Advanced physical/chemical fractionation

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Overview

- Objectives Fractionation work in BioSynergy
- Main processes studied
- Major accomplishments
- Assessment of fractionation routes
- Conclusions
Fractionation of lignocellulosic biomass

Objectives Fractionation:
- Fractionation of lignocellulosic biomass into its **composing fractions** with sufficient quality for production of (bio)chemicals (including lignin).
- **Enhancement (enzymatic) degradability** of cellulose to fermentable sugars.

• To develop methods for fractionation for lignocellulosic biomass into C5 sugars, C6 sugars, and lignin
• To design optimal enzyme systems for an efficient conversion of biomass-derived...
Main routes studied; partners

- Ethanol/water organosolv
- Organic acid organosolv
- Mechanical/Alkaline fractionation
- Mild fractionation of hemicellulose
- HCl-based hydrolysis
- Enzymatic hydrolysis
Activities

- Proof of concept for fractionation work on the basis of same lignocellulosic feedstocks
- Exchange of protocols
- Exchange of samples for enzymatic hydrolysis
- Supply of fractionised products to other WP
- Definition and application of technical benchmarks

Ethanol/H2O Organosolv, ECN
Mech./alk pretreatment A& Partners: WUR, ABNT, ARD, Bioref, ECN, TUD
Acid organosolv Pilot plant ARD
Ethanol/water organosolv (ECN)

- **Method**
  - 160-200 °C, 15-60 min, 5-30 bar.
  - Organic solvent: ethanol (/ acetone)
  - Catalyst: no or H₂SO₄

- **Application in Biorefinery**
  - Carbohydrates for 2nd generation biofuels or chemicals (furans)
  - High-purity Lignin for conversion into chemicals
  - Remaining solids for energy
Major Accomplishments EtOH/water organosolv

- Parameters established that govern organosolv fractionation.
- Suitability organosolv fractionation for various feedstocks assessed.
- Scale-up process to 20L batch reactor.
- Application tests of cellulose and lignin.
- Conceptual design completed
Enzymatic digestibility

<table>
<thead>
<tr>
<th></th>
<th>Wheat straw</th>
<th>Barley straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh (2L, 2008)</td>
<td>17</td>
<td>23</td>
</tr>
<tr>
<td>Product (2L, 2009)</td>
<td>60</td>
<td>92</td>
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<tr>
<td>Product (20L, 2010)</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Product (2L, 2008)</td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>
Organic Acid Organosolv (ARD)

- **Method**
  - 105 °C, atmospheric pressure
  - Organic solvent: acetic acid, formic acid

- **Application in Biorefinery**
  - Carbohydrates for 2nd generation biofuels
  - High-purity Lignin for conversion into chemicals
  - Remaining solids for energy
Major Accomplishments Org. Acid Organosolv

- Improved cellulose digestibility and purity of cellulose
  - By changing acid types
  - By de-acetylation of cellulose pulp
- Experiments performed with woods
- Experiments performed at micro-pilot scale
Mechanical-Alkaline Fractionation (WUR)

- **Method**
  - 75-100 °C, 1 – 4 h, atmospheric pressure
  - Catalyst: NaOH

- **Application in Biorefinery**
  - Combined C5/C6 fermentation to alcohols, organic acids
  - Lignin application as phenolic resins
  - Remaining solids for energy
Major Accomplishments Alkaline Fractionation

- Effect of processing conditions on chemical composition of pretreated straw and yield
- Enzymatic hydrolysis
  - Effect of dry matter on hydrolysis yields
- Isolation of lignin
  - Effect of processing conditions on black liquor properties
  - Properties of isolated lignins established
  - Application tests of isolated lignin
Pretreatment

Efficiency

Lab scale

Semi-technical scale

Chemical composition (wt%)

- Wheat straw
- Stirred reactor
- Conical reactor
- Extrusion (1)
- Extrusion (2)
- Refining (atm P)
- Refining (elev P)

- Other
- Ash (TGA)
- Lignin
- Hemicelluloses
- Cellulose

0 20 40 60 80 100

Wheat straw
Conical reactor
Mild fractionation of hemicellulose (TUDelft)

• Method
  ▪ 120 °C, 15-60 min, 5 bar.
  ▪ Catalyst: HCl, FeCl3

• Application in Biorefinery
  ▪ Selective production of hemicellulose-derived carbohydrates
    ─ Further conversion into furfural, xylitol, surfactants etc
  ▪ Solid residue for enzymatic conversion, or further separation routes
  ▪ Remaining solids for energy
Major Accomplishments hemic. fractionation

- Proof of principle mild (T < 120 °C) fractionation of hemicellulose
  - Relatively simple process, low-cost operation expected
  - Cellulose remains intact after C5 extraction and is free of minerals
  - Enzymatic degradability of cellulose needs improvement
HCl-based Acid hydrolysis (BioRef)

- **Method**
  - 32% - 37% HCl, room temperature

- **Application in Biorefinery**
  - Combined C5-C6 fermentation to alcohols
  - Applications of lignin products in hardboards
  - Remaining solids for electricity and heat
Major Accomplishments Acid hydrolysis

- Improved direct saccharification with a two-step strong hydrochloric acid application
  - No enzymes required
- Remaining lignin with good thermal properties
- Fractionation method is applicable for all feedstocks
Enzymatic hydrolysis (ABNT)

Objectives

• Achieve High productivity strains
• Increased enzyme effective activity which makes a reduction possible of enzyme dosage below 5mg/ g cellulose during enzymatic hydrolysis
• Production of enzymes at competitive cost
Major Accomplishments Enz. hydrolysis

- New supplemental enzymes developed
- Trials performed at 20% wt/wt
- Increased enzymatic activity of commercial enzyme mixes when supplemented
- Yield of SSF with new enzymes 44 g/L ethanol
Benchmarks for evaluating Fractionation

- Delignification
- Lignin purity, quality
- Hemicellulose hydrolysis
- Enzymatic degradability of cellulose
- Fermentability of glucose obtained from cellulose
## Results benchmarking (wheat straw)

<table>
<thead>
<tr>
<th>Method</th>
<th>Delignification</th>
<th>Lignin purity</th>
<th>Hemicellulose hydrolysis</th>
<th>Cellulose degradability</th>
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<tbody>
<tr>
<td>EtOH Organosolv</td>
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<tr>
<td>Acetone</td>
<td>79</td>
<td></td>
<td>82</td>
<td>87</td>
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<tr>
<td>Ethanol; acid catalysed</td>
<td>82</td>
<td>93</td>
<td>74</td>
<td>85</td>
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<tr>
<td>Upscaled process</td>
<td>82</td>
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<td>82</td>
<td>87</td>
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<tr>
<td>Organic acid Organosolv</td>
<td></td>
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<tr>
<td>Base case</td>
<td>53</td>
<td>68</td>
<td>81</td>
<td>52</td>
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<tr>
<td>Formic acid</td>
<td>47</td>
<td>40</td>
<td>63</td>
<td>76</td>
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<tr>
<td>De-acetylisation</td>
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<tr>
<td>Mechanical Alkaline</td>
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<tr>
<td>Extrusion</td>
<td>66</td>
<td>75</td>
<td>39</td>
<td>100</td>
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<tr>
<td>Conical reactor</td>
<td>70</td>
<td>80</td>
<td>38</td>
<td>89</td>
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<tr>
<td>Upscaled process</td>
<td>66</td>
<td>63</td>
<td>26</td>
<td>62</td>
</tr>
<tr>
<td>Hemicell fractionation</td>
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<tr>
<td>Mild hemicellulose fract.</td>
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**Note:** The table above shows the results of benchmarking different processes for wheat straw. The values represent percentages, where higher values indicate better performance.
Delignification (% of total lignin)

- Acetone
- Ethanol; acid catalysed
- Upscaled process
- Base case
- Formic acid
- Extrusion
- Conical reactor
- Upscaled process

- Ethanol Organosolv
- Organic acid Organosolv
- Mechanical Alkaline
Main conclusion

• All technologies lead to significant fractionation into composing elements C5, C6 sugars and lignin
  ▪ High cellulose degradability
  ▪ Differences in hemicellulose hydrolysis, and lignin yield and – characteristics
  ▪ Often trade-off between desired effects

• Fractionation technologies need to be optimized toward a particular goal
  o An integrated approach feedstock-process-endproduct is therefore required!
Remaining Issues

- Feedstock flexibility
- Development of large scale lignin applications
- Recycling of reactants
- Improving enzymes, esp. for upscaling
- Use of organic acids in stead of mineral acids
- Developing continuous reactor systems for fractionation
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