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Co-ordinated Development of Leading Biomass pre-Treatment Technologies for the generation of by-products from Irish Crops

Key external stakeholders:
Farmers, Researchers, Policy Makers, Industrialists, Members of the Bio-economy

Practical implications for stakeholders:

- The optimal pre-treatment chemicals for the conversion of ligno-cellulosic energy crops to ethanol are crop specific and need to be optimised for individual crops
- Ethanol yields can be enhanced considerably through the use of simultaneous saccharification and fermentation.

Main results:

- Chemical and enzymatic pretreatments were demonstrated to be crop specific.
- Bioconversion yields can be significantly improved through the use of simultaneous saccharification and fermentation
- Assessment of the cost of switchgrass pretreatment demonstrated that methanol was the most efficient pretreatment chemical and that ethanol could be produced for €0.50 L^{-1}.
- A Life Cycle Assessment showed that the environmental impact of the pre-treatment process on specific environmental receptors is pretreatment-specific and that no one pre-treatment process had a minimal effect on all environmental receptors.

Opportunity / Benefit:

The results of this project have shown that the optimal pre-treatment chemicals and enzymatic treatments to convert lignocellulosic biomass to ethanol are crop specific and that these processes need to be designed and optimized for each biomass crop. For all crops, yields of ethanol can be optimized through the use of simultaneous saccharification and fermentation. This project has identified the optimal pre-treatment chemical for each of the energy crops which grow best in Ireland and provides the basis for an industry producing ethanol from lignocellulosic biomass feedstocks using second generation technology.

Collaborating Institutions: Carlow Institute of Technology

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1. Project background:

The depletion of fossil fuels, coupled with increased global environmental awareness and related economic concerns, are the major driving forces behind the worldwide transition towards renewable bioresources and agro-industrial wastes for the production of alternative fuels in a sustainable manner. Consequently, the development of more efficient biofuel-producing systems and biofuel-processing technologies are becoming serious challenges for industrialists and researchers in order to provide markets with eco-friendly fuels at competitive prices which contribute to the reduction in CO_2 emissions.

Second generation biofuels utilising lignocellulosic feedstocks and agricultural wastes have been demonstrated as the best alternative to current processing methodologies which use starches and sugars for the production of first generation biofuels. Proven to have a lower environmental impact than first generation biofuels, and more significantly fossil based fuels, second generation technologies have been at the forefront of research and development activities for many years. However, while production technologies are more efficient, second generation processing activities are challenged by lignocellulose recalcitrance, and social and environmental sustainability concerns.

A pre-treatment step is necessary to break-down lingo-cellulosic biomass prior to the conversion of cellulose to ethanol but this this step adds considerable expense to the process but is critical to overall efficiency.

2. Questions addressed by the project:

The objective of this research study was to depreciate the complex structure of selected lignocellulosic feedstocks with the aim of identifying and establishing a leading lignocellulosic biomass pretreatment technology that could be applied to various dedicated energy crops for effective and efficient conversion, generating a high ethanol yield, with little or no inhibitor formation.

3. The experimental studies:

Four Irish grown energy crops were selected for this study; switchgrass (*Panicum virgatum L*), miscanthus (*x-giganteus*), hemp (*Cannabis sativa L*) and willow (*salix*). Dried biomass was milled before being mixed with different concentrations of four different pre-treatment chemicals (Sodium Hydroxide, Sulphuric Acid, Ammonia, Methanol). Three different enzyme preperations (5B06443, C013L,NS22119) were added to the pretreated biomass prior to sugar determination. Pre-treated biomass from the different crops was also subjected to simultaneous saccharification and fermentation where pre-treated biomass was incubated with enzyme and yeast prior to ethanol quantification. Following application and evaluation of various chemical and enzymatic pretreatment processes, SimaPrò life cycle assessment software was used to assess the environmental performance of the pretreatment process and the effect of each approach on the environmental receptors: global warming potential, eutrophication, acidification, photochemical oxidation demand, and marine and human ecotoxicity. In addition, a comparative economic analysis of the ethanol production process was used to help identify the most and least expensive pretreatment option and thus the most commercially viable approach.

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4. Main results:

Chemical and enzymatic pretreatment was demonstrated to be crop specific. Pretreatments employing ammonia proved most effective for willow and hemp saccharification with yields of 59% and 35.7%, respectively. Sulphuric acid pretreatment generated highest saccharification yields for miscanthus - 41.5% (Figure 1). Methanol pretreatment generated the highest yields for switchgrass 69%.

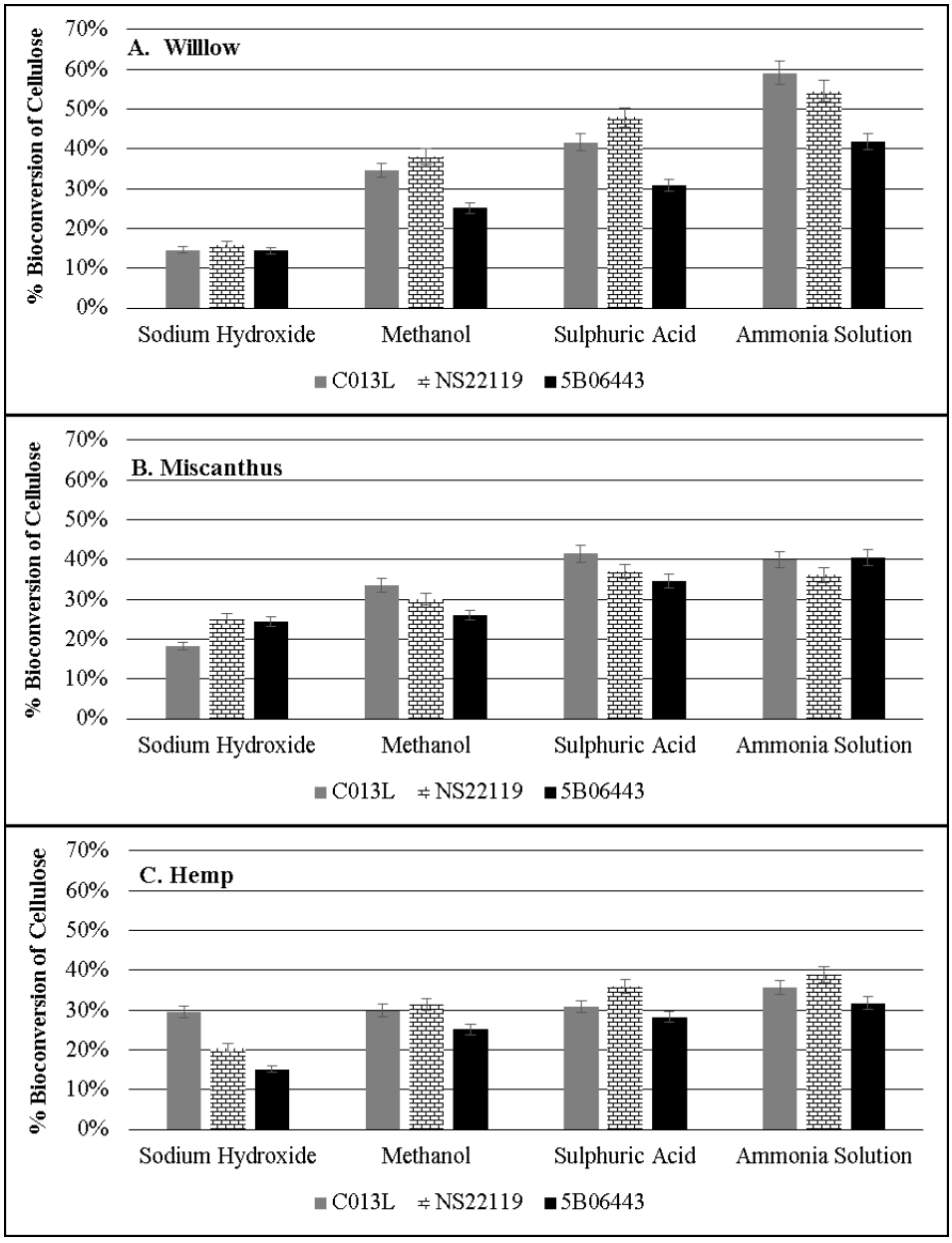

Figure 1: Effect of various commercial enzyme preparations on the bioconversion of willow (**A**), miscanthus (**B**) and hemp (**C**) (cellulose to glucose). Samples were chemically pretreated using 3 mol L^{-1} NaOH, CH_3OH, H_2SO_4 and NH_3 and hydrolysed using C013L, NS22119 or 5B0644.

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Through a series of process refinements and improvements, including the introduction of simultaneous saccharification and fermentation, these bioconversion yields significantly increased to 97% for switchgrass (methanol pretreatment), 80% for miscanthus (ammonia pretreatment), 98% for hemp (sulphuric acid pretreatment) and 99% for willow (ammonia pretreatment).

Assessment of the cost of just the pretreatment step when switchgrass was used as the feedstock for ethanol production demonstrated that methanol was the most efficient pretreatment chemical at €0.55 kg^{-1} glucose and €0.50 L^{-1} ethanol. This compares to sodium hydroxide at €2.52 kg^{-1} glucose and €1.96 L^{-1} ethanol; sulphuric acid at €2.41 kg^{-1} glucose and €1.83 L^{-1} ethanol; ammonia at €0.92 kg^{-1} glucose and €0.80 L^{-1} ethanol.

A life cycle assessment conducted for the pretreatment of switchgrass demonstrated that the effect of the pretreatment process on individual environmental receptors is pretreatment-specific and that there is no one leading pretreatment technique which minimizes the effect of the pretreatment process on all environmental receptors. However, the methanol pretreatment process had the lowest emissions of greenhouse gases which is significant as methanol was the most efficient pretreatment chemical for switchgrass and because the reduction of greenhouse gas emissions is one of the most important drivers for liquid biofuels.

5. Opportunity/Benefit:

The results of this project have shown that the optimal pre-treatment chemicals and enzymatic treatments to convert lignocellulosic biomass to ethanol are crop specific and that these processes need to be designed and optimized for each biomass crop. For all crops, yields of ethanol can be optimized and increased through the use of simultaneous saccharification and fermentation. This project has identified the optimal pre-treatment chemical for each of the energy crops which grow best in Ireland and provides the basis for an industry producing ethanol from biomass feedstocks using second generation technology.

6. Dissemination:

Smullen, E., Finnan, J., Dowling, D. and Mulcahy, P., 2017. Bioconversion of switchgrass: Identification of a leading pretreatment option based on yield, cost and environmental impact. *Renewable Energy*, *111*, pp.638-645.

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