# Ionic Liquid Pretreatment

SBE Special Supplement: Biofuels

# Ionic Liquid Pretreatment

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Ionic liquids show promise as lignocellulosic biomass solvents. But is this approach a scientific curiosity or a commercially viable biofuel pretreatment technology?

# Lignocellulose biomass

- The most abundant and renewable source of carbon on the planet
- It has been estimated that more than a billion tons are available annually in the U.S. alone
- Lignocellulosic biomass can be grouped into four main categories: agricultural residues, dedicated energy crops, wood residues, municipal paper waste

# Plant cell wall

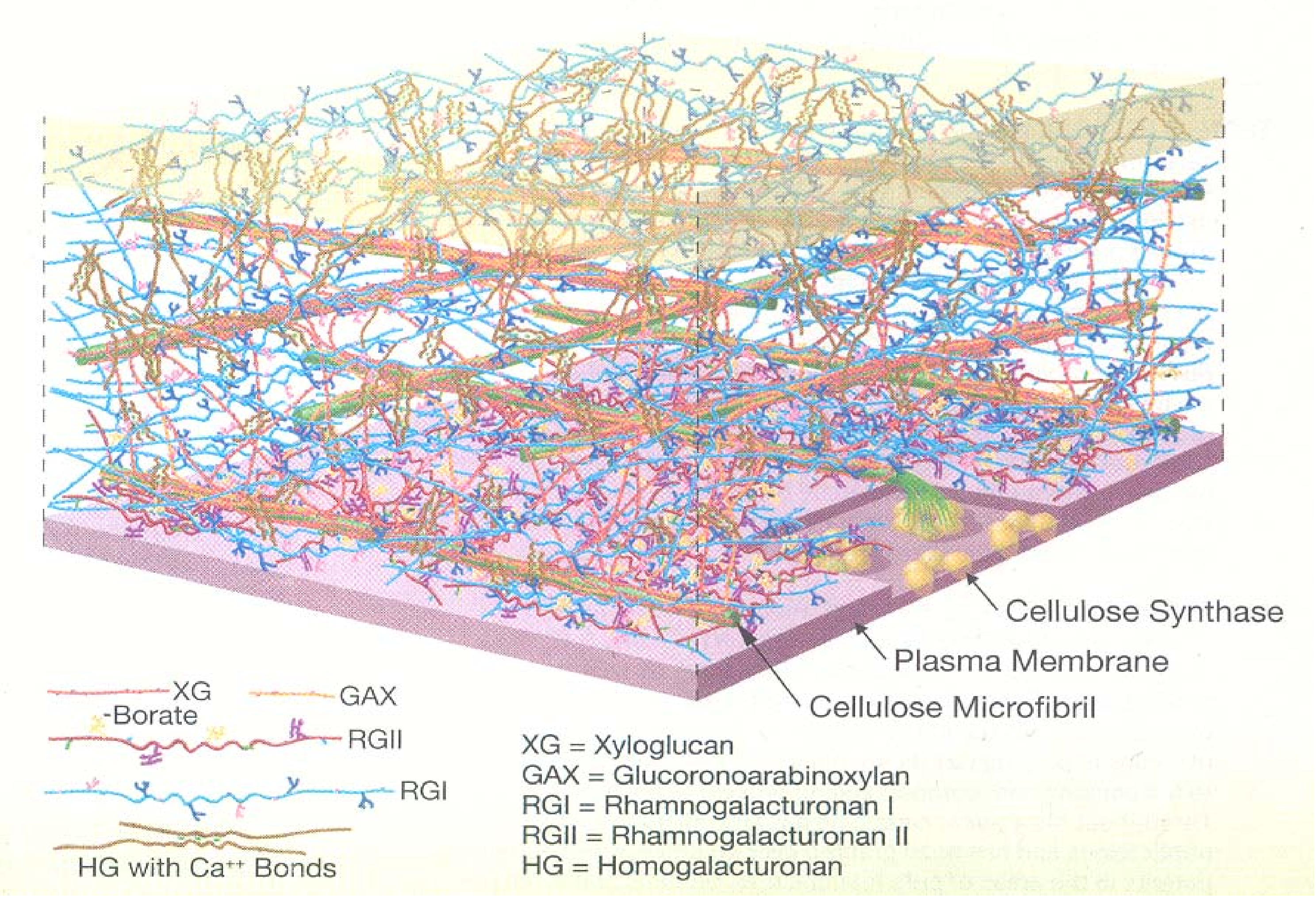



Fig 1. The plant cell wall consists mainly of cellulose, hemicellulose, and lignin.

# Plant cell wall

- plant cell walls are complex structures composed of cellulose, hemicellulose, and lignin
- they are difficult to deconstruct into their component polymers and monomers
- This recalcitrance makes it more expensive and energy-intensive to convert lignocellulose into fermentable fivecarbon and six-carbon monomeric sugars (i.e., xylose and glucose) than the starches in corn or saccharides in sugarcane and sugar beets.

# Cellulose



- It is typically the most abundant molecule in the cell wall
- Making up 20-30% of the cell wall's dry weight
- The ß-l,4-glycosidic linkages between the glucose monomers enable the formation of crystalline cellulose microfibrils during cell wall biosynthesis
- These microfibrils are highly crystalline and provide the primary structural framework within the cell wall

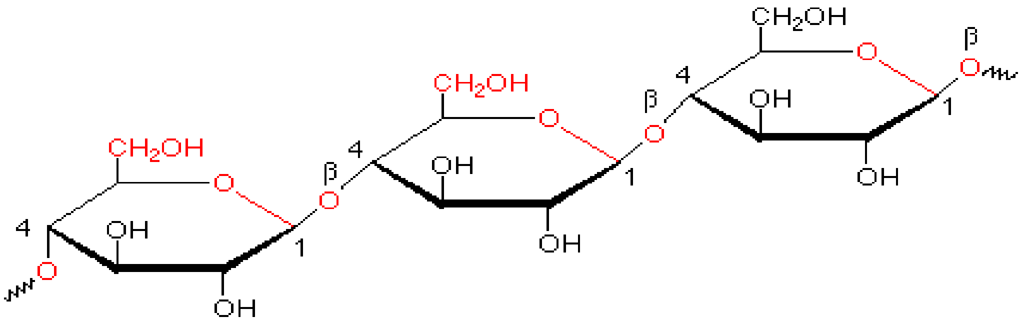
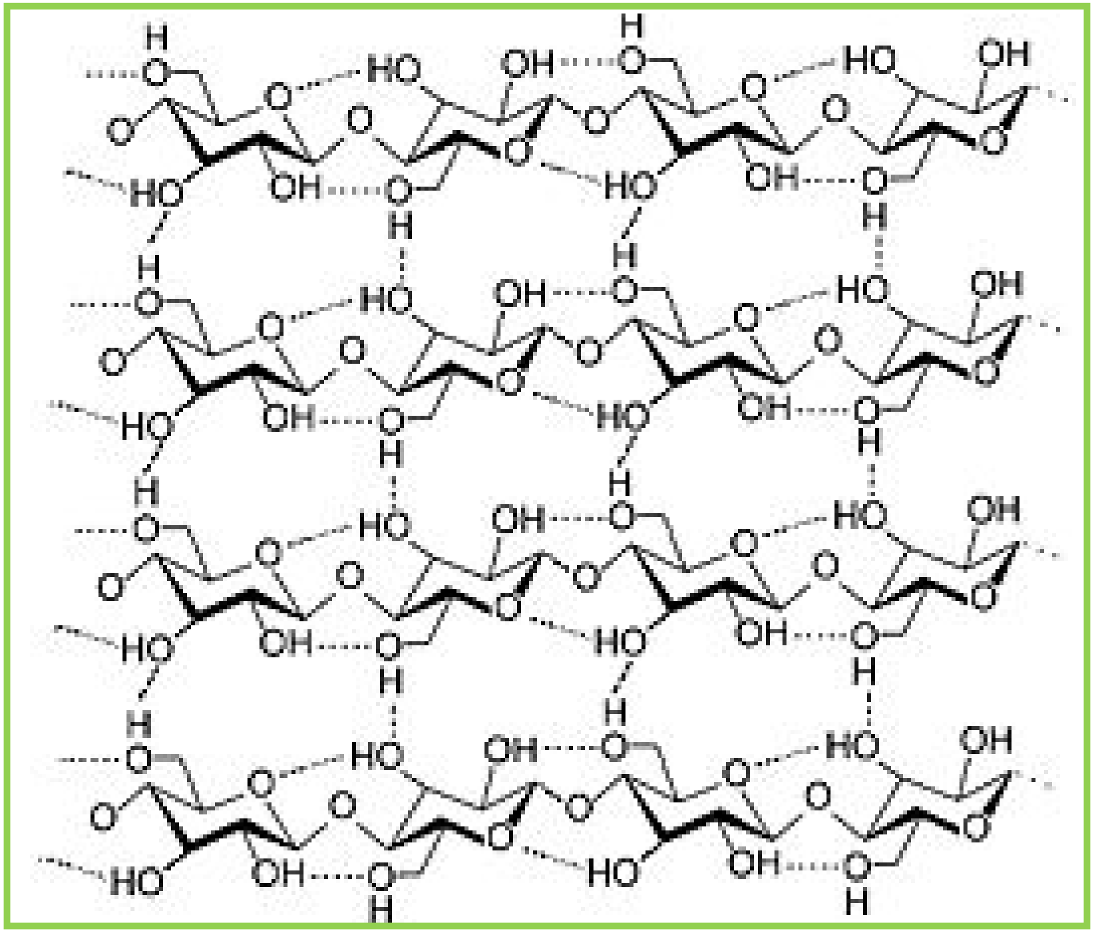



Fig 2. Structure of  Cellulose

# Cellulose structure



# Hemicellulose, Lignin

- Cellulose microfibrils have a coating of hemicellulose that cross-links them together
- The hemicellulose is extensively functionalized during cell wall biosynthesis and can be very difficult to convert into monomeric sugars.
- Lignin, typically the secondmost abundant biopolymer found in vascular plants, is a heterogeneous biopolymer based on phenylpropanoid units.
- Lignin is imparts resistance to insects, microbes, infection, and weather, and it facilitates water transport

# Pretreatment

- The enzymatic conversion of biomass to its component sugars is predicated on a pretreatment step that breaks apart the lignin-carbohydrate complex and increases the surface accessibility of the polysaccharides to the hydrolytic enzymes.

- One of the most critical needs that must be addressed for lignocellulosic biofuels to become a reality is a cost-effective and efficient biomass pretreatment technology. It is estimated that, on a per-gallon basis, biomass pretreatment represents the second-largest (19~22%) cost in biofuel production, after the feedstock (30~32%)

# Pretreatment

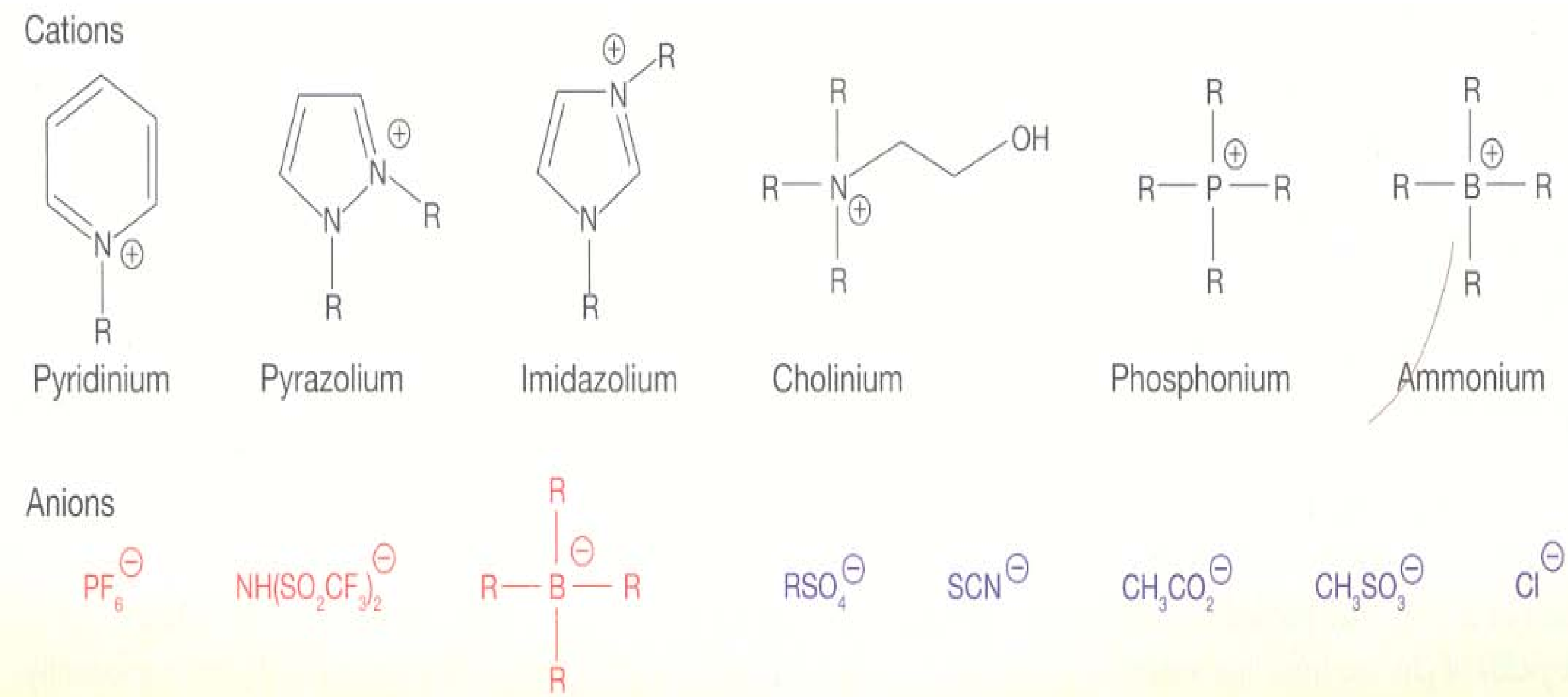
- Several physical and chemical pretreatment methods are being further developed to overcome the recalcitrance of lignocellulose, increase enzyme efficiency, and improve the yields of monomeric sugars from lignocellulose.

- These include dilute acid, ammonia fiber expansion, lime, steam explosion, and organic solvent pretreatment methods.

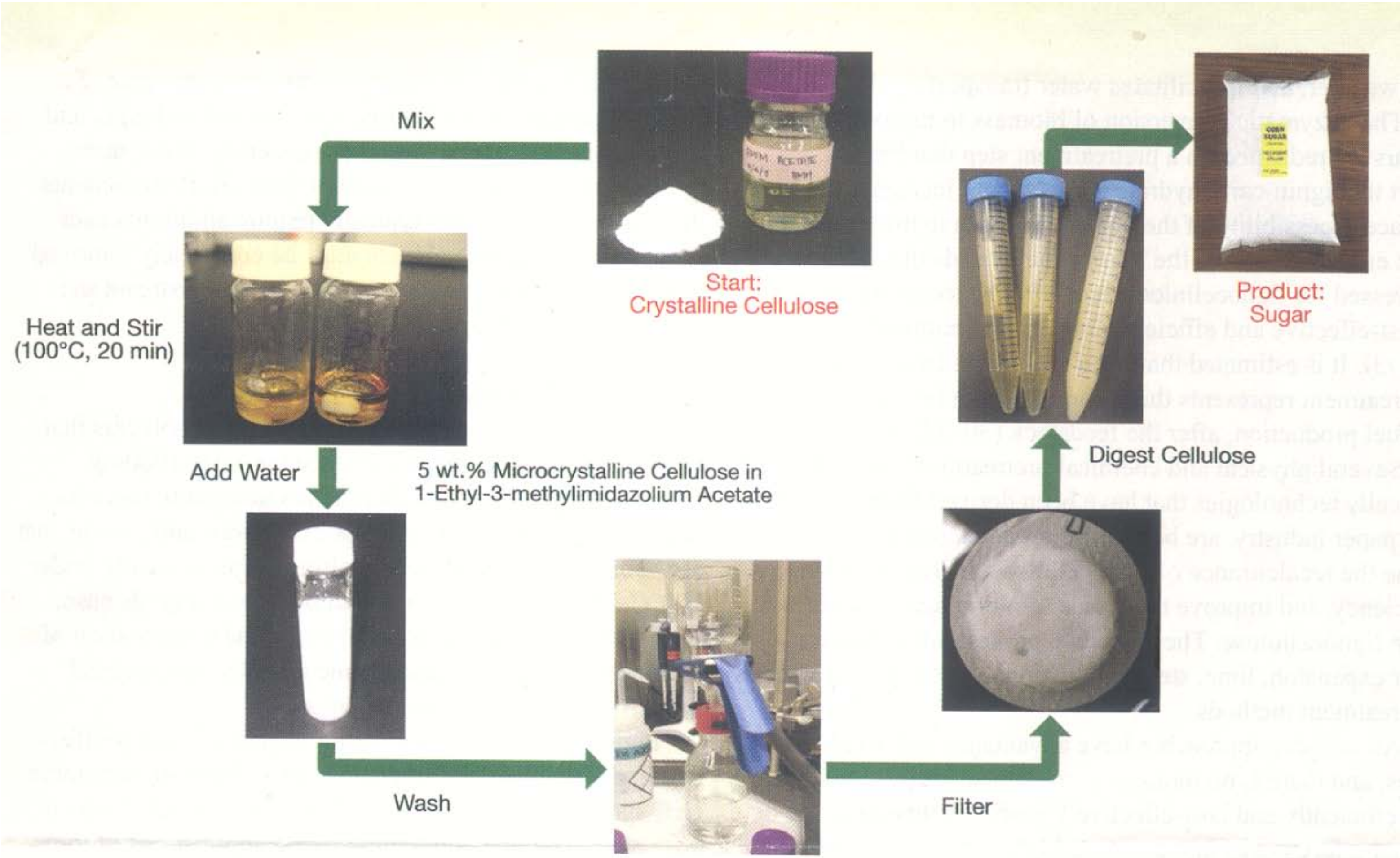
# Ionic Liquid

- Ionic liquids are a relatively new class of solvents as environmentally friendly alternatives to organic solvents
- It is a salt composed of anions and cations that are poorly coordinated, with melting points typically under 100°C
- There are thousands of known ionic liquids based on a wide range of anions and cations, the combination of which defines the thermodynamic and physicochemical properties of the ionic liquid

# Ionic liquid is a salt composed of a cation (top) and an anion.

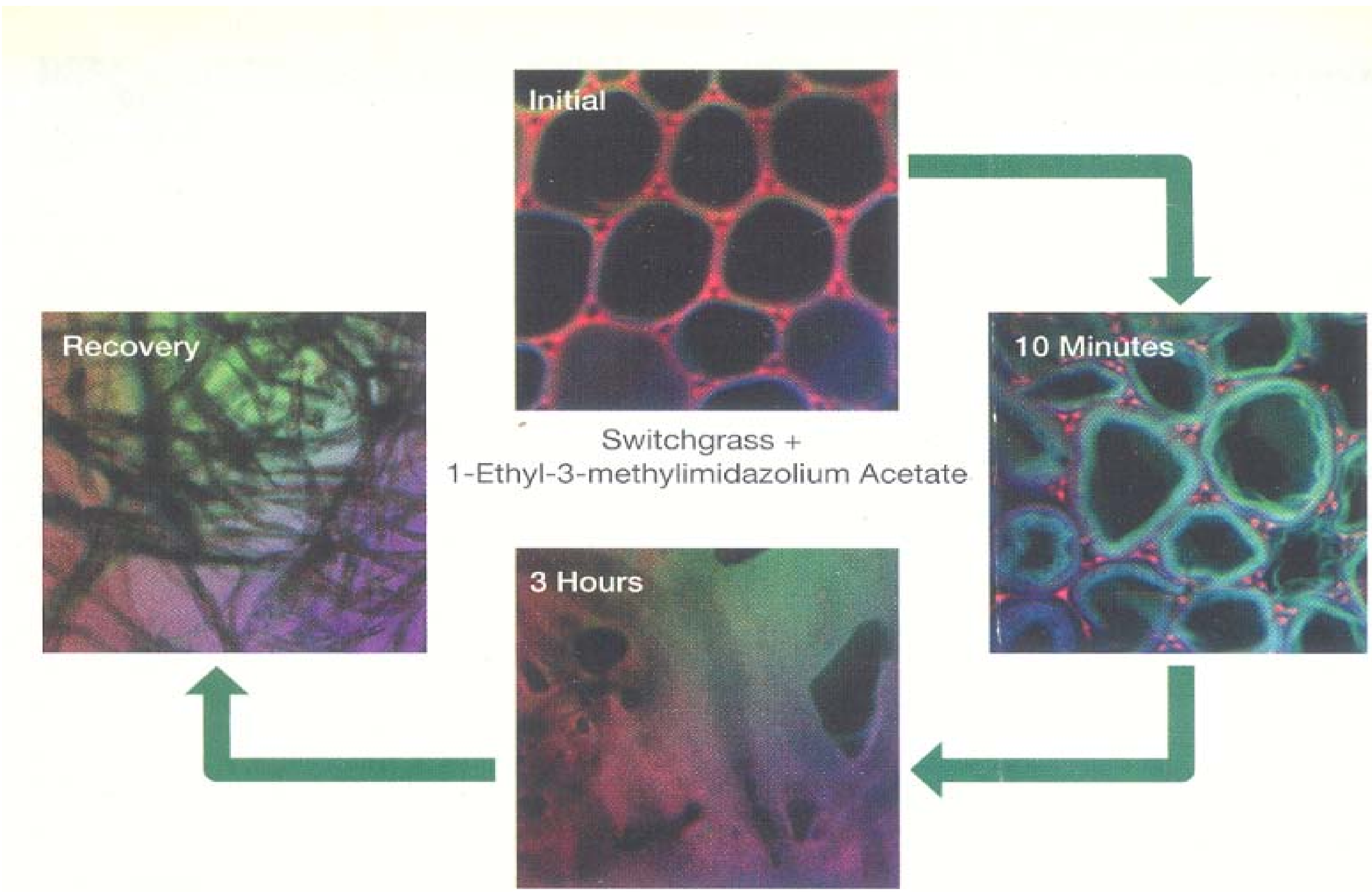


# Cellulose to glucose by ionic liquid



| Table 1. The solubility of cellulose and lignin in alkyl-imidazolium ionic liquids is a function of the specific anion and cation. | | | | | |
|---|---|---|---|---|---|
| **Cation** | **Anion** | **Cellulose Solubility** | **Lignin Solubility** | **Temperature** | **Reference** |
| 1-Allyl-3-methyl-imidazolium | Formate | 21% | N/A | 85°C | 21 |
| 1-Ethyl-3-methyl-imidazolium | Acetate | N/A | ~30% | 90°C | 16 |
| | Methylphosphonate | 10% | N/A | 45°C | 22 |
| | Methyl Methylphosphonate | 10% | N/A | 55°C | 22 |
| | Dimethylphosphonate | 10% | N/A | 65°C | 22 |
| 1-Butyl-3-methyl-imidazolium | Chloride | 3% | 10% | 90°C | 10 |
| | Chloride | 3% | 1.4% | 75°C | 23 |
| | Bromide | N/A | 1.75% | 75°C | 23 |
| | Trifluoromethanesulfonate | N/A | ~50% | 90°C | 16 |
| | Methylsulfate | N/A | 31.2% | 50°C | 23 |
| | Methylsulfate | N/A | 6.18% | 25°C | 23 |
| 1-Butyl-2,3-dimethyl-imidazolium | Hexafluorophosphate | N/A | Insoluble | 70–120°C | 23 |
| 1-Hexyl-3-methyl-imidazolium | Tetrafluoroborate | N/A | 1.45% | 70–100°C | 23 |
| | Trifluoromethanesulfonate | N/A | 27.5% | 50°C | 23 |
| | Trifluoromethanesulfonate | N/A | 1.0% | 25°C | 23 |
| 1,3-Dimethylimidazolium | Methanesulfonate | N/A | 34.4% | 50°C | 23 |
| | Methanesulfonate | N/A | 7.42% | 25°C | 23 |
| Benzyldimethyl (tetradecyl) ammonium | Chloride | 39% | N/A | | 24 |

# Autofluorescent microscopy images : Pretreatment of switchgrass and polysaccharide recovery.



# Results

- The high temperatures and long residence times required for complete hydrolysis increase the risk of sugar degradation and the formation of inhibitory compounds.
- Several major challenges must be overcome before ionic liquid pretreatment can become a viable commercial process. The most pressing issue is the current cost of ionic liquids.
- Even if the ionic liquid can be purchased at sufficiently low cost, the process will need to operate in a closed-loop fashion with recycling to minimize the replenishment of the ionic liquid.
- An efficient means of recovering and removing any remaining lignin and plant cell wall constituents that remain in the ionic liquid after the initial addition of the anti-solvent must also be in place.