTRY**



# RENEWABLE FEEDSTOCKS



Image: Wikimedia Commons, Author: R. Möhler

**DAY 2 SESSION III**  
**4-DAY PRESENTATION**

[www.greenchemistry-toolkit.org](http://www.greenchemistry-toolkit.org)



## USE OF RENEWABLE FEEDSTOCKS

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**A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.**



Image: Wikipedia, Pongamia Pinnata Seeds

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## Topics To Be Covered

1. Energy and Feedstock Consumption
2. Petroleum
3. Renewable Feedstocks
  - Biomass Feedstocks
  - Carbohydrate Feedstocks
  - Lipid Oils and Terpenes as Feedstocks
  - Protein Feedstocks
4. Renewable Feedstocks as a Source of Energy
5. First, Second, and Third Generation Feedstocks
6. The Advantages and Drawbacks of Biofuel

# RENEWABLE vs. DEPLETING FEEDSTOCKS



## Feedstock:

- A raw material to supply or fuel or industrial process.

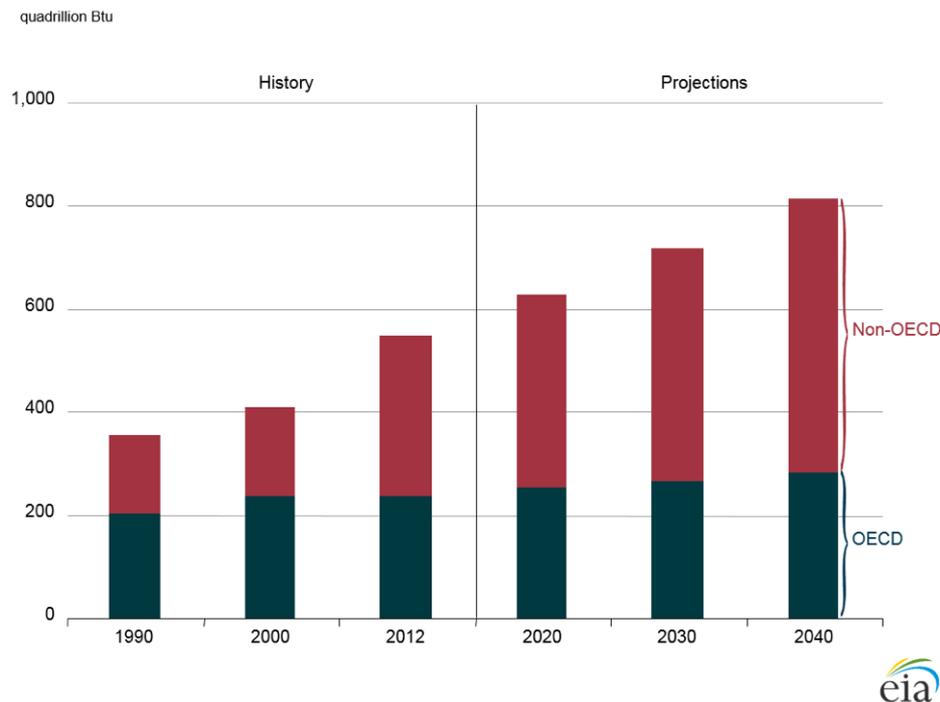
## Renewable or Depleting is a question of time:

- A renewable resource is determined to be renewable if it can be replenished in a relevant amount of time.
- Fossil fuels are depleting because they cannot be replenished in a practical timeframe from vegetation.



Image: Wikimedia Commons, Author: Johnlacrosse

# ENERGY CONSUMPTION: DATA AND PROJECTIONS



Increasing world energy consumption since 1990.

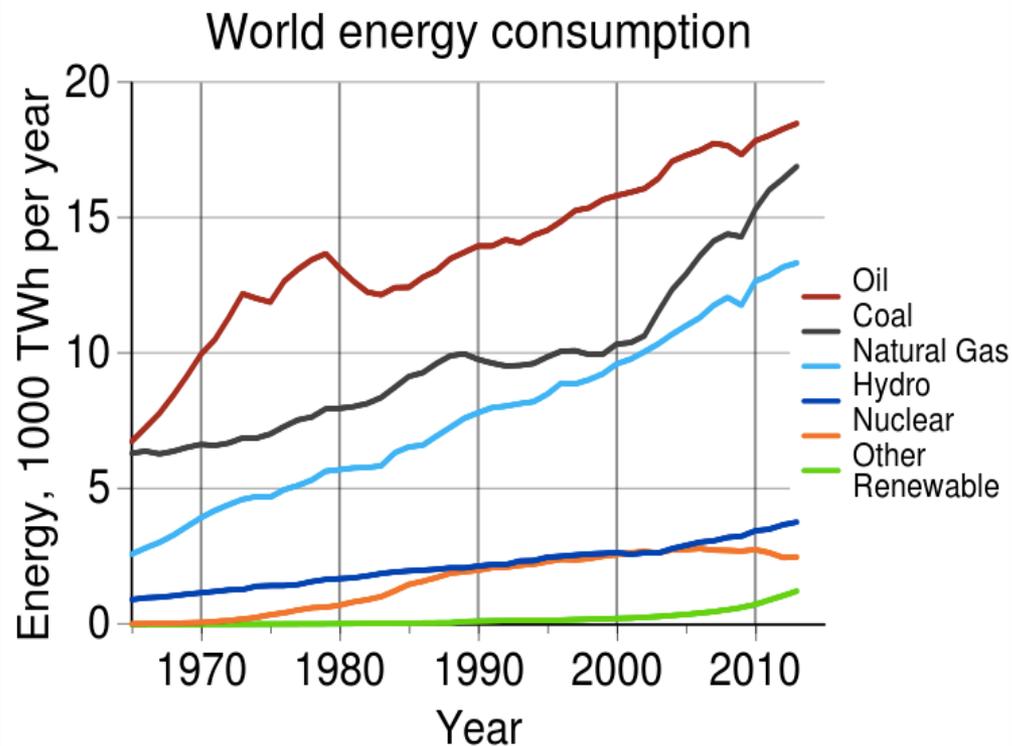
The graph includes a prediction for year 2035, where the projected energy consumption will reach 770 quadrillion British Thermal Unit [BTU].

Source: U.S. Energy Information Administration [U.S. EIA].



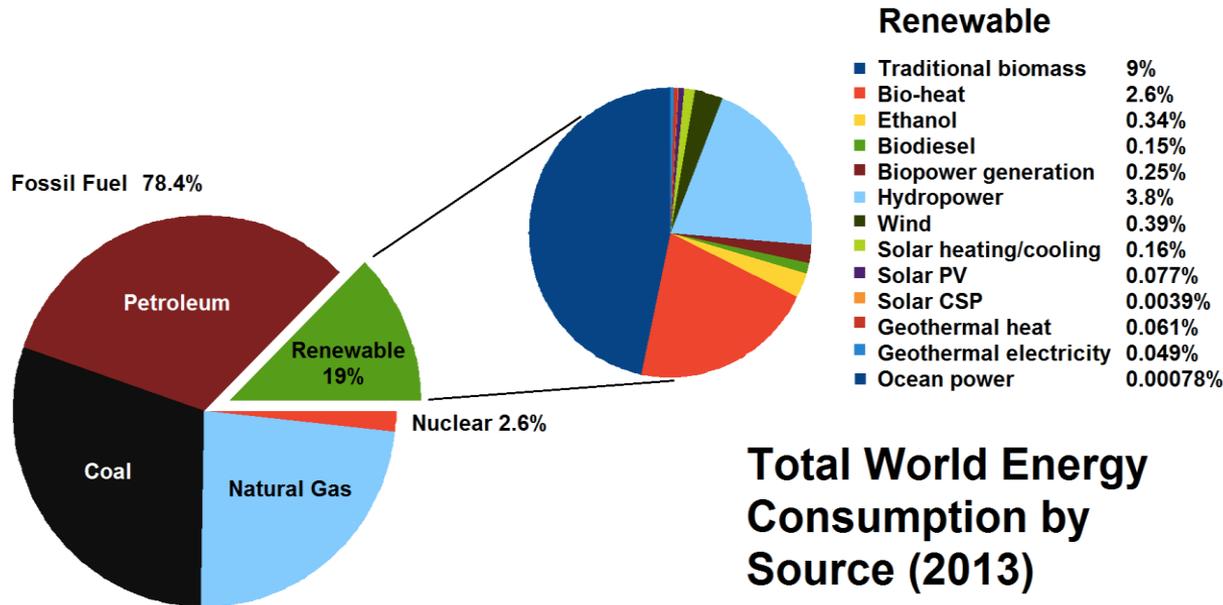
Oil, coal and natural gas remain the predominant sources of energy, but the use of renewables is still increasing.

Source: Statistical Review of World Energy



Increasing world energy consumption: 1970-2010.

# ENERGY FEEDSTOCKS SOURCES



World energy consumption by source as reported in 2013.

While the use of fossil fuels is still predominant, by 2013 there was an increase in the use of renewable sources of energy. Most renewable energy comes from biomass.

Source: REN21 Renewables 2014 Global Status Report.

# WHAT ARE THE MOST COMMON FEEDSTOCKS TODAY?

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Image: Creative Commons

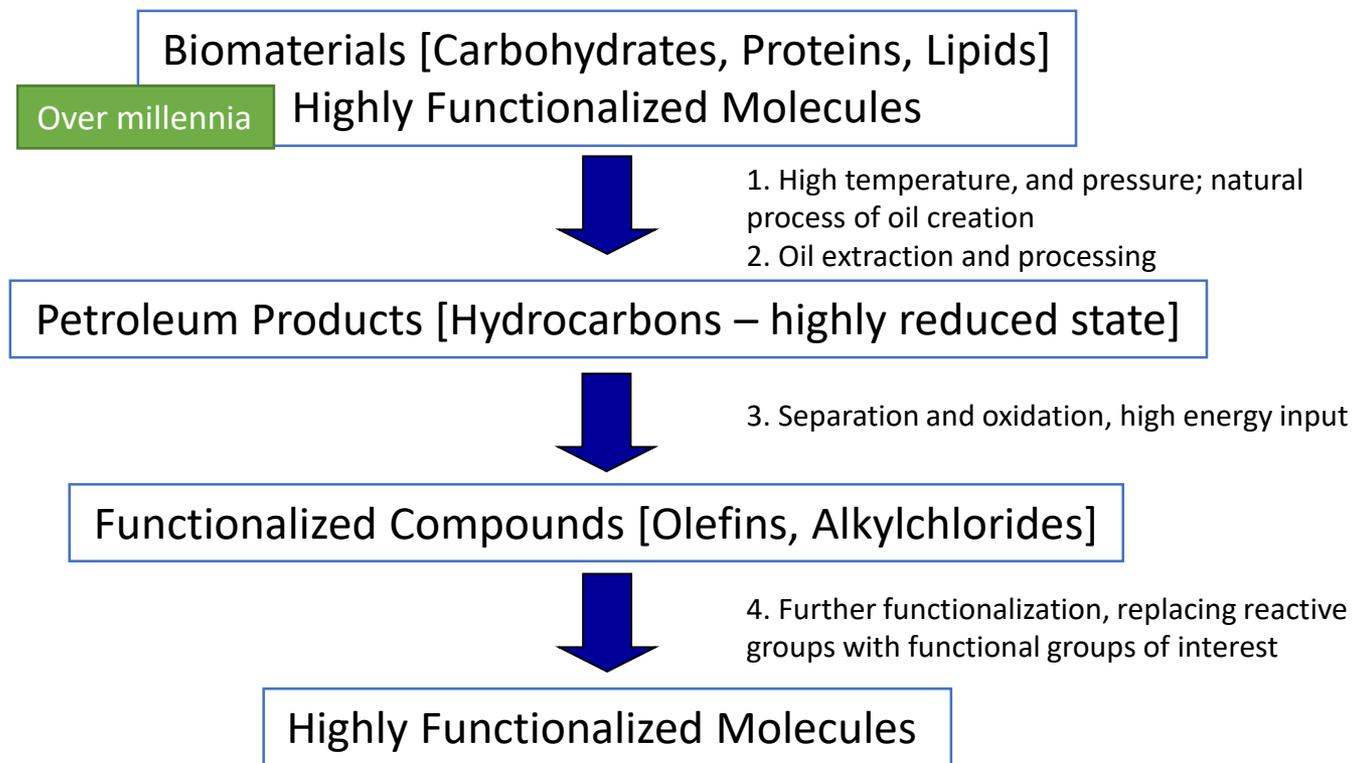
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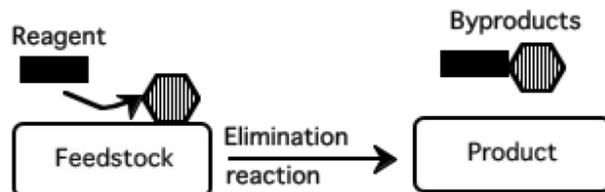
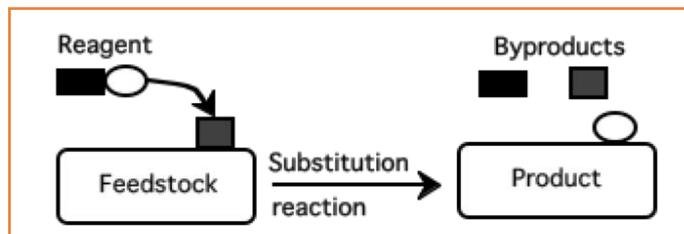
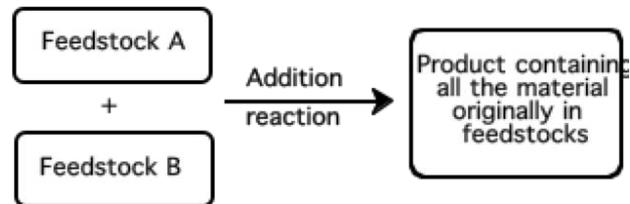


# HOW IS PETROLEUM GENERATED AND USED?





## Three major categories of reaction processes by which feedstocks are acted upon by reagents to yield products



Petroleum hydrocarbon molecules are in a highly reduced chemical state and often must be oxidized to be used as a feedstock.

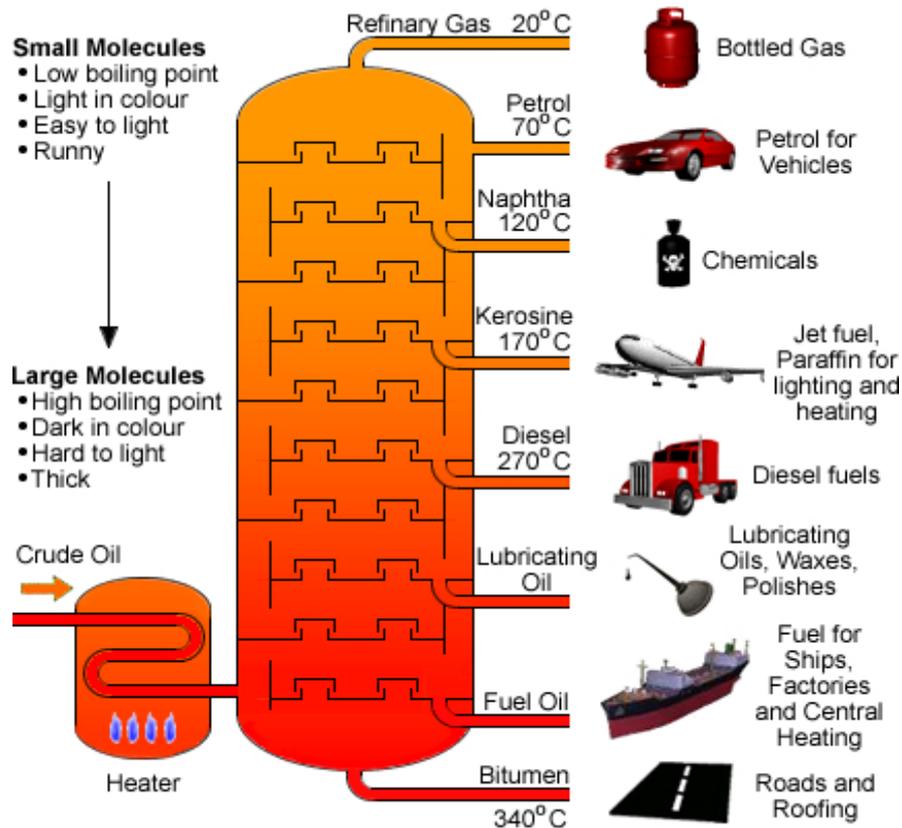
The oxidation process consumes energy and often uses severe and hazardous reagents which are capable of oxidations of non reactive molecules.

The majority of reactions for petroleum feedstocks are substitutions since reactive groups need to be replaced with the desired group.

This process generates several byproducts, which oftentimes are considered a waste.

# HOW ARE PETROLEUM PRODUCTS MADE?

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**Small Molecules**  
• Low boiling point  
• Light in colour  
• Easy to light  
• Runny

**Large Molecules**  
• High boiling point  
• Dark in colour  
• Hard to light  
• Thick

1. By using a fractionation column.
2. By oxidation (typically by a powerful oxidizing agent like chloride) and adding numerous additives.

Fractioning Column  
Copyright © 2009 science-resources.co.uk

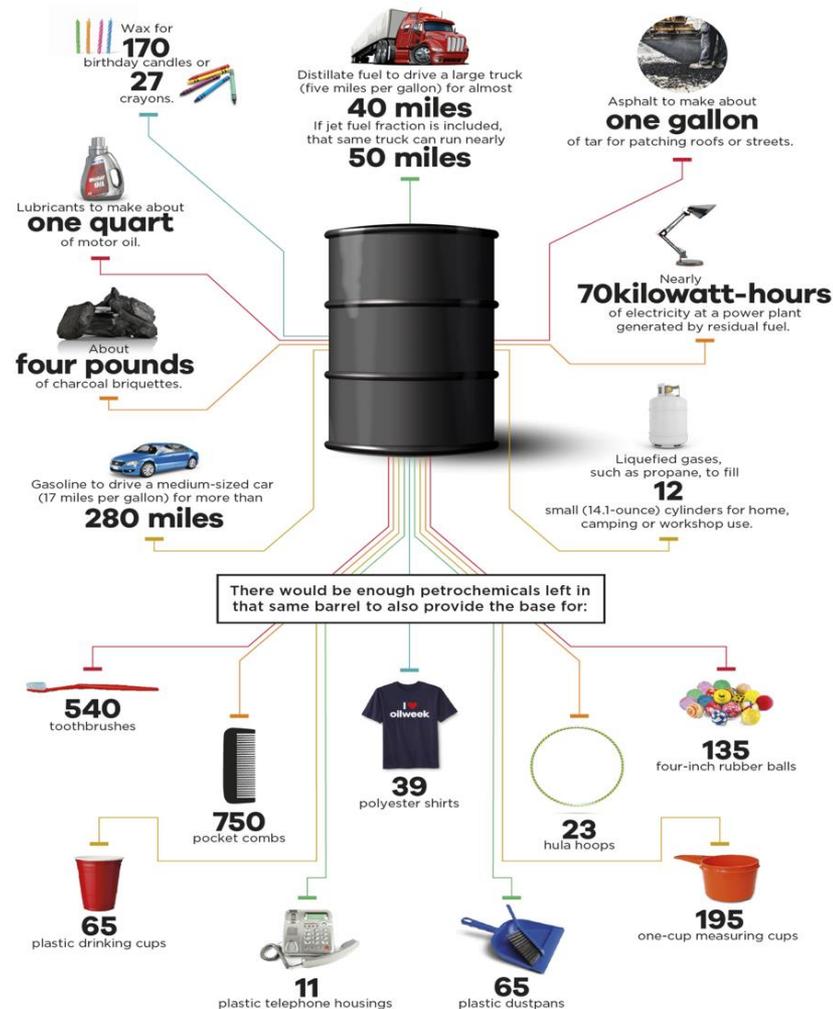
# WHAT CAN BE MADE FROM ONE BARREL OF OIL?

Researchers broke down a typical barrel of domestic crude oil into what could be produced from it. The average domestic crude oil has a gravity of **32 degrees** and weighs **7.21 pounds per gallon**. Here's what just one barrel of crude oil can produce:

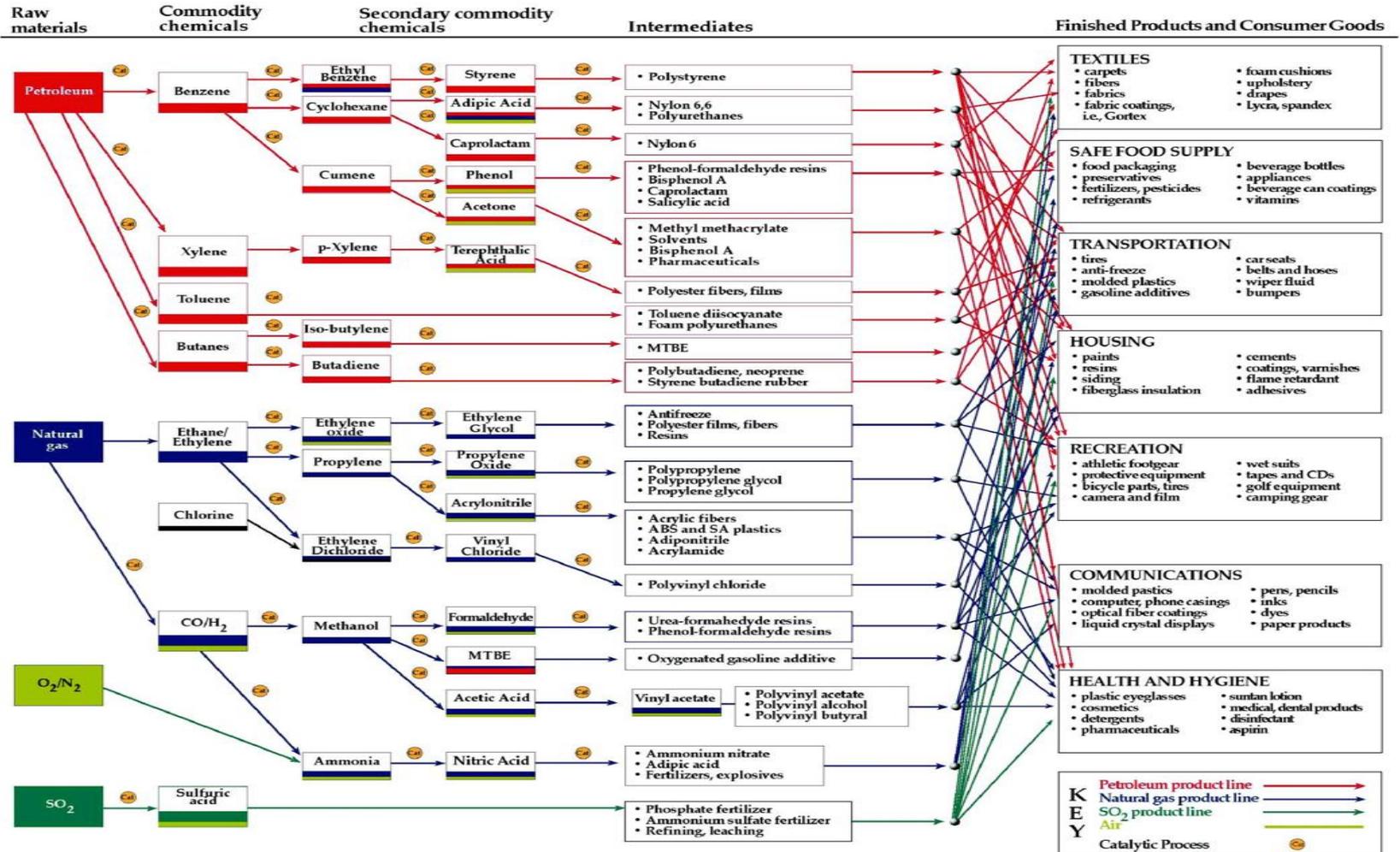
The lighter materials in a barrel are used mainly for paint thinners and dry-cleaning solvents, and they can make nearly a quart of one of these products. The miscellaneous fraction of what is left still contains enough byproducts to be used in medicinal oils, still gas, road oil and plant condensates.

<http://www.visualcapitalist.com/can-made-one-barrel-oil/>

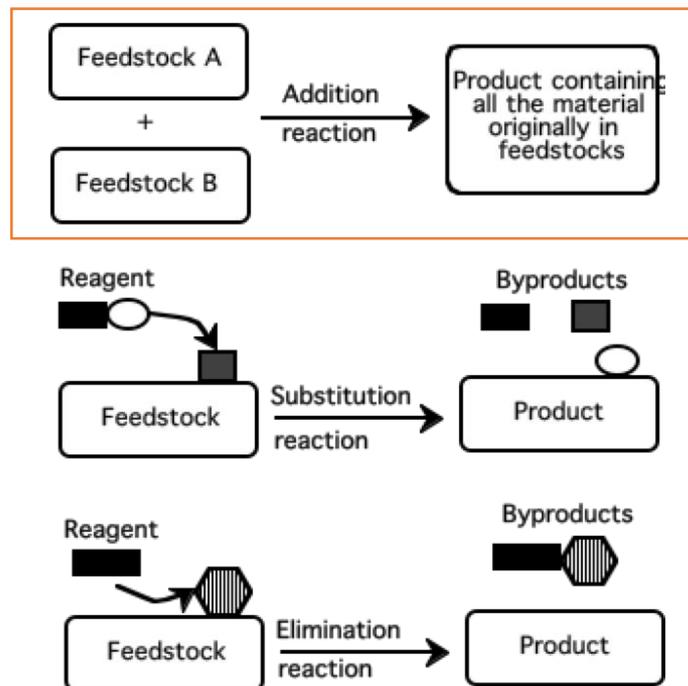
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# WHAT CHARACTERIZES AN IDEAL FEEDSTOCK?



An ideal feedstock is renewable and poses no hazards to humans or the environment.

An ideal feedstock can be converted to the desired product using only a few steps.

The reaction gives a 100% yield and has 100% atom economy.



## Renewable feedstocks include the following materials:

- Biomass (algae, corn, switchgrass, poplar, willow, sorghum, and bamboo)
- Agricultural waste (ex. manure)
- CO<sub>2</sub>



# WHAT CAN BE MADE FROM RENEWABLE FEEDSTOCKS?

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<b>Defense and aerospace</b> <ul style="list-style-type: none"><li>• Adhesives</li><li>• Coatings</li><li>• Corrosion, inhibitors</li></ul>	<b>Automotive</b> <ul style="list-style-type: none"><li>• Solvents</li><li>• Polymers</li><li>• Fuels</li></ul>	<b>Household cleaners</b> <ul style="list-style-type: none"><li>• Surfactants</li><li>• Fragrances</li><li>• Dyes</li></ul>
<b>Electronics</b> <ul style="list-style-type: none"><li>• Solder</li><li>• Housings</li><li>• Displays</li></ul>	<b>Agriculture</b> <ul style="list-style-type: none"><li>• Pesticides</li><li>• Fungicides</li><li>• Fertilizers</li></ul>	<b>Cosmetics</b> <ul style="list-style-type: none"><li>• Builders</li><li>• Chelating agents</li><li>• Dyes</li></ul>
<b>Specialty Chemicals</b>	<b>Pharmaceuticals</b>	<b>Used in Academic Research Labs</b>

[www.rethinkalumni.org](http://www.rethinkalumni.org)







**Organisms have provided a huge share of the materials used by humans throughout their existence.**

**Biomass:** Plant material generated by photosynthesis

- Biomass is the leading candidate to replace petroleum as a feedstock for the organic chemicals industry.
- Partially oxidized biomass material avoids expensive, and sometimes difficult oxidation steps in oxidizing petroleum

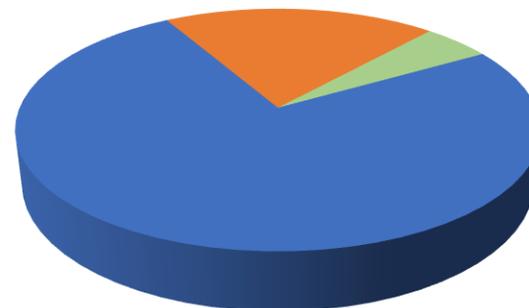


Image: Wikimedia Commons, Author: Daniel Schwen



Biomass production in nature:  
180 billion metric tons/year

Only about 4% utilized by humans  
(food, ethanol, sweeteners)



■ Carbohydrates ■ Lignin ■ Fats, proteins, terpenes, etc.

Building blocks for a diverse  
chemical platform.

Nature's richest source of  
aromatic carbon. Used in  
polymers, adhesives,  
production of phenolic  
chemicals.

Converted into polymers,  
lubricants, and detergents.

## Carbohydrates can be used as feedstocks for chemical processes

### Carbohydrates are created in several forms:

- Sucrose sugar,  $C_{12}H_{22}O_{11}$ , is squeezed from sugar cane as sap and is extracted from sugar beets and sugar cane with water.
- Starch, a polymer of glucose readily isolated from grains (such as corn) and from potatoes, and is readily broken down by adding water to produce glucose.
- Huge amounts of cellulose, which occur in the woody parts of plants, can be broken down to glucose with cellulase enzymes.



Lipid oils can be extracted from the seeds of some plants.

- Volatile solvent *n*-hexane,  $C_6H_{14}$ , is used to extract the oils.
- Solvents are distilled off from the extract and recirculated through the process.



Image: Wikimedia Commons, Marula - Sclerocarya birrea – Seeds, Author: Genet

Hydrocarbon terpenes can be tapped from rubber trees as a latex suspension in tree sap.

Steam treatment and distillation are used to extract terpenes from sources such as pine or citrus tree biomass.



Image: Wikimedia Commons, Rubber trees in Kerala, India, Author: M.arunprasad



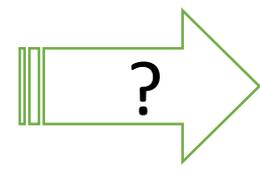
Grain seeds can be used as sources of protein.

- Grain seeds are generally used for food.
- They are potentially useful as chemical feedstocks for specialty applications.
- Transgenic plants can be used to make specialty proteins, such as medicinal agents.



Image: Wikimedia Commons, Brown Flax Seeds, Author: Sanjay Acharya

# HOW ARE BIOLOGICAL FEEDSTOCKS PROCESSED?



- Fermentation
- Microorganisms (aerobic, anaerobic)
- Enzymes

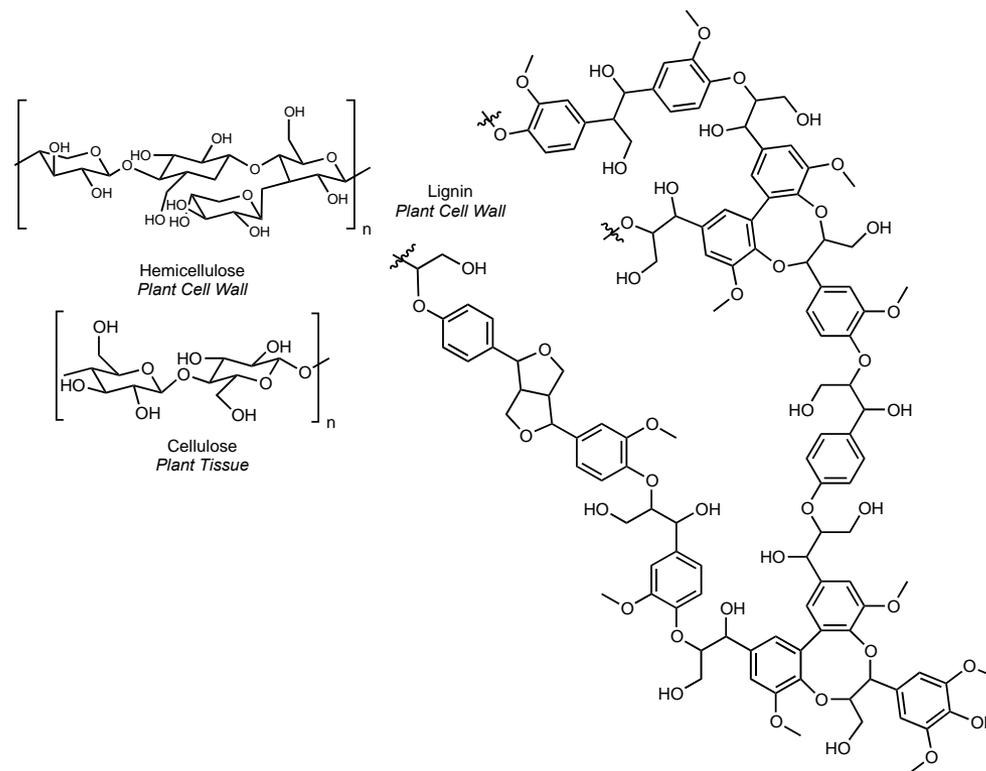
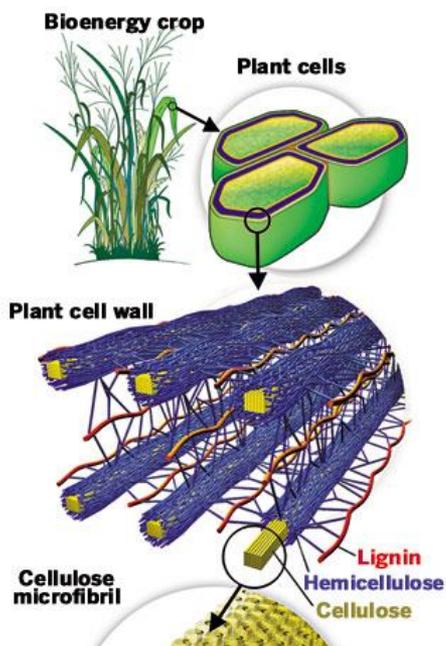


Images: Creative commons

# EXAMPLE: ENZYMATIC LIGNOCELLULOSE BREAKDOWN

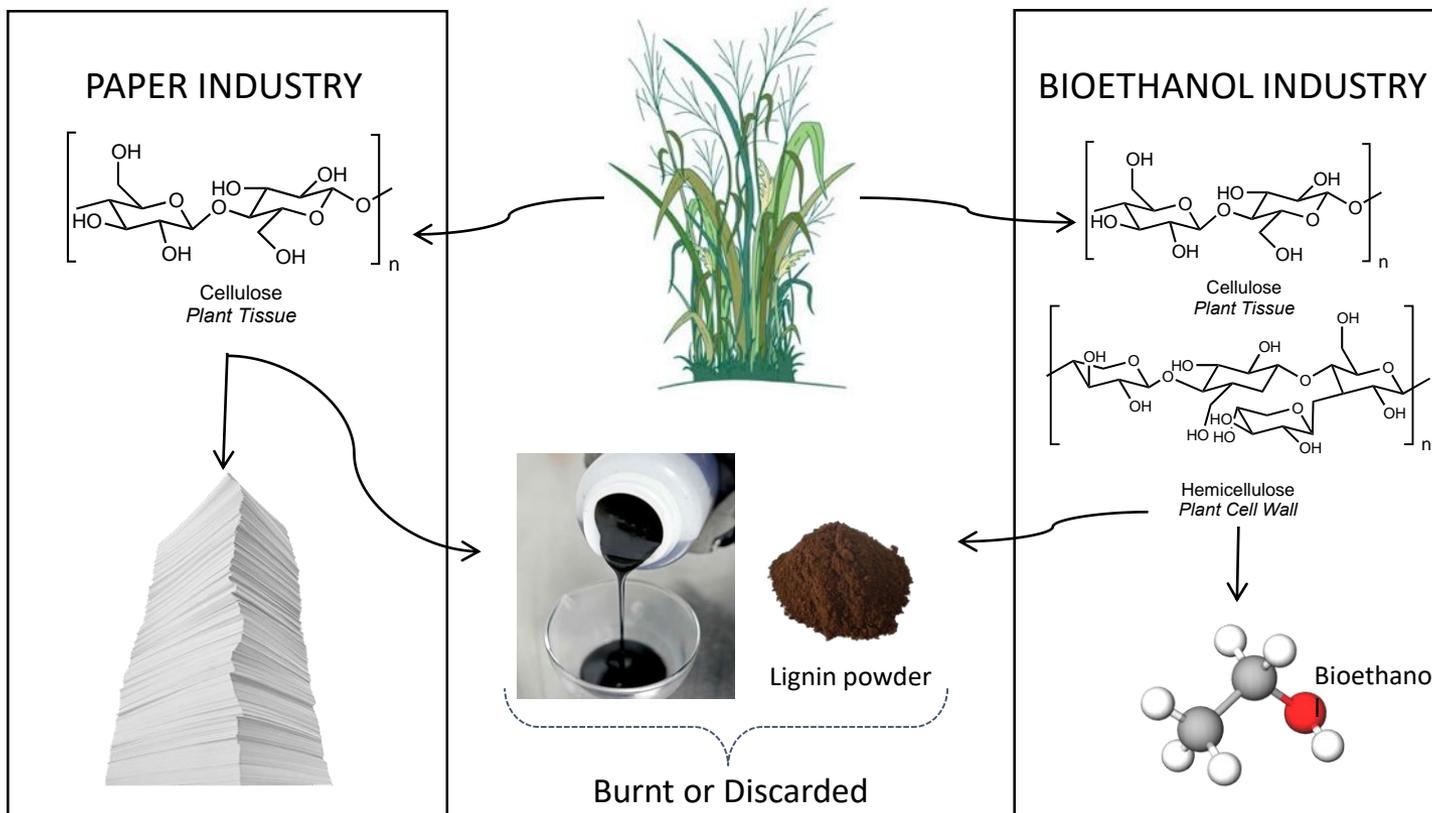


Lignocellulose is a complex polymer obtained from plant cell walls.  
It has many aromatic subunits.



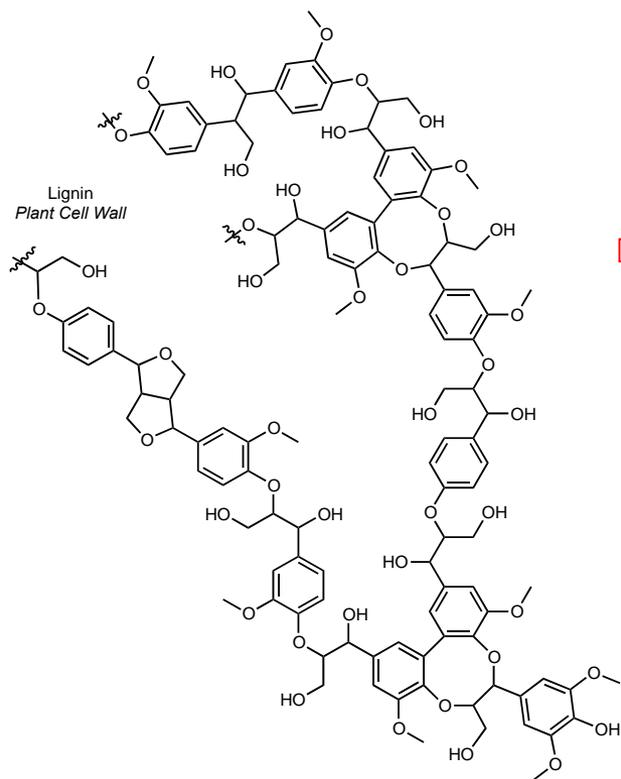
# MAIN INDUSTRIES FOR LIGNOCELLULOSE

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# LIGNIN: A SOURCE OF RENEWABLE 'DROP-IN' PLATFORM CHEMICALS

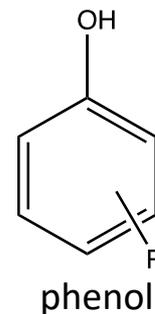
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A Need of New Technology:



Economical  
Sustainable  
Selective  
Efficient



The lignin structure includes aromatic (ring) structures.

If it is broken down selectively, it can be a source of drop-in platform chemicals such as phenol.



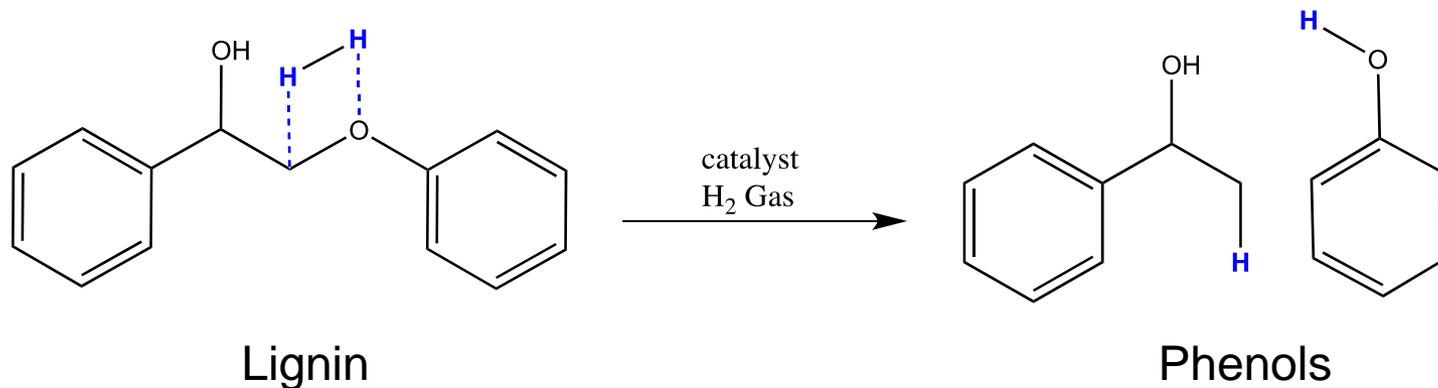
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# A DEPOLYMERIZATION STRATEGY FOR THE VALORIZATION OF LIGNIN



With the addition of hydrogen and a selective catalyst, lignin can be broken down into phenols.



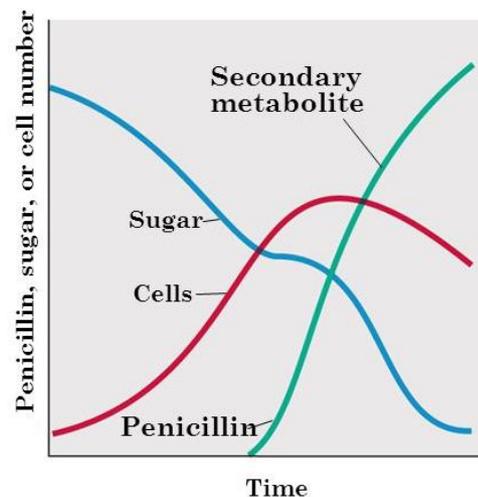
# EXAMPLE: PENICILLIN PRODUCTION USING FERMENTATION



Penicillin antibiotics were among the first medications to be effective against many bacterial infections caused by staphylococci and streptococci. They are still widely used today, though many types of bacteria have developed resistance due to the extensive use.

The secondary metabolite of a fungus - *Penicillium chrysogenum* - grows using a carbon source of glucose and lactose.

Once the fungus reaches a stationary phase, it starts producing the antibiotic.

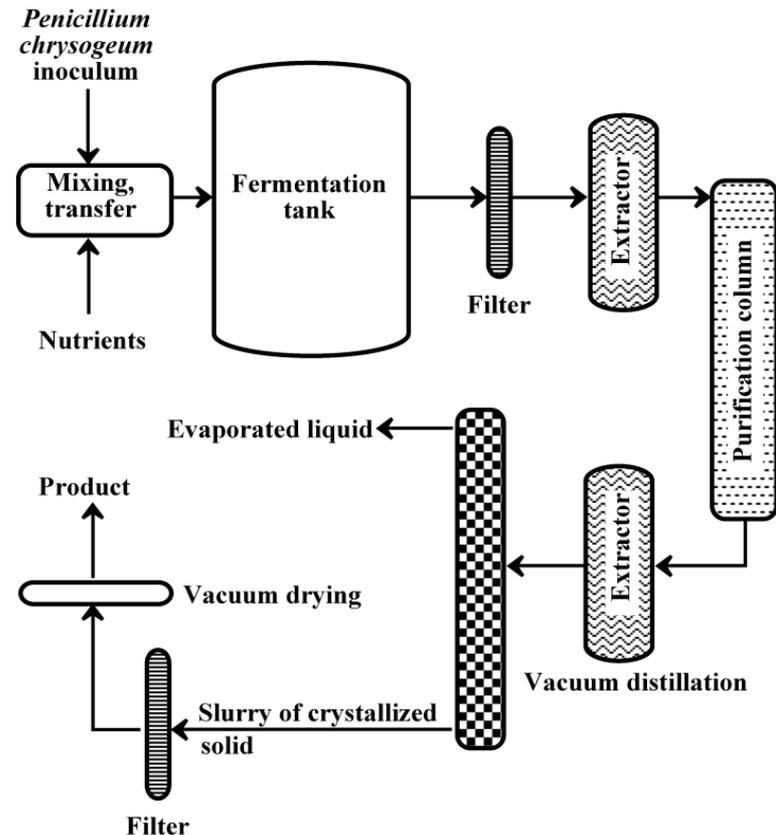


# REQUIREMENTS FOR A SUCCESSFUL FERMENTATION PROCESS



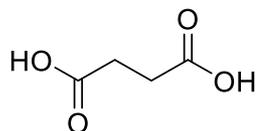
- Proper nutrients
- Sterile conditions
- Temperature regulation
- Oxygen level
- pH control

The fermentation process is similar for other commodity products, such as antibiotics, insulin, ethanol, organic acids, vitamins and enzymes.

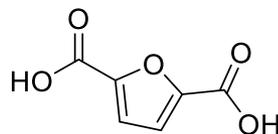


# THE TOP 10 CHEMICAL TARGETS (PLATFORM CHEMICALS FROM BIO-FEEDSTOCKS)

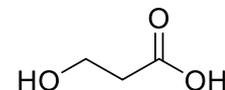
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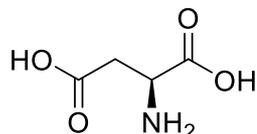
succinic acid



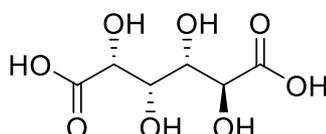
2,5-furandicarboxylic acid



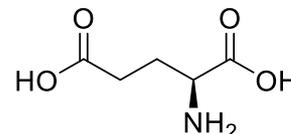
3-hydroxypropionic acid



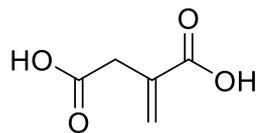
aspartic acid



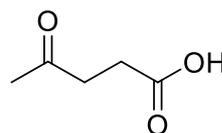
glucaric acid



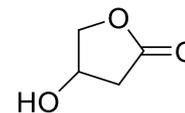
glutamic acid



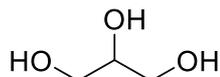
itaconic acid



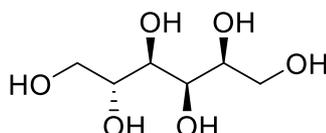
levulinic acid



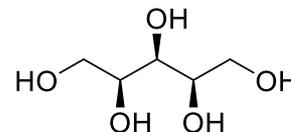
4-hydroxydihydrofuran-2(3H)-one



glycerol



sorbitol



xylitol



# WHY USE RENEWABLE FEEDSTOCKS?

## ❑ **Economic reasons:**

- The inherent long-term tendency for petroleum price increases.
- A fluctuation of a few cents in the price of crude oil can result in massive price swings for downstream products.
- The constant decrease in cost of renewable resources.

## ❑ **Scientific reasons:**

- The constant improvement in quality of renewable feedstocks.
- Modern plant breeding.
- Genetic manipulation.
- Breakthroughs in catalysis (enzymes, etc.).

## ❑ **Environmental reasons:**

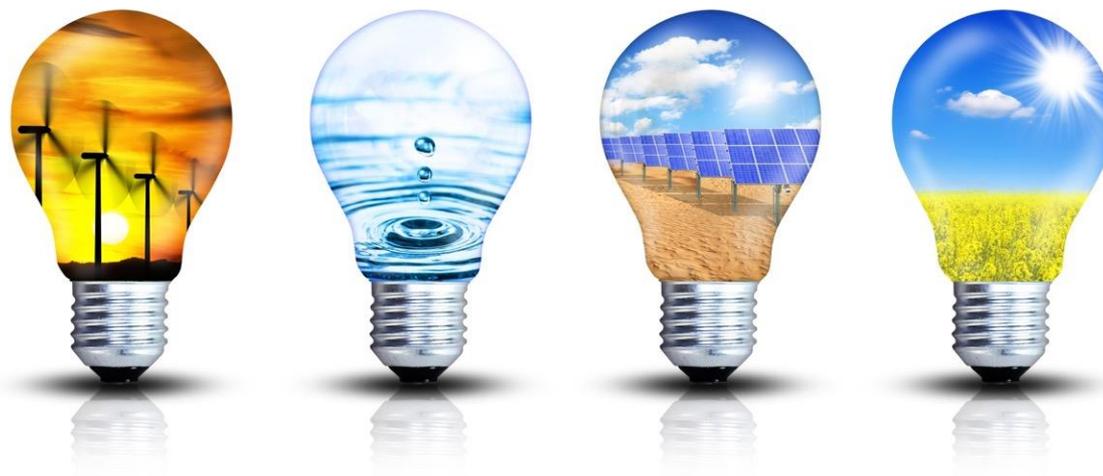
- Biological compatibility (to an extent).
- The use of waste streams (wood pulping, agriculture, etc.).

# SOME POTENTIAL CHALLENGES OF USING RENEWABLE FEEDSTOCKS

- Feedstock cultivation
  - Competition with food supply
  - Land demand
  - Nutritional needs
  - Diseases
  - Initial investment
- Harvesting method to maximise yields and minimise degradation of product
- Post harvest processing
- Product extraction and purification
- Product standardization
- Complexity
- Product storage, packing, and distribution
- New methodologies for alternative feedstocks

# WHAT ABOUT ENERGY FROM RENEWABLE RESOURCES?

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At first glance, we might think that biofuels are inherently environmentally friendly, but is this true?

That depends on how the biofuels are produced.



Image: Flickr, Tribal Biofuel, Author: U.S. Department of Agriculture

## **Bioenergy can have positive impacts:**

- Green house gas reduction (through fossil-fuel substitution).
- More agrobiodiversity, soil carbon increase, less erosion.

## **But these impacts can also be negative:**

- Green house gas from cultivation, soil carbon, life-cycle, direct and indirect land-use changes.
- Loss of biodiversity from land-use changes, water use, agrochemicals, erosion.

## First Generation Biofuels

- Grains are used to produce ethynol
  - Food versus fuel

## Second Generation Biofuels

- Using agricultural wastes  $\leftrightarrow$  lignocellulosics
  - Lignocellulosics for ethanol
  - Oils for biodiesel
  - Grasses
    - These crops were not domesticated for use as biofuels

## Third Generation Biofuels (looking to the future)

- Algae

# FIRST GENERATION: THE CORN-BASED ETHANOL PRODUCTION PROCESS



- ❑ Grind up the feedstock so it can be easily and quickly processed.
- ❑ Sugar is dissolved out of the material.
- ❑ The sugar is fed to microbes that use it for food, producing ethanol and carbon dioxide in the process.
- ❑ Purify the ethanol to desired concentration.

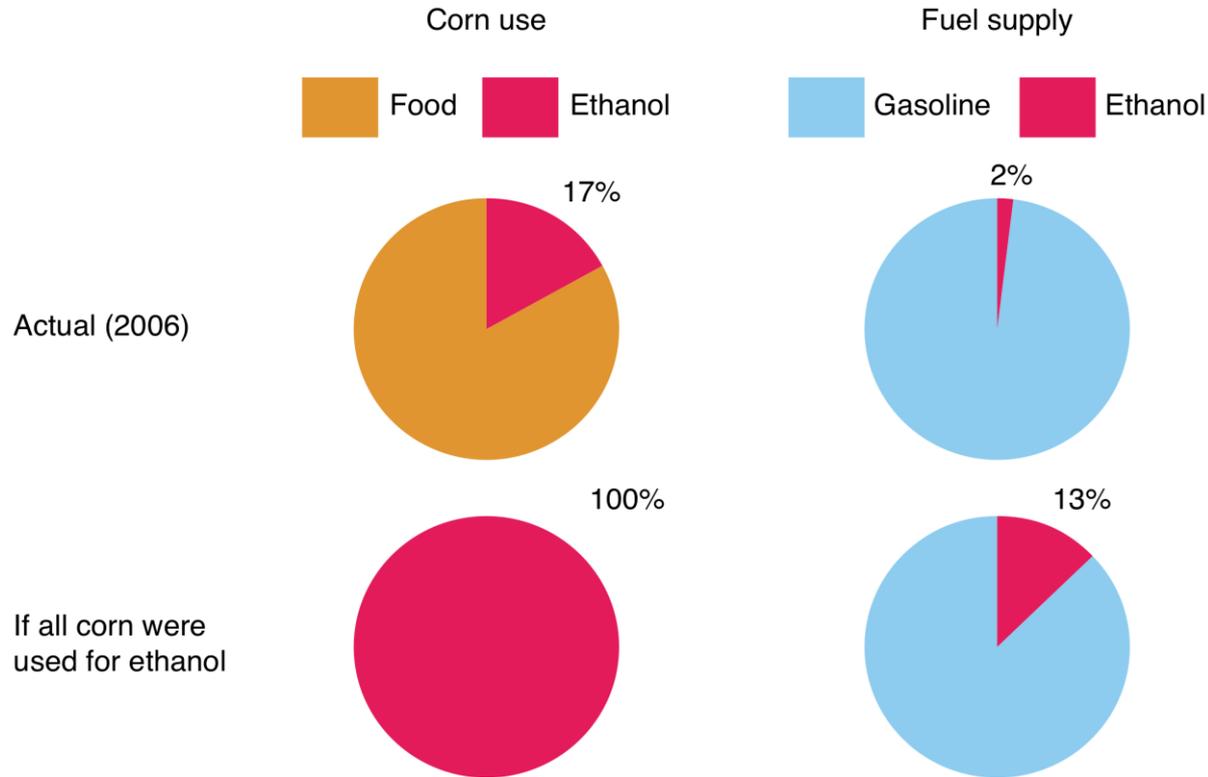


Images: Wikipedia Commons, Corncobs, Author: Sam Fentress; Wikimedia Commons, Biofuel Pumps, Author: Mario Roberto Duran Ortiz



- ❑ To fill up an average 25 gallon SUV gas tank with ethanol requires the same amount of grain as it takes to feed 1 person for 1 year.
- ❑ Every person in the U.S. uses 500 gallons of gasoline per year.
- ❑ That means that each year, every person in the U.S. would use enough gasoline to feed 20 people for one year.
- ❑ There are 300 million people in the U.S. – if each person was using enough food to feed 20 people to run their cars, that alone would require enough grain to feed 6 billion people.

# ETHANOL SUPPLY: THE EFFECT ON CORN SUPPLY AND ON GASOLINE SUPPLY



# ETHANOL DEMAND AND CORN PRICES



There is a large increase in demand for corn for ethanol production.

- Current production capacity is at over 5 billion gallons.
- This is projected to increase to over 9 billion gallons with plants currently under construction.

Corn prices continue to fluctuate. Bushels of corn sold for over \$8 (USD) each in July 2012.



Graph: <http://www.macrotrends.net/2532/corn-prices-historical-chart-data>

## First Generation Biofuels

- Grains are used to produce ethynol
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## Third Generation Biofuels (looking to the future)

- Algae

# SECOND GENERATION BIOFUELS: CELLULOSIC FEEDSTOCK

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Switchgrass



Wheat Straw



Hybrid Poplar



Corn Stalks

Image, Wikimedia Commons, Author: David Hawgood



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To qualify as second generation, a feedstock must not be suitable for human consumption and meet the following criteria:

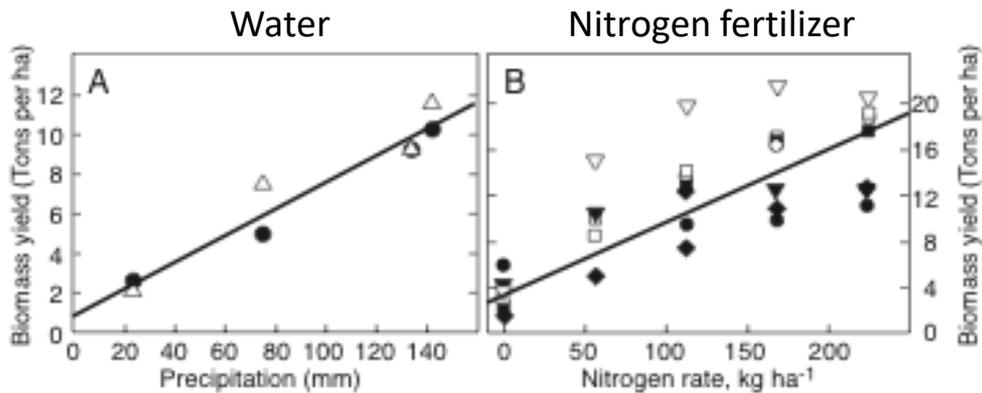
- Should grow on marginal (non-agricultural) land.
- Should not require large amounts of water or fertilizer.
- Certain food products can become second generation fuels when they are no longer useful for consumption:
  - Waste vegetable oil (2<sup>nd</sup> generation feedstock).
  - Virgin vegetable oil (1<sup>st</sup> generation feedstock).

# SWITCHGRASS AS A FEEDSTOCK



Switchgrass still needs water and fertilizer to grow.

Nutrients needed: corn versus switchgrass.



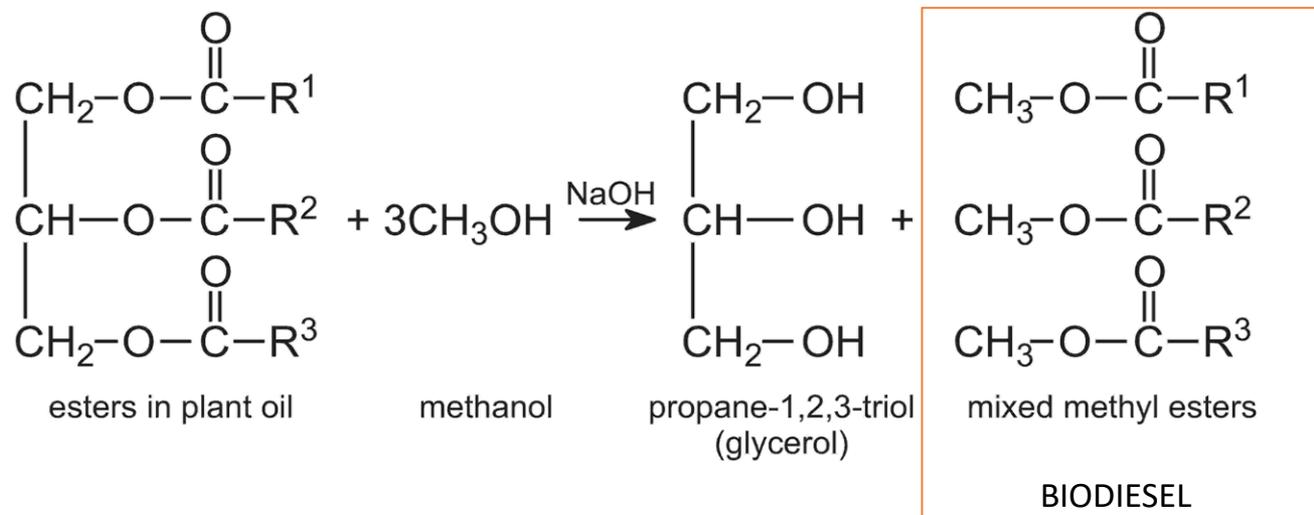
kg ha <sup>-1</sup> yr <sup>-1</sup>	Corn	Switchgrass
N	148	0
P	23	4
K	50	6

Data of Lee et al. and Muir et al, collated in Gressel, "Genetic Glass Ceilings, Hopkins, 2007"

# SECOND GENERATION BIOFUELS: OILS AND BIODIESEL

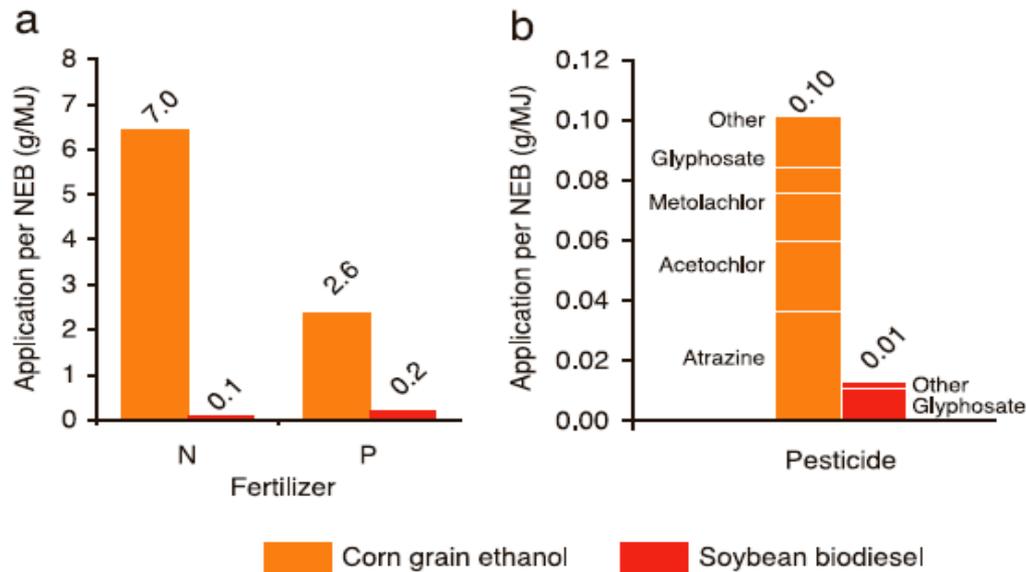


Biodiesel refers to vegetable oil or animal fat-based diesel fuel consisting of long-chain esters. The main component of vegetable oil is triglycerides, which require transesterification prior to usage as a fuel.



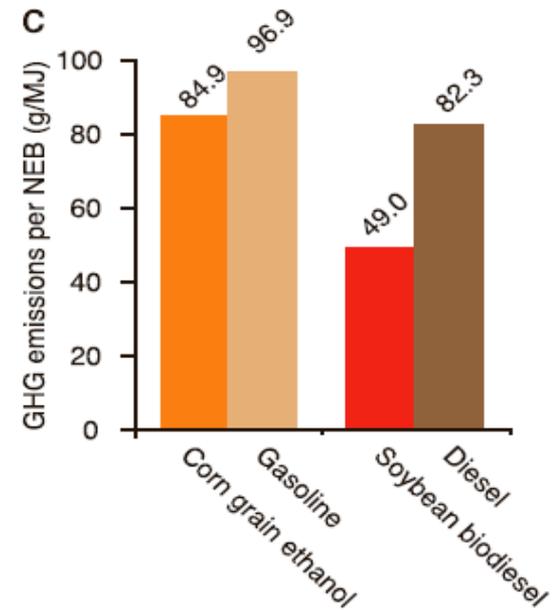
# COMPARING THE ENVIRONMENTAL IMPACT

## Environmental Consequences per Unit Energy



Soybean biodiesel needs less fertilizer and pesticide than corn ethanol.

## Greenhouse Gas Emissions per Unit Energy



Soybean biodiesel produces significantly less green house gas.

Data of Lee et al. and Muir et al, collated in Gressel "Genetic Glass Ceilings, Hopkins, 2007

[www.thinkalliance.org](http://www.thinkalliance.org)

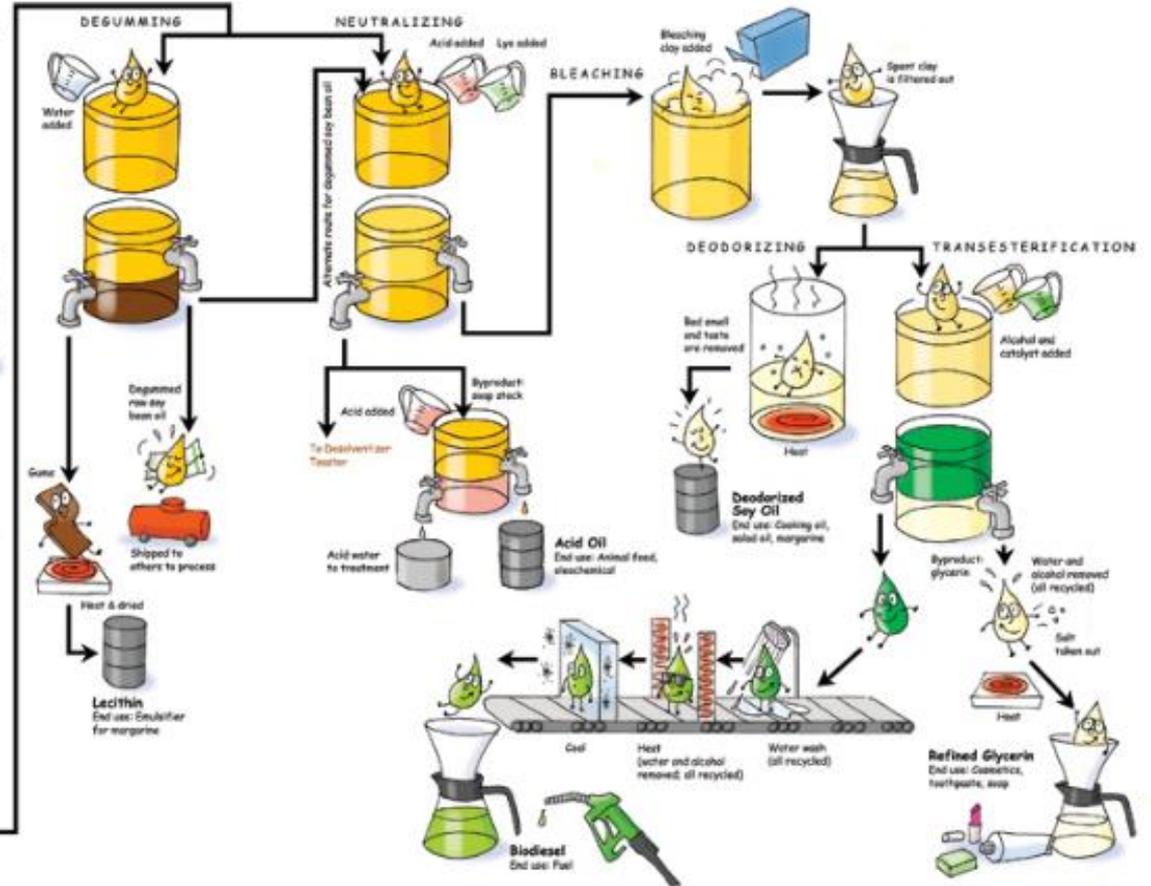
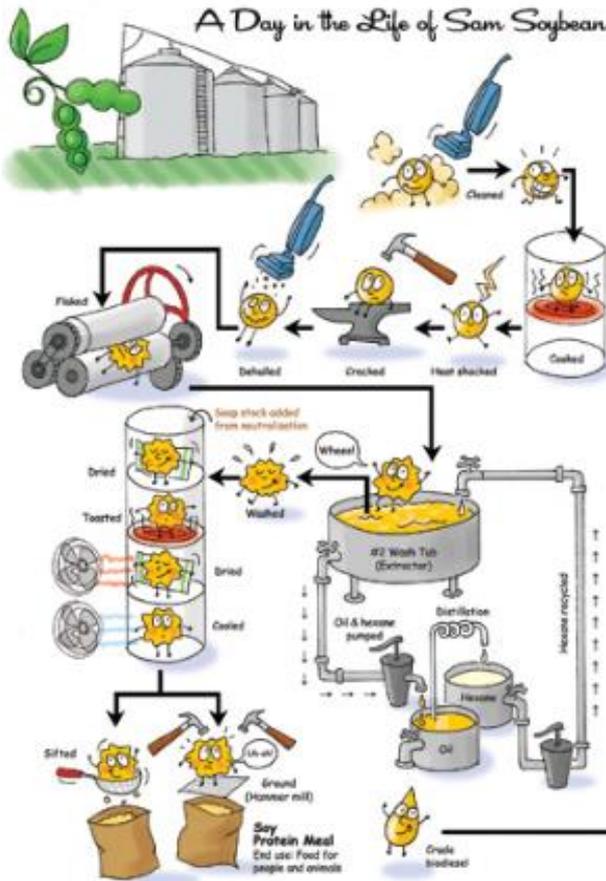
# ADVANTAGES OF BIODIESEL

- Reduces other pollutants.
- 35% reduction in unburned hydrocarbons through life cycle. Hydrocarbons are smog and ozone precursors.
- 8% reduction in sulfur oxides. The release of sulfur oxides can lead to acid rain.
- 3% reduction in methane.
- 32% reduction in particulate matter (PM10 68%).
- 83.6% reduction in particulate matter soot.
- 79% reduction in wastewater.
- 96% reduction in hazardous waste, but double the non-hazardous waste.

Compared to conventional diesel processing, biodiesel requires additional processing and has a lower overall energy return. Energy return is one of the important parameters that enables engineers to evaluate the efficiency and viability of a process. Energy return describes the amount one can gain from the production versus the amount of energy input. Biodiesel lags far behind conventional diesel processing in this regard.

# STEPS REQUIRED TO PRODUCE BIOFUEL FROM SOYBEANS

# GREEN CHEMISTRY



Retrieved: nancymeyersdesign.com



## First Generation Biofuels

- Grains are used to produce ethynol
  - Food versus fuel

## Second Generation Biofuels

- Using agricultural wastes  $\leftrightarrow$  lignocellulosics
  - Lignocellulosics for ethanol
  - Oils for biodiesel
  - Grasses
    - These crops were not domesticated for use as biofuels

## Third Generation Biofuels (looking to the future)

- Algae

# THIRD GENERATION BIOFUELS: ALGAE FEEDSTOCK

# GREEN CHEMISTRY



[www.rhenkollinsid.org](http://www.rhenkollinsid.org)

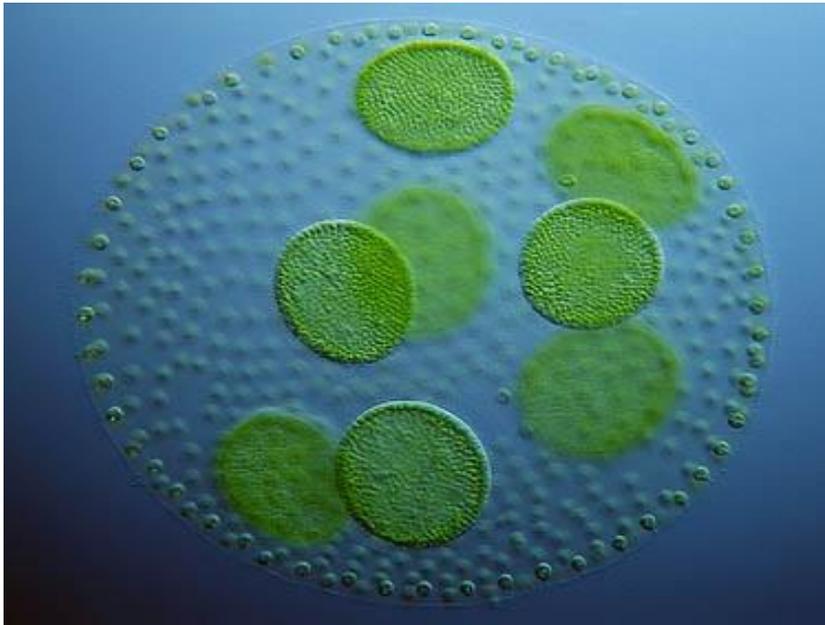


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# WHAT IS ALGAE?



Algae is a large and diverse group of simple, usually autotrophic, organisms that can have either unicellular or multicellular forms.



# WHAT DOES ALGAE NEEDS TO GROW?



- Carbon dioxide
- Sunlight
- Water



# IS ALGAE “GREEN GOLD”?



- ❑ Currently being developed.
- ❑ 30 times more oil per acre than current crops that are being used.
- ❑ No sulfur.
- ❑ Non-toxic
- ❑ Highly biodegradable,
- ❑ Not subject to a commodity risk like crude oil, corn, and soybeans are.





## Pros

- Versatility in growth methods
- Versatility in uses
- Speed of production
- Potential for huge production levels
- CO2 reduction

## Cons

- Energy intensive
- Not competitive against foreign oil (yet)
- Needs funding
- Technology not ready (yet)

# HOW TO OVERCOME THE TECHNICAL ROADBLOCKS TO LOW-COST ADVANCED BIOFUEL PRODUCTION

**GREEN  
CHEMISTRY**



Make all of the components of biomass available for biofuel and co-product production:

**Use the appropriate parts of specific plants.**

Improve the efficiency of biomass to biofuel conversion:

**Do it faster, cheaper, and sustainably.**

Minimize the cost of biomass transportation.

**Move more for less.**

[www.greenalliance.org](http://www.greenalliance.org)



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- ❑ Biofuels are not THE answer to sustainable energy, but biofuels may be part of the answer.
- ❑ Biofuels may offer environmental and economic advantages over fossil fuels, but the magnitude of these advantages depends on how a biofuel crop is grown and converted into a usable fuel.



1. Energy and Feedstock Consumption
2. Petroleum
3. Renewable Feedstocks
  - Biomass Feedstocks
  - Carbohydrate Feedstocks
  - Lipid Oils and Terpenes as Feedstocks
  - Protein Feedstocks
4. Renewable Feedstocks as a Source of Energy
5. First, Second, and Third Generation Feedstocks
6. The Advantages and Drawbacks of Biofuel



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**GREEN  
CHEMISTRY**



**THANK YOU!**  
**QUESTIONS?**

This training material was developed in close collaboration with the **Center for Green Chemistry and Green Engineering** at Yale University.

[www.greenchemistry-toolkit.org](http://www.greenchemistry-toolkit.org)