University of Birmingham, School of Chemical Engineering, College of Engineering & Physical Sciences, UK

FAPESP
Workshop Centro Paulista de Pesquisa em Bioenergia, Universidade de Nottingham e Universidade de Birmingham
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The Utility of Critical Fluids for Efficient Processing of Lignocellulose as Part of an Integrated Biorefining Concept

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Outline

- The University of Birmingham
- The School of Chemical Engineering
- The concept of an “Integrated Biorefinery”
- Biorefinery Technologies
- Critical Fluids
- Biomass to Bioenergy

Outline

- Lignocellulosic Biomass
- Lignocellulosic Biomass Biorefinery
- Example of a Research Project in Birmingham
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The University of Birmingham

- The University of Birmingham was founded in 1900.
- The University is home of around 28,000 students with one of the largest international student communities in the UK with over 4,000 international students from nearly 150 different countries and with 27% of the academic staff being from outside the UK.
- According to the university's research output it is ranked 12th in the UK overall (out of 159 institutions).

in the Research Fortnight University Power Ranking, based on the quality and quantity of UK.



The School of Chemical Engineering

- Around 30 academic teaching staff,
- 120 postgraduate students,
- Each year approximately 100 students enter the undergraduate School.

The RAE (Research Assessment Exercise):

- Places the school in the Top 5 Chemical Engineering Schools in the country;
- 20% of our outputs were in the highest 4* category (highest-international, world-leading);
- 45% in the 3* (high international) ranking.

The concept of an "Integrated Biorefinery"

The integrated biorefinery is to biomass what the traditional refinery is to oil

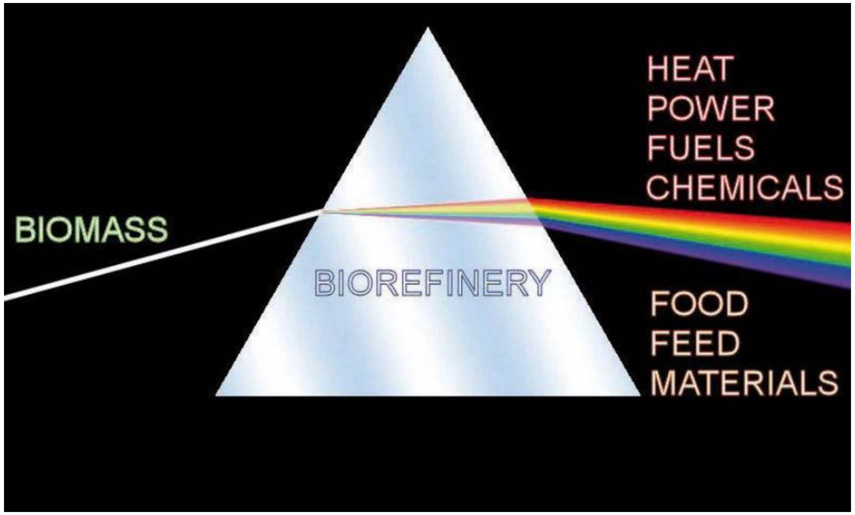
Biorefinery is understood as a further stage in the development of technologies based on biomass as feedstock

The concept of an “Integrated Biorefinery”

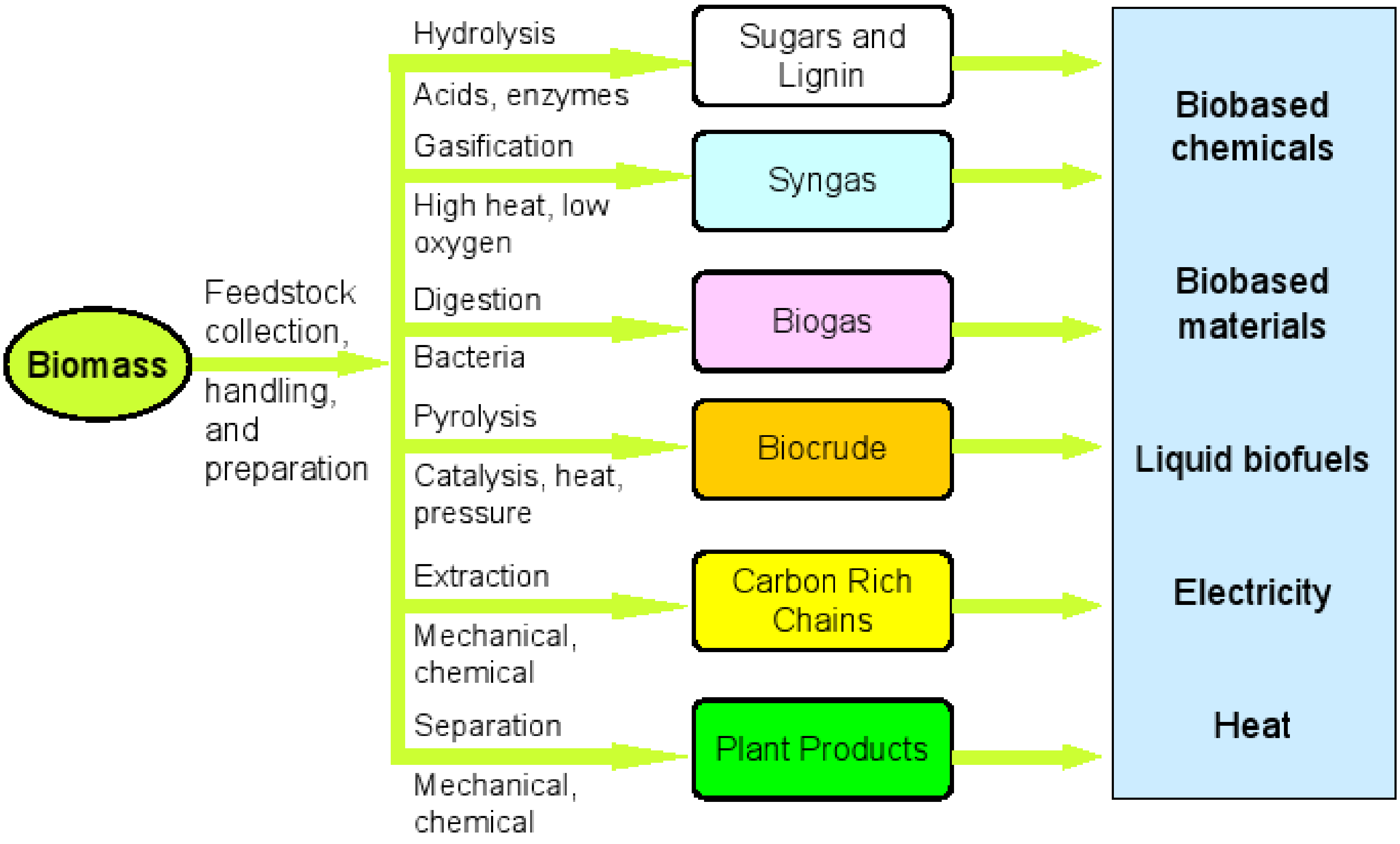
Definition:

A sustainable combination of biological, thermo-chemical, and chemical processes, aimed to produce a complete range of marketable products, using a wide range of feedstock, and getting advantage of synergies between technologies.

(definition IEA (International Energy Agency) Bioenergy task 42)



Biorefinery Technologies

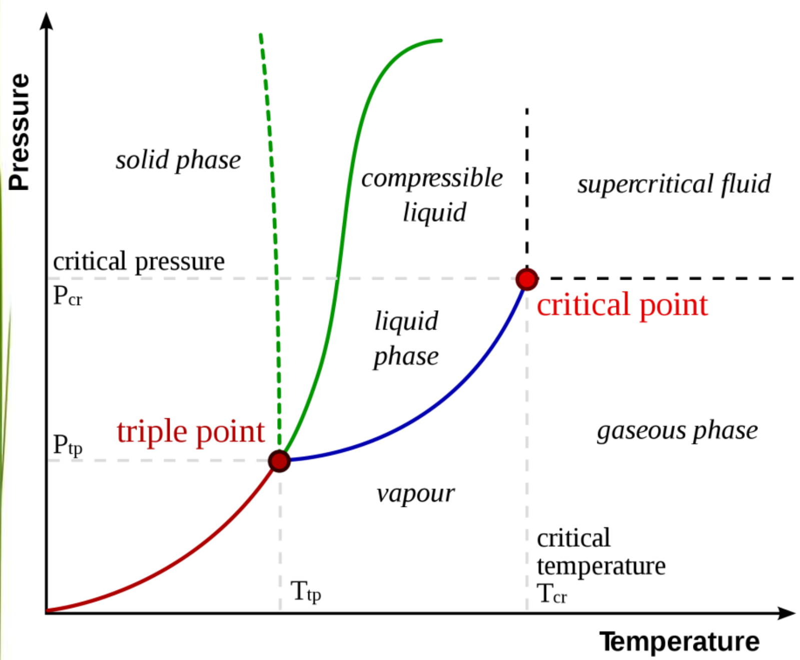


Critical Fluids

In 1822, Baron Charles Cagniard de la Tour discovered the critical point of a substance.

Definition:

The critical point of a pure substance or a mixture of them, is the point of highest temperature and pressure at which its vapour and liquid coexists in equilibrium. At pressure and temperature higher than the critical point, a supercritical fluid is obtained.



Solvent	Molecular weight	Critical temperature	Critical pressure
	g/mol	ºC	bar
Carbon dioxide	44.01	31	73.8
Water	18.01	374	220.6
Methanol	32.04	240	80.9
Ethanol	46.07	241	61.4
Acetone	58.08	235	47.0

Critical Fluids

- In the Supercritical region the substance is neither a gas nor a liquid – it is a fluid that has properties of both.
- There are no sharp boundaries between gas and liquid.
- Properties of SCFs can be very different from the normal liquid phase.

Advantages:

- Increased solubilities of reactants or products
- Single homogeneous phase, no transport limitations
- Reaction conditions can be fine-tuned by varying pressure and/or temperature
- Separation step can be eliminated
- SCFs such as water, CO_2 can be recovered, or disposed of with little or no environmental impact.
- Organic compounds are soluble in supercritical water, inorganic salts are insoluble $\Rightarrow$ Supercritical water oxidation

Critical Fluids

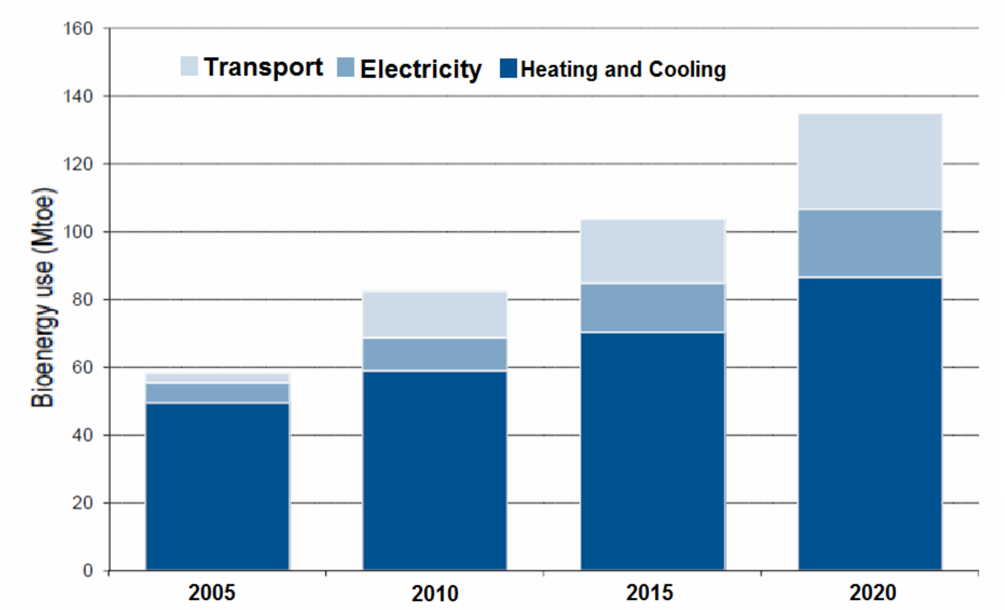
Applications:

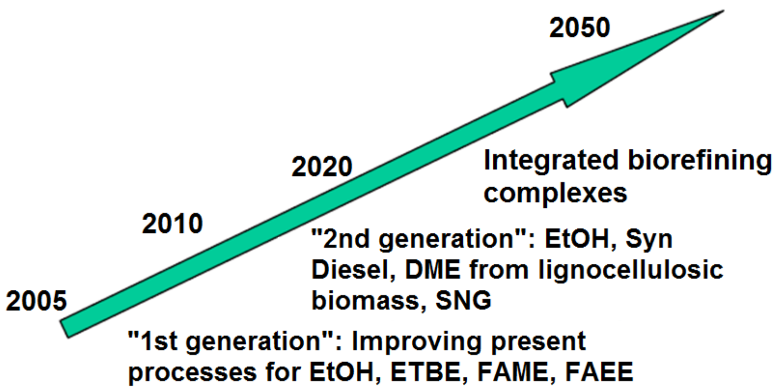
- Supercritical Fluid Extraction (SFE)
- Supercritical Fluid Chromatography (SFC)
- Catalysis/Reaction Feed
- Injection Molding and Extrusion
- Particle Formation
- Cleaning
- Plastics Production
- **Integrated Biorefinery Concept, due to the relatively easy tuneability of the fluids.**

Biomass to Bioenergy

According to the EU Renewable Energy Directive:

- Agreement to use 20% of renewable energy by 2020
- UK-specific target of 15% by 2020.





EU estimates of bioenergy use towards reaching 2020 Renewable Targets, according to National Renewable Energy Action Plans (to March 2011)

Lignocellulosic Biomass

Plant material that is principally composed of cellulose, hemicellulose, and lignin. Its sources are:

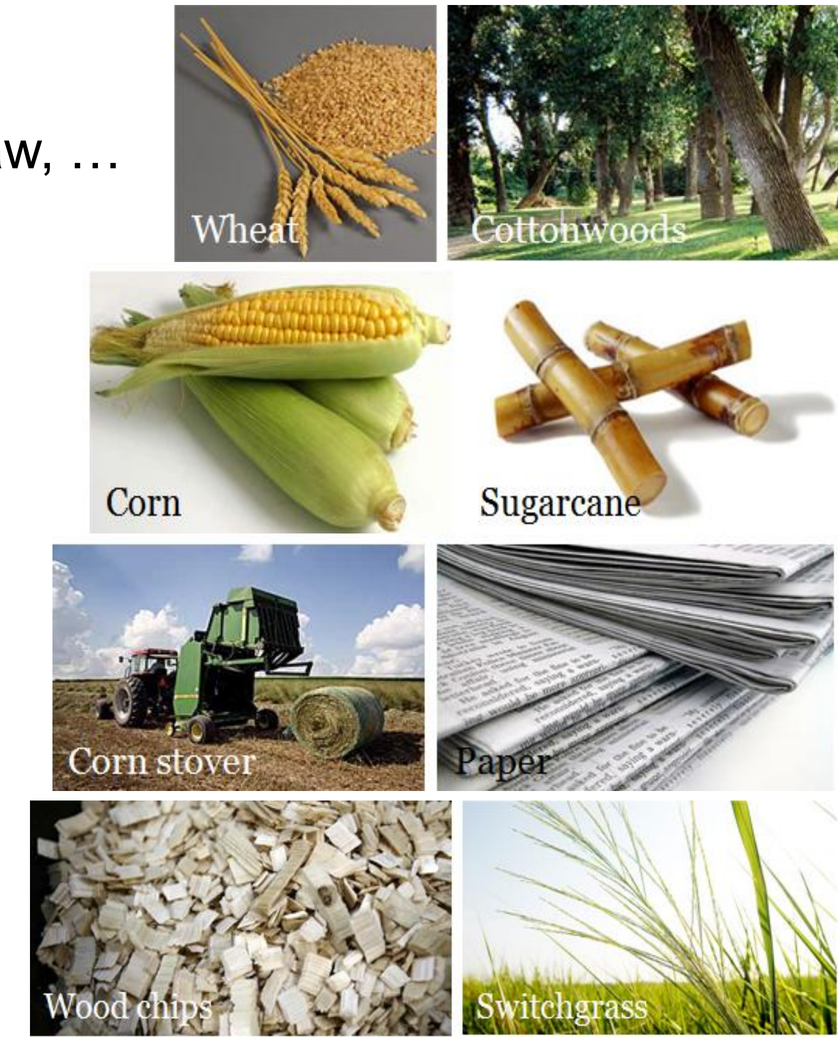
- Hardwood: poplar, willow, ...
- Softwood: spruce, pine, ...
- Herbaceous: Miscanthus, wheat, straw, …

Available in form of:

- (Forestry / agricultural) residues.
- Energy crops.

Advantages compared to other types of biomass:

- Wide range of low cost feedstocks.
- No direct competition with food production.
- High CO_2 reduction of derived fuels and products.



Lignocellulosic Biomass – Enzymatic Hydrolysis

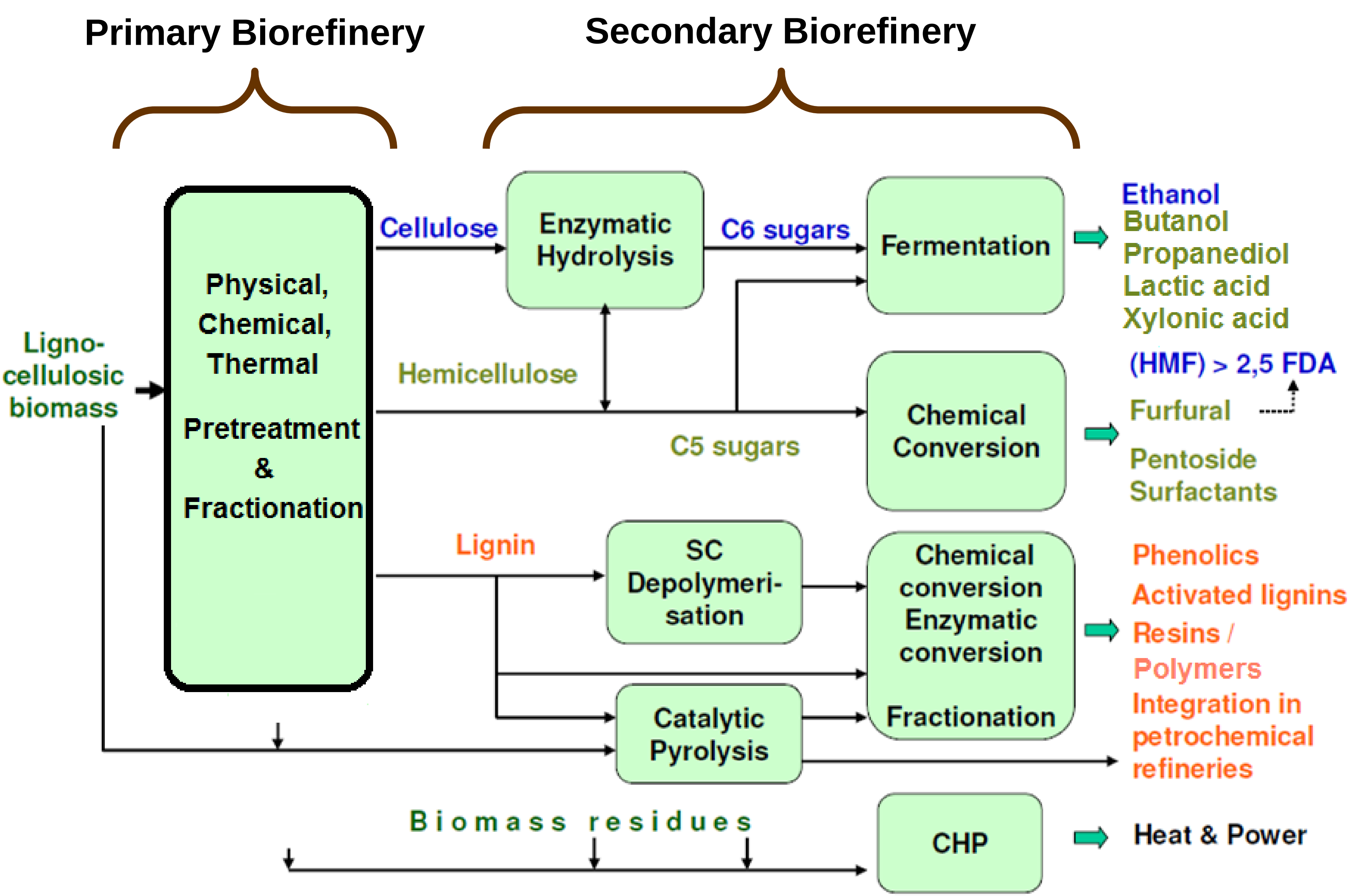
Some disadvantages of direct enzymatic saccharification of lignocellulose :

- Structural components strongly linked (physically & chemically).
- Cellulose protected against decomposition by lignin.
- Crystallinity cellulose.

Pretreatment needed to overcome biomass “recalcitrance” by:

- Removing hemicellulose and lignin to improve accessibility for hydrolytic enzymes.
- Removing / altering lignin to reduce cellulase binding and the production of inhibitors.
- Reducing crystallinity of cellulose.

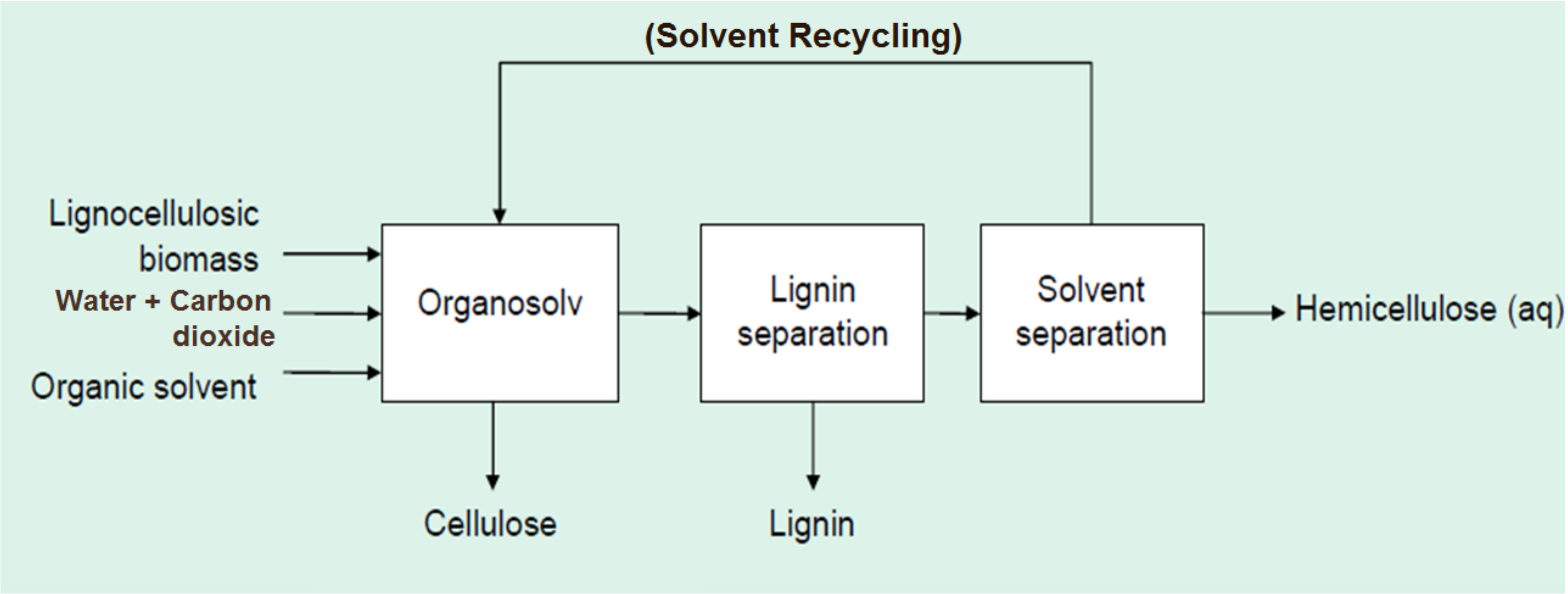
Lignocellulosic Biomass Biorefinery



Example of a research project in Birmingham applying the integrated biorefining concept

Modified organosolv pretreatment:

Evaluate the impact of sub-critical water processing parameters, such as temperature, load size, addition of ethanol and CO_2 as modifiers, in order to optimise the solubilisation and delignification of the *Miscanthus* χ *giganteus, the lignocellulosic feedstock*



Miscanthus χ giganteus

In the last 15-20 years it has attracted a lot of interest as a potential feedstock for bioenergy.

- **10- 40 oven-dried tonnes ha^{-1}** - Annual yields across Europe, from established trials depending on soil type and climate.
- It is relatively **easy to establish.**
- Requires **low inputs** in terms of nitrogen and water.
- Does not **compete** with food production.

- It is a perennial rhizomatous grass and its stems are harvested annually which can attain 3m in height.

Miscanthus χ giganteus

- Miscanthus was first cultivated in Europe in the 1930s, introduced from Japan.
- US are exploring the closely related “cousins” such as switch grass but the interest in Miscanthus is rising.

The *Miscanthus χ giganteus*, was provided by Institute of Biological, Environmental & Rural Sciences (IBERS) in collaboration with Phytatec (UK) LTD and is composed of 44% cellulose, 20% hemicellulose and 26% Klason lignin.

Research Methodology

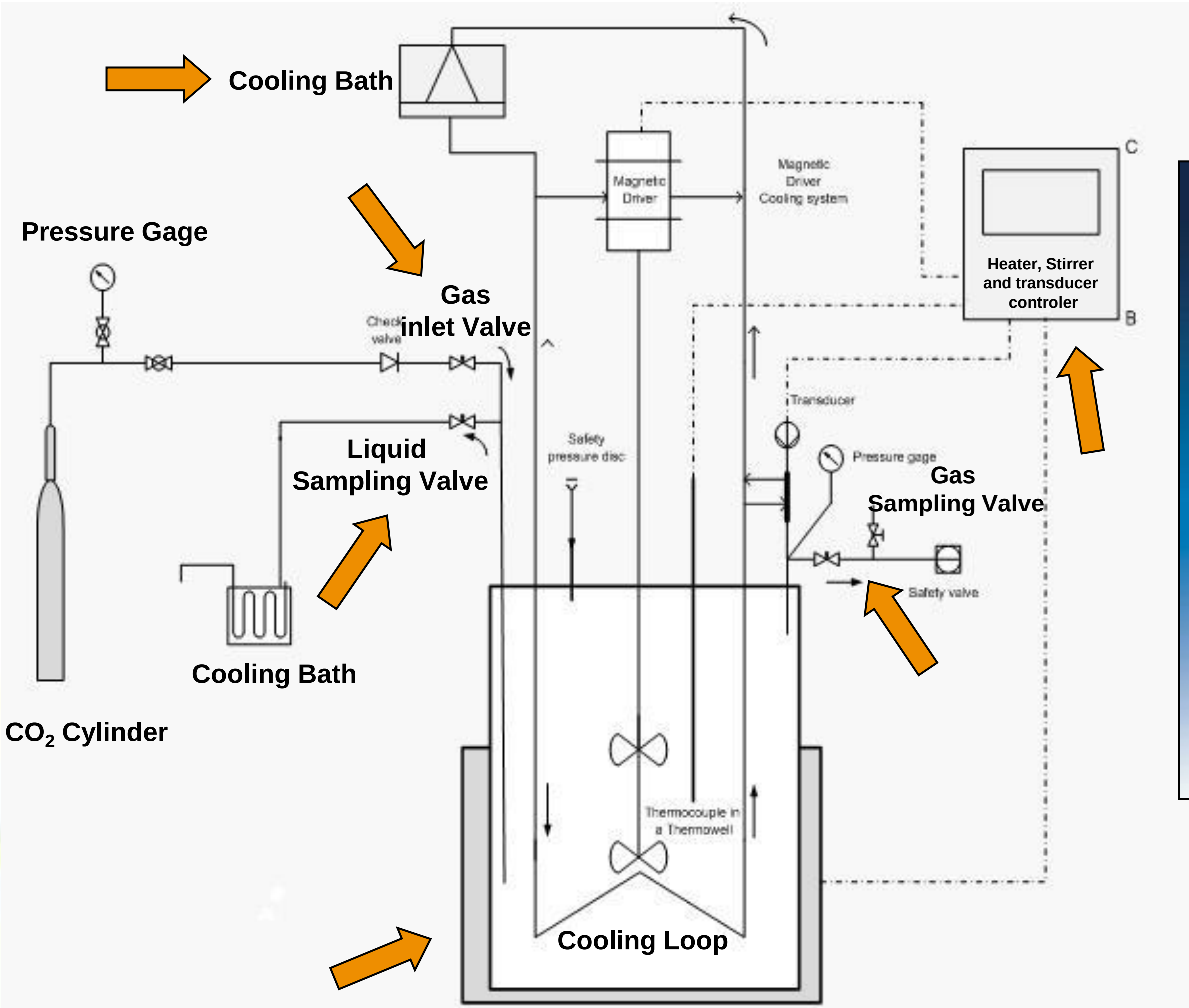
Samples Preparation

- Samples (2.5, 5, 10, 15g) were rehydrated in 250 ml of water:ethanol solution (0, 33, 50, 67% in ethanol) at 50ºC for 20 min.
- Mixture was ground in a blender for 3 min.
- Grinding conditions had been optimised and an average particle size of approximately 500μm was obtained.

Lignin Recovery

- After hydrolysis, the the resulting slurry was vacuum filtrated.
- Lignin in the filtrate was recovered by precipitation with the addition of water to adjust ethanol concentration to 25% and centrifuged at 4ºC and 10K RPM for 10 min.
- The supernatant was decanted and the resulting precipitated lignin was air-dried.

Sub-critical Water Mediated Hydrolysis



A Parr 500ml high pressure stirred reactor manufactured in Alloy C276 is used for the hydrolysis experiments.

Analytical Methods

Klason lignin determination:

There are many different methods for quantifying lignin, like Acid Detergent Lignin. But we have chosen the Klason assay because it measures the total lignin directly.

- Residual insoluble fraction was analysed for lignin using Klason lignin assay

(ASTM Standard Method E1721-01: Determination of acid-insoluble residue in biomass).

- The amount of Klason lignin remaining in the insoluble fraction was compared to the amount present in the biomass giving the percentage lignin solubilised (delignification).

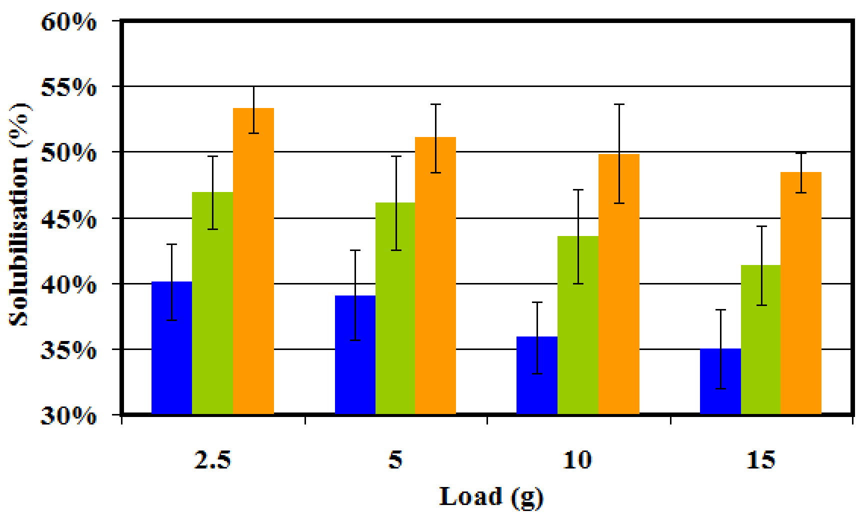
Sub-critical Water Mediated Hydrolysis - Lignin

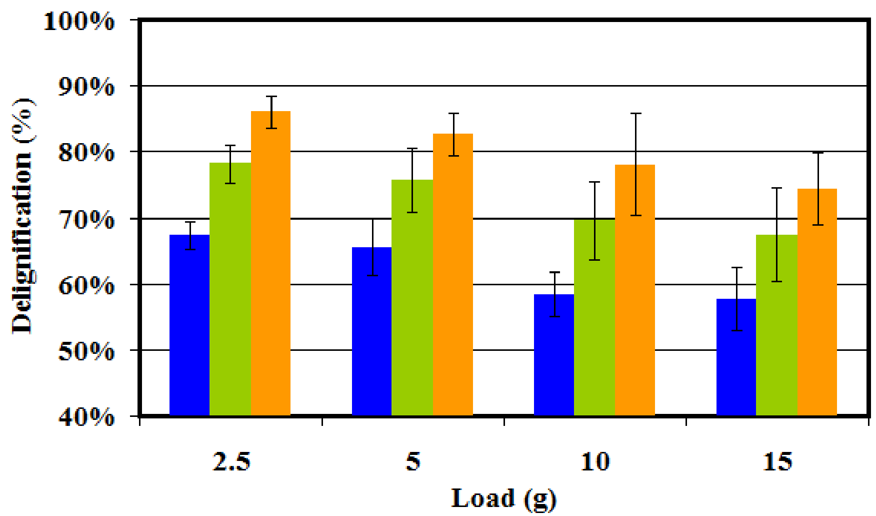
Pretreatment parameters:

- Temperatures: 80 - 200ºC, (T>200 cause cellulose hydrolysis and sugars degradation)
- Load sizes: 2.5 -15 g of biomass
- In 250 ml of ethanol:water mixture at different concentrations 0 - 67%
- Carbon dioxide: 2 to 55 bar.
- Hydrolysis time: 5 to 60 min

Results

Effect of temperature and biomass:solvent ratio (load size) on sub-critical water mediated hydrolysis of Miscanthus



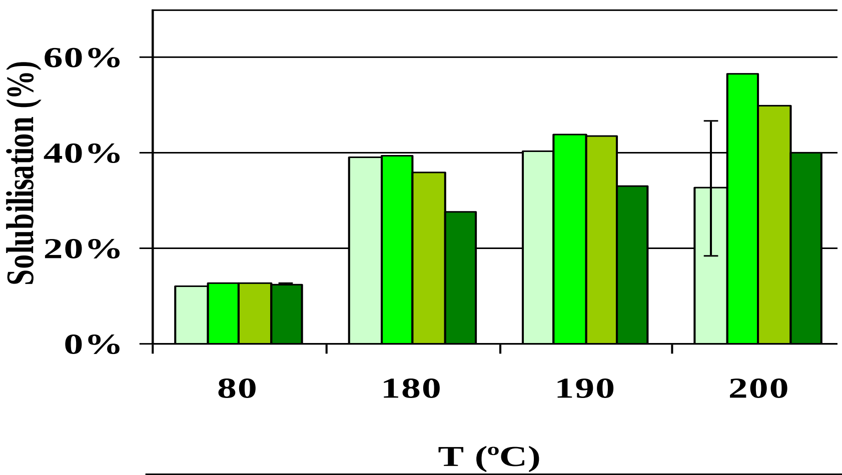


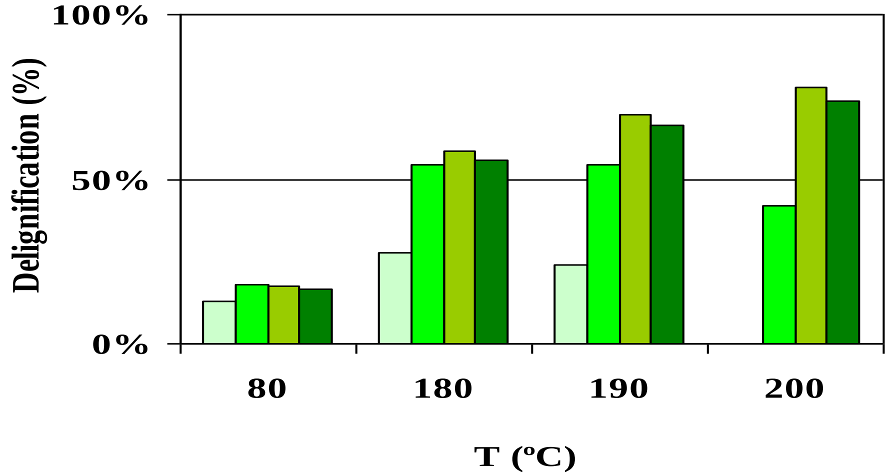
40%	39%	36%	35%		180°C	67%	66%	58%	58%
47%	46%	44%	41%		190°C	78%	76%	70%	67%
53%	51%	50%	48%		200°C	86%	83%	78%	74%

- Solubilisation range 35 - 53%.
- Delignification range 58 - 86%.
- Temperature has a greater effect than biomass:solvent ratio on both solubilisation and delignification.

Results

Effect of temperature and ethanol concentration on sub-critical water mediated hydrolysis of Miscanthus





12%	39%	40%	33%	10g, 0%Et-OH	13%	28%	24%	n.d
13%	39%	44%	57%	10g, 33%Et-OH	18%	54%	55%	42%
13%	36%	44%	50%	10g, 50%Et-OH	18%	58%	70%	78%
12%	28%	33%	40%	10g, 67%Et-OH	16%	56%	66%	74%

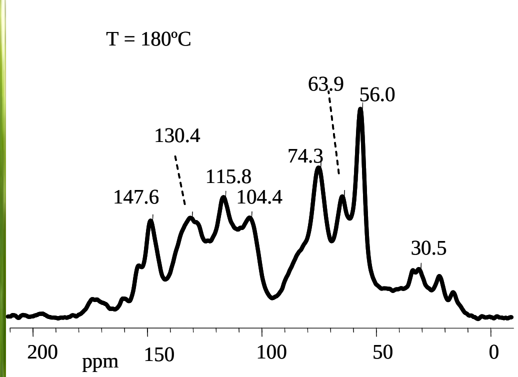
- Temperature affects biomass solubility in a range 12 - 57%.
- Delignification range 0 - 78%.
- Solubility tends to be reduced for both highest and lowest ethanol concentrations.
- Lower etanol concentration (0 and 33%) reduces the delignification particularly at higher temperatures. (50% ethanol - optimal concentration).

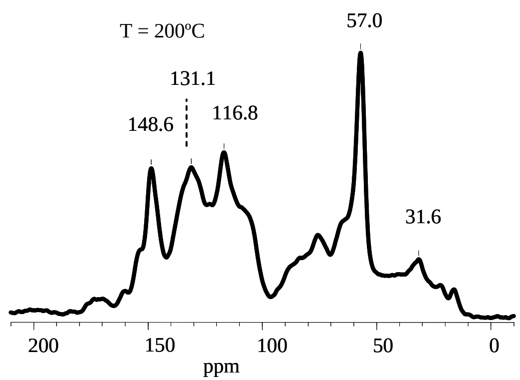
Results - Characterisation of Lignins

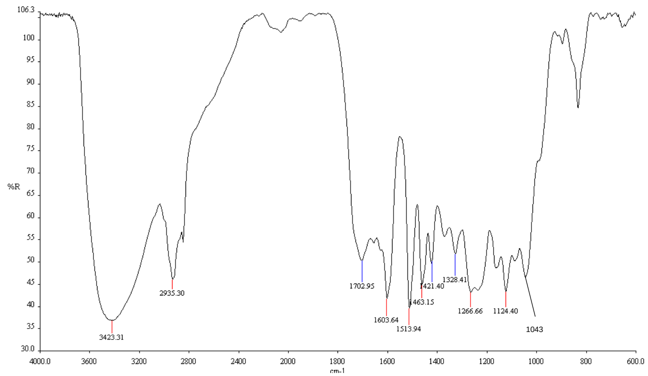
Solid-State CP/MAS ^{13}C NMR Analysis / FTIR Analysis

- Analyses were performed to evaluate the effect of temperature on the lignin quality recovered by precipitation.

- The hydrolysis conditions used were 180 and 200ºC with 10g load size and 50% ethanol concentration.





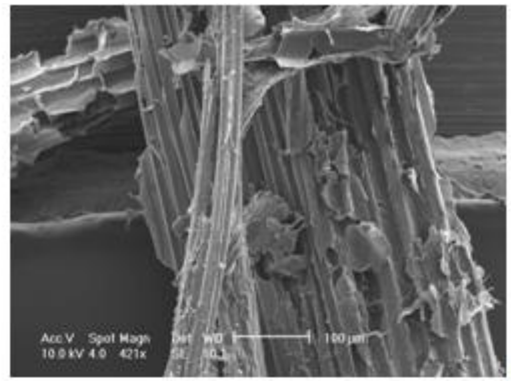


- NMR and FTIR analyses show that at these working hydrolysis conditions lignin was successfully removed from biomass and recovered by precipitation.

- At higher hydrolysis temperatures recovered lignin seems to have higher purity.

Sub-critical Water Mediated Hydrolysis - Cellulose

SEM Images



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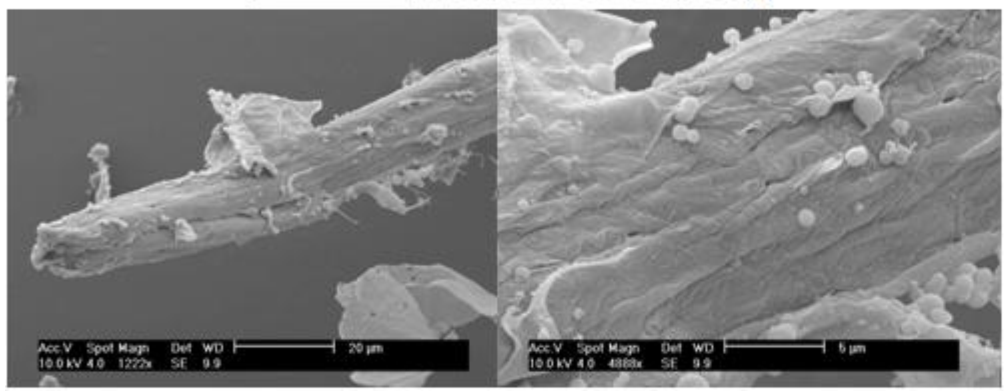

- Fibres structure has been preserved and the majority of lignin has been removed.
- The use of sub-critical water, ethanol and CO_2 at working conditions supports delignification without destroying cellulose fibres.

Sub-critical Water Mediated Hydrolysis - Hemicellulose

Hydrolysis parameters:

- Temperatures: 120°C to 180°C
- Load sizes: 5 -15 g of biomass in 250 ml of water
- Volume: 250 ml of water
- Carbon dioxide: 55 bar
- Hydrolysis time: 0 – 60min

Results

The degree of hydrolysis of hemicellulose can be determined by the concentration of xylose on the hydrolysate .

Other studies on wheat straw confirmed hemicellulose is hydrolysed at these range of conditions. [1]

1. Harmsen, P., et al., *Literature review of physical and chemical pretreatment processes for lignocellulosic biomass*. 2010, ECN Biomass, Coal and Environmental Research

Conclusions

- Under sub-critical water mediate hydrolysis in presence of ethanol and CO_2 at working conditions, the temperature seems to be the most significant parameter.
- 50% ethanol – Considered the optimal ethanol concentration for delignification.
- Optimal delignification condition: 200ºC, 10g load size, 50% in ethanol, 55bar, 60min.
- Lignin was successfully removed from biomass and recovered by precipitation as illustrated by NMR and FTIR analyses .

Conclusions

- The use of this modified organosolv method can be implemented as part of an integrated biorefinery concept for lignocellulosic biomass.

- The biorefinery business is considered a way to increase the competitiveness of the biomass to ethanol process in the long term. Valorization of biomass fractions not converted into ethanol is necessary to make the process competitive.

Future Work

- Apply this modified organosolv process with CO_2 to other lignocellulosic biomass.
- Why not sugarcane bagasse?
- Studies into new lignocellulosic biomass resulting in the breeding between Miscanthus and sugarcane (MISCANE):
  - Combining the high productivity of both species
  - Adaptation to colder climates
  - Improving cell wall composition and its digestibility to enhance sugar extraction efficiency and the overall economy of cellulosic ethanol production.[1]

1. Jakob, K., F. Zhou, and A. Paterson, *Genetic improvement of C4 grasses as cellulosic biofuel feedstocks.* In Vitro Cellular & Developmental Biology - Plant, 2009. **45**(3): p. 291-305.

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Thank You

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