Wood Saccharification: A Modified Rheinau Process

After *Chemistry of Wood* by Erik Hägglund

1976

INTRODUCTION (UPDATED)

The Rheinau (or Bergius) Process was one of the means by which Nazi Germany obtained sufficient fuel for their "war machine," even though they did not capture the oil fields of the Middle East: They were able to convert wood from their extensive forests into alcohol, which could serve as fuel in combustion engines. Ultimately, as other means of energy production were more efficient (including the better-known Bergius Process, of converting coal to fuel oil) and as food became very scarce in war-torn Germany, this Bergius process was used mostly to produce yeast, as a food supplement for both cattle and people.

Although this old process uses concentrated hydrochloric acid (HCl) as a catalyst, mostly at room temperature, and a later, more-utilized (Scholler) process uses sulfuric acid, at lower concentrations but higher temperatures, a new process uses "cellulase" enzymes (like those found in the gut flora of termites), which operate without the problems associated with concentrated acids or high temperatures—energy costs were prohibitive for the Scholler process during the fuel shortages of the 1970s, when I originally made this report and when the U.S. Army was doing the state-of-the-art (enzyme) research, for national security purposes.

The utilization of cellulose (and chemically related "hemi-cellulose" molecules) as a fuel and/or food source (cellulose and hemicelluloses are polymers of sugar molecules) is particularly intriguing because cellulose—not any fossil fuel—is the most abundant source on Earth of carbon-to-carbon bonds, burnt by our engines, fermented by yeasts, or respired by our bodies.

And given the fact that the bulk (typically 70%) of the waste in garbage dumps is "ligno-cellulosic" (that is, composed of cellulose, hemicelluloses, and "lignin"—the stuff of bark etc.), and the fact that garbage around the world is piling up faster than it is being recycled, and the fact that there are limited amounts of materials on Earth, the prospect of "mining" dumps for their cellulose, from which we can produce fuel, is a "win-win situation."

Also, because cellulose is ultimately produced from the photosynthesis of green plants, the amount of carbon dioxide *added* to the atmosphere by the burning of ethanol produced from cellulose is *equal to* the amount of carbon

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

dioxide *subtracted* from the atmosphere by the growth of plants producing cellulose: There is no net addition to the Greenhouse Effect.

The hydrolysis of cellulose, catalyzed by acids or enzymes, remains an intriguing, potentially massively profitable and strategic enterprise: It is currently (2009) the subject of much research, for the production of "cellulosic ethanol" as from switchgrass; an alternative method of producing this "bio-fuel" involves gassification of the cellulose. There is also competition from the growing corn ethanol industry, although growing corn is such an energy-intensive practice that there is reportedly a net addition of carbon dioxide to the atmosphere by growing and burning corn ethanol.

Note: Numbers etc. in the chart below refer to a diagram I created in the 1970s, which no longer exists.

Step I. Preparation of raw cellulose for hydrolysis. Procedures adapted from wood pulping industries. Methods for alternative cellulose sources differ.

#	Name	Function	Notes
1	Woody plants, especially trees	Raw cellulose and fuel source	Native or minimum cultivated stands especially on otherwise unproductive land. Individual or parts of individual plants will be selected with ecological considerations: Light, humus, effect on photosynthesis, etc.
2	Debarking operation	Removes bark.	This and other operations possibly powered by steam-generated electricity fueled with bark and lignin (smoke/smog problems?)
3	Bark	Fuel and/or soil-conditioner	Unwanted for hydrolysis: High percentage of fatty suberin (cork) restricts its amount of available carbohydrate (?)

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

4	Branches, twigs, sawdust, and other plant waste	Raw cellulose contributors	This is waste in pulping operations, in which difficultly soluble materials (12) must be dissolved to isolate solid cellulose. Here, the intractable materials are left as solids and the cellulose is dissolved (10).
5	Wood	Chief raw cellulose contributor	Usually 40 - 50% by weight cellulose
6	Wood chipper	Chops up wood to facilitate hydrolysis (increases reaction surface area).	See power notes at (2).
7	Wood drier	Dries chips.	Heat from condensed gases (15, 18, 19)
8	Dried wood chips	Prepared raw cellulose	Dry chips reportedly give better glucose yields.

Step II. Dissolution and hydrolysis of cellulose: The Rheinau (or Bergius) Method.

9	40% $HCl_{(aq)}$	Hydrolysis catalyst in reagent, water	Concentrated acid dissolves carbohydrates via partial hydrolysis.
10	Diffusion battery (Key operation)	Repeated dissolution in a countercurrent system: <———— wood acid ————> Most completely dissolves cellulose and associated carbohydrates.	Wood absorbs acid from solution;thus, in left-most vessel most concentrated acid contacts least soluble carbohydrate.

11	Systematic washings	Rinse away absorbed acid from insoluble material (12).	Possibly salt water
12	Carbohydrate-free insoluble material	Briquetted and used for fuel and/or used as soil-conditioner.	Contains mostly lignin. Also contains some gums, resins, pigments, and tannins that may possibly be isolated and utilized or marketed.
13	Evaporator with agitator	Evaporates off excess acid and volatile impurities but leaves carbohydrate in solution.	Operation below 70°C prevents sugar decomposition.
14	Heat source	Heats carbohydrate solution to depressed boiling point under vacuum.	—
15	Condenser	Retrieves concentrated HCl.	Concentration re-adjustment necessary. Heat must be dissipated: See wood drier (7).
16	Recovered $HCl_{(aq)}$	Re-used in hydrolysis upon concentration correction.	As a catalyst, HCl is typically regenerated and here economically (?) recovered, via vacuum distillation.
17	Vacuum pump	Allows evaporation of concentrated HCl at depressed boiling point: Prevents sugar decomposition.	Energy requirement = ? (significant cost factor)

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

18	Lime tower	Removes traces of HCl from volatile impurities.	Heat dissipation possibly used in wood drier (7). Possibly also connected to lignin output and wood input openings.
19	Recoverable volatile impurities, which may include acetic acid, methanol, acetone, aliphatic aldehydes, terpenes, aromatic hydrocarbons, and furfural (which treated with hydrogen gas, heat, and pressure, in the presence of Ni, produces furfuryl alcohol, an anti-corrosive, as possibly useful for lining tanks and pipes in contact with acid)	Industrially useful and marketable.	All formed in small amounts but marketable. Methanol and acetic acid are formed from hydrolysis of methylated and acetylated carbohydrates present in wood. Heat decomposition of wood is main source of impurities. Furfural is formed from the dehydration of pentoses derived from wood pentosans. Furfuryl alcohol's use here is questionable (For one thing, it is poisonous). However, furfural is (presently) prepared from hydrolysis of high-cellulose- containing waste; and this similar preparation should yield a marketable product.
20	Hot water	Dilutes the slightly acidic carbohydrate solution for completion of hydrolysis.	Possibly salt water

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

21	Inversion tank	Hydrolyzes to monosaccharides the oligosaccharides formed by reversion of soluble sugars and the incompletely hydrolyzed cellulose dextrins.	Sugars formed (as approximate percentages of total carbohydrate): Glucose (62%), mannose (25%), xylose (8%), galactose (4%), & fructose (1%).

Step III. Concentration of the sugar solution and collection of purified sugar crystals.
Procedures adapted from sugar cane (sucrose) and corn sugar (glucose) industries.

22	Evaporator with agitator	Evaporates off water and HCl while concentrating sugar solution to syrup.	—
23	Hot steam or other heat source	Heats dilute sugar solution to boiling under vacuum.	—
24	Vacuum pump	Facilitates evaporation of water and acid from syrup without decomposing sugar at higher boiling temperature.	Spent HCl either neutralized and disposed of or re-used with concentrated acid in hydrolysis.
25	Lime, limestone, or other cheap, readily obtainable alkaline material	Neutralizes HCl left in syrup.	Na_2CO_3 used similarly in corn sugar production.
26	Crystallization vat	Isolates raw glucose crystals from molasses.	Molasses contains liquid and soluble impurities, such as unhydrolyzed carbohydrate and sugars.
27	Filter press	Presses molasses from raw crystals.	—

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

28	Fermentation vat	Produces ethanol from waste molasses.	Ethanol is useful as fuel additive, in "gasohol."
29	Yeast culture with nutrients. *Torula utilis* is recommended.	This yeast gives good yields of protein and vitamins in addition to ethanol. Using Rheinau hydrozylates, NH_3 is the only nitrogen source needed. Ferments both pentoses and hexoses.	Yeast after fermentation must be washed and dried (and perhaps mixed with dextrose (37)) for human or animal consumption. Addition of conventional edible yeast reportedly aids in glucose/protein assimilation by human digestive system. Yeast is grown in vat (28), a portion retained for next run-through.
30	Flashing	Aids fermentation, by removing remaining furfural.	Done before adding yeast.
31	$Al_2(SO_4)_3$	Clears wort to facilitate fermentation.	Lignin-like substance may otherwise deposit on yeast.
32	NH_3	Nitrogen source for *Torula utilis*.	Ammonium salts have alternatively been used in Jamaica.
33	Ethanol	Industrially useful and possibly used in solution vat (34) to aid in re-crystallization: Glucose is insoluble in cool ethanol.	—
34	Solution vat	Used to mix raw glucose crystals, water, and possibly ethanol (33) for re-crystallization.	Ethanol may keep many organic impurities in solution.

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930

35	Recrystallization vat	Used to recrystallize glucose crystals.	As done for corn sugar, slow agitation gives best results. Seeding and an experienced eye are necessary.
36	Centrifuge with crystal scrapers	Spins off sugars and impurities in solution, which is returned to solution vat (34). Isolates recrystallized glucose.	—
37	Dextrose hydrate (glucose plus chemically bound water), "Wood Sugar"	Human food supplement. Fodder for animals.	Yield and purity tests may show that further refining is required for human consumption. Careful re-crystallization may well be sufficient.

Doug@DouglasDrenkow.com · 5760 Main St., South Gate, CA 90280 · 562-531-6643 · Cell: 310-570-8930