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Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method

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ABSTRACT

Biomass pretreatment aims at separating and providing easier access to the main biomass components (cellulose, hemicellulose and lignin), eventually removing lignin, preserving the hemicellulose, reducing the cellulose crystallinity and increasing the porosity of the material. Pretreatment is an essential step towards the development and industrialization of efficient 2nd generation lignocellulosic ethanol processes. The present work reviewed the main options available in pretreatment. Autohydrolysis and steam explosion were then selected for further investigation. Experimental work was carried out on batch scale reactors, using Miscanthus as biomass feedstock: the effects on sugar solubilization and degradation products generation have been examined for each of these two pretreatment systems. A new process using only water and steam as reacting media was then developed, experimentally tested, and results compared to those achieved by the autohydrolysis and steam explosion processes. Products obtained with the new pretreatment contained a lower amount of usual fermentation inhibitor compounds compared to that typically obtained in steam explosion. This result was achieved under operating conditions that at the same time allowed a good xylan yield, preventing degradation of hemicelluloses. The new pretreatment process was also able to act as an equalization step, as the solid material from the pretreatment phase had a similar composition even under different operating conditions. As regards the effect of pretreatment on enzymatic hydrolysis, the new process achieved yields similar to steam explosion on glucans: however, this was obtained reducing the formation of degradation products from sugars, mainly from C5 sugars. These results made the proposed pretreatment system suitable for further development and industrialization on pilot and industrial scale.

1. Introduction and scope of work

The production of lignocellulosic ethanol represents one of the main routes for new generation biofuel production. Based on the IEA definition [1], the term second generation biofuels refers to biofuels produced from lignocellulosic biomass, i.e. from cellulose-hemicellulose-lignin composed feedstock. A wider biofuel class, "next generation" biofuels, is sometimes also defined: it includes those biofuels produced from hydrotreating of vegetable oil, or from other unconventional

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Glossary

AH	Autohydrolysis
AFEX	Ammonia Fiber Explosion
BTL	Biomass To Liquid
CBP	Consolidated Bio-Process
DME	Di-Methyl Ether
FEP	Furfural Equivalent
HMF	5-HydroxymethylFurfural
HPLC	Hugh Performance Liquid Chromatography
LSR	Liquid Solid Ratio
OXEP	Xyloolygomers
PRX	Xylan remained in the solid phase
SE	Steam Explosion
SHF	Separate Hydrolysis and Fermentation
SSF	Simultaneous Saccharification and Fermentation
SSCF	Simultaneous Saccharification and Co-Fermentation
SY	Solid Yield
WIS	Water Insoluble Solid content
XEP	Equivalent Xylane

feedstocks (as algae). The recent European Directive on the Promotion of Renewable Energies [7] also introduced a well defined legal distinction between biofuels and bioliquids, the former referring to liquid fuels of biomass origin in transport applications and the later at the same fuels when used in stationary generation.

Second generation biofuels have excellent quality characteristics, and these high standards can be better controlled and maintained in time, i.e. a constant fuel quality can be assured. In addition, first generation biofuels are less stable to both biological and chemical decomposition, are more corrosive than fossil fuels and can act as solvent towards sediments in the fuel tank and paint coatings: this especially occurs when blends higher than 5% are adopted [2].

Examples for second generation biofuels are those produced either through the biochemical route, e.g. lignocellulosic ethanol, or from the thermochemical pathway. Processes combining both the thermochemical and the biochemical approaches are also under investigation, such as syngas fermentation [3–6].

Schemes summarizing possible routes towards new generation biofuels have been elaborated by various authors (as Bradley [8]). In a more general approach, intermediate and final products of new generation biofuel chains can also be seen as elements of biorefinery platforms, where not only fuels but also chemicals are produced in a “no-waste” plant (Fig. 1):

Today, the lignocellulosic ethanol chain probably represents one of the most developed route towards industrialization of 2nd generation biofuel production. It can be developed according to different levels of process integration [1]: it is commonly distinguished between Simultaneous Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), Simultaneous Saccharification and Co-Fermentation (SSCF) and Consolidated Bio Processing (CBP) (Fig. 2).

The pretreatment phase in general represents at least 20% of total production costs in all these different approaches, and it can be considered as the single most expensive process step [10].

The expected/desired characteristics for pretreatment can be summarized as follows:

- The more the pretreatment system is able to process biomass pieces of large dimension, the better the energy balance and the overall process efficiency.
- Pretreatment is a major energy-consuming step in the lignocellulosic ethanol process. Energy demand should be kept at the lowest possible level, while maintaining high process performances.
- The dimensions of the pretreatment reactor should be limited to reduce volume and costs, the use of expensive materials should be avoided (this is also dependent on process operating conditions, such as temperature and pressure). Optimum design is a compromise between performances and costs.
- Pretreatment process conditions should minimize sugar losses, especially C5 sugars.
- Yeasts suffer from the presence of inhibitors and various chemicals formed or added during pretreatment. The use of chemicals should be reduced as much as possible or even totally avoided, since they must be neutralized before hydrolysis and fermentation. This means a further intermediate conditioning step, which add costs and complexity to the whole process, and produce chemicals (to be disposed off).

In addition, performances of downstream processes are linked to the pretreatment phase. In fact:

- Sugars must be concentrated at a sufficient level to operate the downstream steps in the economically efficient way: a concentration of sugars not less than 10% is recommended.
- Yeasts must be able to ferment both cellulose and hemicelluloses derived sugars. While C6 sugars fermenting yeasts are well known and available, microorganisms able to ferment C5 sugars are still under development.
- It is desirable to operate the fermentation phase in the shortest possible period, i.e. no more than 5 days (preferably 4 or even 3 days), in order to reduce the capital cost associated to the installation of fermenters.

Today, various authors consider that only those pretreatment steps adopting chemicals can be competitive in terms of performances (i.e. yields) and costs (among others, Yang et al. [10]).

The present research work aims at examining current pretreatment options for lignocellulosic ethanol production, identifying main strengths and weaknesses of the different concepts, and to develop a revised pretreatment solution suitable for industrial scale demonstration. The strategy, validated through the experimental campaign reported here, is to develop an innovative and efficient pretreatment system (two-stage hydrolysis) which is not using chemicals and that