

Biomass exploitation – a challenge finding its way to reality

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Lignocellulosic biomass holds the key to supplying the basic needs of society for sustainable production of chemicals and fuels without impacting the human food supply. The production of second-generation biofuels and chemicals from lignocellulosic biomass has not yet been commercialized due to its complex and recalcitrant structure. Therefore, the challenges involved in the production of lignocellulosic biomass-derived fuels and chemicals must be addressed. Search for economic pretreatment methods has been recognized as one of the main hurdles for processing of biomass to biofuels and chemicals. The conversion of all biomass components, lignin in particular, would greatly contribute to the economic viability of biomass-based processes for second-generation biofuels and chemicals. Hydrolysis of lignocellulose carbohydrates into fermentable sugars requires a suitable cellulase enzyme cocktail acting on both raw as well as pretreated biomass. Depending on raw material and pretreatment technology, the enzyme mixtures must be designed to degrade biomass carbohydrates. Recent publications on GVL-pretreatment to solubilize and degrade carbohydrates in biomass and CelA enzyme acting on raw biomass would probably meet the challenges in biomass conversion technologies.

The abundantly available lignocellulosic biomass consists of almost 70% carbohydrates made up of fermentable sugars which can be converted to second-generation biofuels and chemicals. These carbohydrates can be either used as such in polymeric forms or de-polymerized to their respective monomers, glucose, xylose and arabinose. Isolation of individual components of biomass in pure form is rather tricky requiring appropriate pretreatments using solvents such as ionic liquids (IL), which disrupt the lignin and hemicellulose network¹. These individual components will be sustainably available in abundance as renewable feedstock biopolymers and biocomposites with properties matching those of petroleum-based compounds. In an oil refinery, a crude product is converted into individual compounds of high purity. Similarly, in the bio-refinery concept, the biomass is converted to a variety of products such as fuels and chemicals, including high-cost specialty chemicals². The lignocellulosic biomass needs to be subjected to different pretreatments to separate individual components of the biomass. Pretreatment processes are supposed to be the entry point for any bio-refinery scheme.

All biomass pretreatments reported till today produce insoluble solids that are hydrolysed using costly enzyme cocktails, the availability of which is another threat to the economics of biomass refinery. Hydrolysis of treated biomass results in less concentrated sugar syrups containing glucose and xylose degradation

products causing problems in sugar fermentation. A recently published article in *Science*³ reports the laboratory-scale production of soluble carbohydrates from biomass such as corn stover, hardwood and softwood using a solvent mixture consisting of biomass derived γ -valerolactone (GVL), water and dilute H₂SO₄. GVL is known to solubilize biomass components, including lignin. The soluble carbohydrates in the solvent mixture can be recovered as a concentrated solution (127 g/l) by addition of NaCl or liquid CO₂. The liquid CO₂ recovered monomer fraction was converted to ethanol by a robust *Saccharomyces cerevisiae* strain with 87% yield. Considering the preliminary economics based on various assumptions, the proposed approach appears to be economically competitive to present biomass-derived processes involving pretreatment followed by simultaneous saccharification and fermentation (SSAF). One of the major advantages in this approach is the synthesis of GVL from biomass-derived levulinic acid and recycling of this solvent back to the system. This approach could be a turning point in the biomass conversion technologies, since it does not require costly enzymes to hydrolyse the biopolymers in the pretreated/untreated biomass to their respective monomers. In addition, this treatment can be used for any type of biomass, including hardwood and softwood, unlike other pretreatments in which the type of biomass decides their suitability. The only disadvantage is that the major solid

obtained in all streams is lignin, which is utilized for burning. Hence the fate of the important biomass component, lignin, still remains unclear.

Lignin conversion to value-added products is still in its infancy due to its complex and irregular structure, and even now lignin is incinerated as an inefficient energy source. It is also the most abundant carbon source available in nature and hence its valorization is essential to improve the economics of biomass conversion. Ragauskas *et al.*⁴ have discussed various challenges in lignin conversion to high-value products such as low-cost carbon fibre, engineering plastics and thermoplastic elastomers, polymeric foams and membranes, and a variety of fuels and chemicals. These high-value products are currently sourced from petroleum. Many of those working on bio-refinery pay more attention to carbohydrate conversion without paying much attention to lignin valorization by transforming it into multiple product streams. Commercial success of bio-refinery depends on the conversion of all lignocellulosic components into high-value products. Lignin can serve as a potential source of aromatic platform chemicals, although such conversion is still challenging⁵. Deconstruction of biomass with specific ionic liquids (IL) is promising because lignin extracted in IL can be precipitated and recovered by the addition of anti-solvent, usually water¹. This recovered lignin can be used in the manufacture of wood adhesives, cement additives or various products such

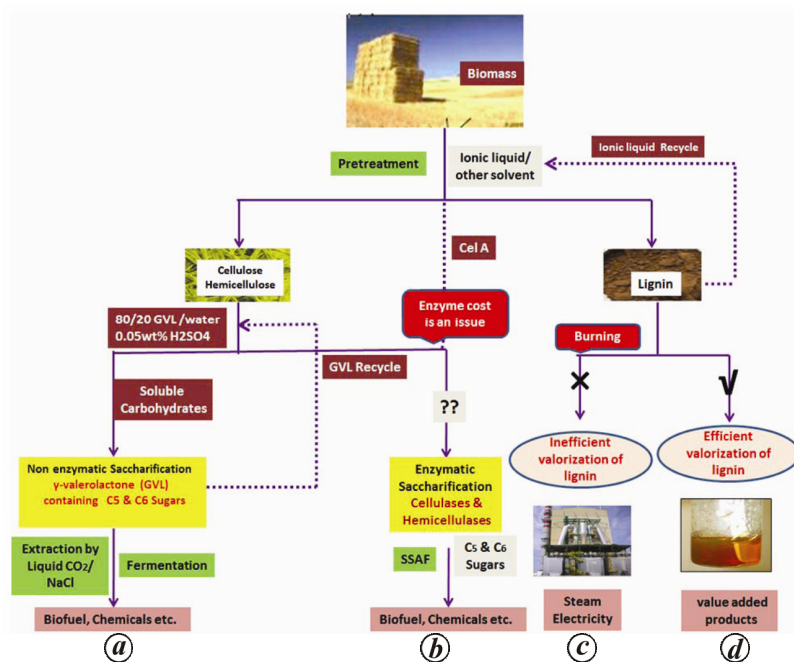


Figure 1. Schematic presentation of overall process for efficient conversion of biomass components to fuels and chemicals. **a**, Feasible process for biomass conversion into biofuels and biochemicals; **b**, Feasibility depends on cost of enzymes involved in biomass conversion; **c**, Inefficient way of lignin valorization as it is burnt; **d**, Efficient way of lignin valorization since it can be used as a source for production of value-added chemicals.

as vanillin and cinnamic acid that are commercially used as sweeteners and precursors of pharmaceuticals. In addition, lignin can be de-polymerized and the released substituted monomers can act as precursors of a wide range of products, including fuels such as cyclohexane. Recently, Sathitsuksanoh *et al.*⁶ have used non-toxic and recyclable ionic liquid, [C2mim][OAc], for pretreatment of wheat straw, *Miscanthus* and loblolly pine followed by enzymatic hydrolysis of the treated material. They found that IL pretreatment process conditions play a major role in obtaining lignin structures suitable for its valorization, thereby improving the economics of bio-refinery. Though the ionic liquids are costly, they can be recycled to make the IL-pretreatment processes economically feasible. We suggest that the IL-pretreated biomass (rich in cellulose and hemicellulose) can be treated with a mixture of GVL and water to depolymerize it to the respective sugars without the use of costly enzymes. This may help in the utilization of all the three biomass components for production of biofuels and value-added chemicals. The developments in the use of solid acids⁷ in biomass hydrolysis may also establish the

efficient and economically viable process for biomass hydrolysis in the near future. The possible means of utilizing all biomass components with commercial success is given in Figure 1.

Brunecky *et al.*⁸ reported an unusually large multidomain cellulase, CelA that may give a complete solution to biomass conversion technology. CelA could be the ideal biocatalyst since it acts preferably on raw/native biomass releasing cellobiose and glucose. In addition, it is active at even higher temperatures (80°C), which will avoid the bacterial contamination problems during hydrolysis of raw biomass. This enzyme has great potential in biomass to fuel technologies compared to most commercial biomass degrading enzymes that are enzyme cocktails with extremely less specific activity on raw biomass. Hence there is scope for development of new classes of enzymes such as hemicellulases preferentially degrading hemicellulose in raw or CelA-treated biomass. Specific xylanases capable of producing xylo-oligosaccharides (XOS) from xylan in raw biomass could add new dimensions to the economics of hemicellulose (biomass) conversion to value-added products⁹. Thus the search for the exist-

tence of such unknown enzymes may provide new avenues for efficient utilization of lignocellulosic biomass.

Suitable biomass pretreatment and low-cost production of biomass degrading enzymes still remain as challenges in biomass processing¹⁰. However, recent publications on GVL-pretreatment and CelA enzyme acting on raw biomass would probably meet these challenges to make the biomass conversion technologies eco-friendly as well as cost-effective. The Environmental Protection Agency (EPA) in USA has a mandate of adding 10% ethanol to fuel (E10 mix), which requires 51 billion litres of ethanol. The US is already producing 53 billion litres of ethanol from corn. The excess ethanol is sold to other countries, leaving no market for cellulosic ethanol¹¹. Hence only 1.1 million litres of ethanol is produced in the US from a handful of cellulosic plants. However, most of the Asian countries like India have to depend on cellulosic ethanol-based technologies to meet their E10 mix requirements. Such innovations in biomass conversion would benefit highly populated countries, where food is not available even to humans.

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