Levulinic acid production by acid-hydrolysis of lignocellulosic biomass

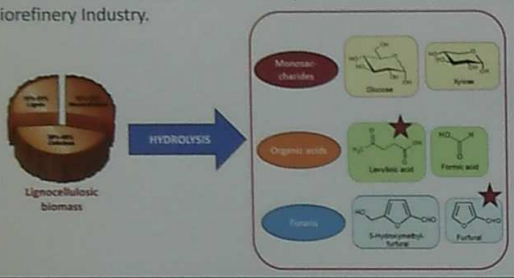
B. Girisuta, K. Dussan, D. Haverty, J.J. Leahy, M. H.B. Hayes

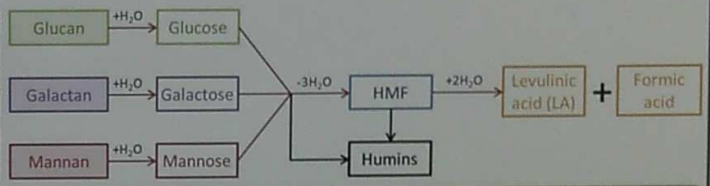
Carbolea Research Group
www.carbolea.ul.ie
University of Limerick, Limerick, Ireland

About the acid-hydrolysis

Acid-catalysed hydrolysis of biomass proceeds via a complex series of reactions involving the conversion of carbohydrates into furan compounds and further Levulinic Acid (LA). During the reaction, the intermediates compounds can also undergo parallel reactions to yield undesirable degradation products, namely humins.

Experimental work carried out at the University of Limerick has been oriented towards the evaluation and modelling of different lignocellulosic feedstocks (Miscanthus *x giganteus*, Sugarcane Bagasse, and others) through hydrolysis and dehydration in aqueous phase catalysed by mineral acids (H_2SO_4) at mild temperatures (130-200°C) in batch and continuous reactors of small and pilot scale in order to maximize Levulinic Acid (LVA) and Furfural (FURF) yields, as the two platform chemicals with great potential in the Biorefinery Industry.

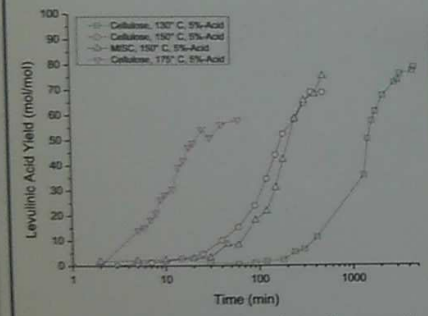


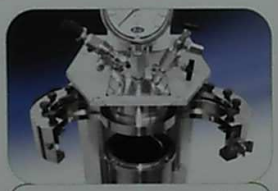


Mechanism for the conversion of hexoses through hydrolysis and dehydration to Levulinic Acid (LVA) and Formic Acid (FA).

Kinetic studies of acid hydrolysis of Miscanthus *x giganteus* and Sugarcane Bagasse

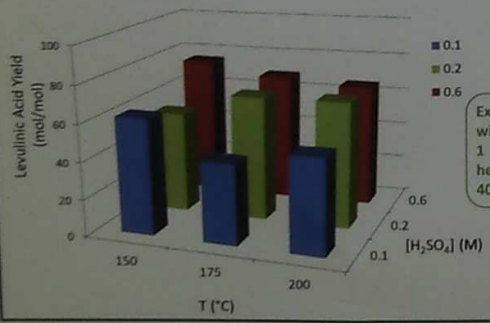
The study of the kinetics of the acid hydrolysis (H_2SO_4) of Miscanthus *x giganteus* (MISC) and Sugarcane Bagasse (SCB) has indicated that despite the fact that reaction rate decreases with lower temperatures, they favoured the production of levulinic acid and reduces the formation of humin type residues.





Experiments carried out with an initial concentration of 4.0% w/w of hexoses available for conversion, in a 8-L Parr reaction vessel with sampling ports.

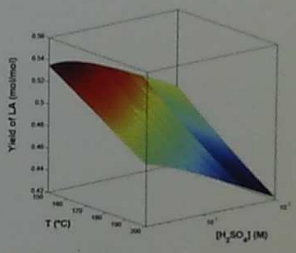
Experiments with pure cellulose (Avicell) at considerably lower temperatures (130° C) have shown a potential increase in the final Levulinic Acid yield (up to 80% mol/mol).



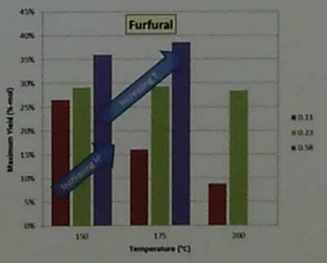
Experiments carried out with MISC (Particle size < 1 mm) with an average hexoses content of 40% w/w.

The kinetic models developed as part of the investigation in University of Limerick has allowed the development of new tools for optimisation of the LVA production. The following graphs shows the response of the LVA yield at different temperatures and H_2SO_4 concentrations for SCB: A yield up to 53% mol/mol for these material (10% initial biomass loading) can be reached at low temperatures and high acid concentrations.

Simulation derived from the kinetic modelling of the acid hydrolysis of sugarcane bagasse catalysed by Sulfuric acid (H_2SO_4). SCB contains about 35-40% w/w of hexoses.



Furfural formation is occurring simultaneously from the hydrolysis and dehydration of pentoses. Nevertheless, pentoses in hemicellulose are more reactive and easily hydrolysed even in autocatalytic hydrolysis at moderate temperatures. Similar humin-type condensation reactions occurs during the formation of FURF. Shorter residence times are required in order to get high molar yields of furfural.

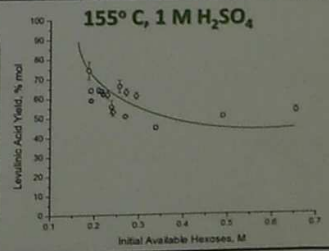


Furfural molar yields obtained during acid hydrolysis of MISC at different [H_2SO_4] (0.11, 0.23, 0.58 M).

Diversifying Biorefinery feedstocks

Following the principle of the integrated network of the DIBANET project, several South American feedstocks considered as agricultural residues and wastes from different sectors have been processed through acid hydrolysis catalysed by Sulfuric acid at different conditions to evaluate their potential on the production of LVA. One important parameter during the acid hydrolysis conversion of carbohydrates is the initial concentration (availability) of the substrate: the higher the biomass loading (thus the hexoses intake), the lower the LVA yield possible at a certain set of conditions (T, [H_2SO_4]). There is a great potential in the use of agricultural residues in the Biorefinery industry due to their significant content of carbohydrates and abundant availability.

LVA yields obtained after 4 hours at 155°C, 1M H2SO4 from several feedstocks, including agricultural wastes from Brazil such as coffee husks, banana field residues, sugarcane trash, rice husks, and energetic crops from Ireland such as willow coppice and Miscanthus.



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