

How can we best solubilize lignocellulosic biomass for hydrolysis?



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Annual global biomass production is about 220 billion dry tons or 4500 EJ, equivalent to 8.3 times the world's energy consumption in 2014 (543 EJ). Most biomass is in lignocellulosic form that contains 75% sugar units (e.g. wood and grass plants: 50% cellulose and 25% hemi-cellulose). The key is determining how to release these abundant biopolymers into water-soluble sugars that can then be easily converted into ethanol or other biofuels, lipids, various chemicals, food, and medicine by physical, chemical, and biochemical technologies. There are three typical methods for hydrolyzing lignocelluloses into sugars, but what are the advantages and disadvantages of each method?

(1) Enzymatic hydrolysis at low temperatures (e.g. 50 °C)

Pre-treatment with bio, chemical, and physical methods is the first and the most crucial step to break down the lignin that binds cellulose and to destroy the crystalline structure of cellulose and increase its surface area, so that fragments are accessible to the enzyme active sites for hydrolysis. In addition to the issue of the high cost of enzymes, pre-treatment is a process-intensive step. It is the single most expensive processing step in cellulosic ethanol production, making up approximately 20–40% of the product cost. Solubilization of biomass with a non-toxic solvent for direct enzymatic hydrolysis, or pre-treatment by subsequent precipitation and fractionation, may be a green, safe, and inexpensive approach.

(2) Catalytic hydrolysis at mild temperatures (e.g. 180 °C)

Hydrothermal hydrolysis of wood with dilute acid (0.4–0.8% H₂SO₄, 12–13 atm., 180–190 °C) to sugars for ethanol production was commercialized in the former Soviet Union (and a few other countries) around a century ago.

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However, homogenous acids are hard to recover and corrosive to reactors. Recyclable heterogeneous magnetic catalysts, such as sulfonated carbonaceous solid acid, may be used in this process. Another issue is that the process can only operate in a batch or a percolating semi-flow reactor because wood is water-insoluble and blocks flow reactors. This therefore results in low production rate capabilities because material flow is low and interrupted.

(3) Fast hydrolysis at high temperatures near critical point (e.g. 350 °C)

Microcrystalline cellulose can be completely dissolved in water at temperatures above 320 °C and become a 'cellulose solution' for fast hydrolysis in a continuous flow reactor. Continuous hydrolysis of cellulose (20 wt%) in supercritical water (>374 °C and 22.1 MPa) is facilitated by the homogeneous phase in a short reaction time (ca. 0.05 s) into water-soluble products (with 100% conversion) containing 80% hydrolyzates (glucose and oligomers). By adding 0.8 wt% Na₂CO₃, actual wood particles can be completely dissolved to form a 'wood solution' at 329–367 °C and rapidly (ca. 15 s) hydrolyzed to sugars/sugar oligomers under homogeneous conditions. The results show that fast refining of 'biomass solution' is possible on a continuous basis (US patent: 8268126).

It is very important to solubilize biomass into a homogenous phase for reaction and pre-treatment, because a homogenous biomass solution is easily processed in a flow system for practical applications. Organic solvents (e.g. γ -valerolactone), ionic liquids, and supercritical fluids can be used to dissolve biomass for hydrolysis. However, we still need to find a green and inexpensive solvent that is able to solubilize biomass at mild conditions for novel biorefineries.

Once the biomass is in a soluble state, how can we further improve the methods for practical uses and commercialization?

- (i) For enzymatic hydrolysis, determining how to recycle enzymes, keeping activity rates high, and reducing costs are the challenges for industrial production.
- (ii) For catalytic hydrolysis, a flow process can be established to increase production efficiency. At the same time, solid catalysts may replace liquid acids for greener processes. However, their stability and activity need to be studied further.
- (iii) Even though fast hydrolysis method can be very efficient, because of the severe operating conditions (high temperatures and pressures), engineering issues (such as reactor design, materials, and continuous operation) become the key obstacles to commercialization.

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