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Assessment of Pre-Treatment Methods for Bio-ethanol Production from Sugarcane Bagasse

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Lignocellulosic biomass such as sugarcane bagasse is non-food biomass that can be used to produce ethanol. Lignocellulose is a complex network of cellulose, hemicellulose and lignin, which requires pre-treatment to improve access to cellulose for hydrolysis which produces glucose for fermentation. Lignin prevents access to cellulose thus delignification using alkaline is often included before hydrolysis. A variety of pre-treatment methods exist requiring different raw materials and operating conditions thus having different economics and environmental impacts. This paper aims to use computer modelling in an optimisation environment called GAMS (General Algebraic Modelling System) to screen a host of pre-treatment options of sugarcane bagasse for bio-ethanol production. The criteria to determine the best pre-treatment option evaluates both economic and environmental objectives. Pre-treatment options included steam explosion, with and without acid catalysis, and acid pre-treatment. Methane was produced from xylose formed in pre-treatment in all options. Delignification using NaOH was included in some investigated pre-treatment flowsheets. The delignification was included in these flowsheets prior to the hydrolysis stage which used either acid or enzymes. The solution space was used to evaluate possible flowsheets in terms of the two aforementioned objectives. For a scenario where methane is the only desired product, steam explosion would be recommended. Adding acid hydrolysis to steam explosion (SA) to produce bio-ethanol increases profitability and reduces environmental impact however the glucose flowrate from this flowsheet is low. For a scenario where higher glucose flowrate is desired, steam explosion with enzymatic hydrolysis pre-treatment flowsheet is recommended however the environmental impact of this flowsheet may be large depending on the energy efficiency of enzyme production.

1. Introduction

Various bioproducts can be obtained from biotransformation of pre-treated lignocellulosic materials. Garcia et al. (2013) used Aspen Plus to evaluate some of these biotransformations. The authors also simulated the separation and product recovery stages. Chiaramonti at al. (2014) presented a review of biofuel producing plants in the United States of America and the European Union. The authors found that most of these plants use lignocellulosic biomass as their feedstock. They also found that biochemical based processes were dominant, however thermo-chemical biofuel processes were also coming on stream. Bio-ethanol production from lignocellulosic biomass can be divided into a few process steps: pre-treatment, hydrolysis, fermentation and separation. Figure 1 below shows a block flow diagram of a bio-ethanol plant.

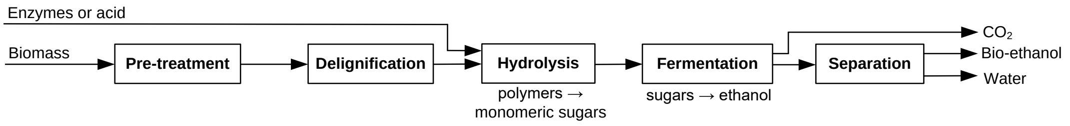

Figure 1: Block flow diagram of bio-ethanol plant (adapted from Galbe and Zacchi, (2007))

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This paper focusses on screening various pre-treatment options, including delignification, and hydrolysis of sugarcane bagasse. Pre-treatment breaks up the structure of the lignocellulosic biomass in order to enable effective hydrolysis. Lignocellulosic biomass is comprised of three main components: lignin, cellulose and hemicellulose, in a matrix. Lignin is an aromatic polymer which is hydrophobic (Sarkar et al., 2012). Cellulose is a straight chain glucose polymer but is structurally different from starches and forms both crystalline fibres and amorphous chains (Menon and Rao, 2012). Hemicellulose is a branched glucose polymer that also contains sugars such as xylose, mannose, galactose and arabinose (Menon and Rao, 2012). The presence of lignin and the way in which molecules in crystalline cellulose are so tightly packed makes enzymatic attack difficult (Menon and Rao, 2012). Pre-treatment is a crucial step in bio-ethanol production as it reduces cellulose crystallinity to facilitate hydrolysis. Delignification is sometimes included prior to hydrolysis. Alkalis are used to solubilise lignin which increases access to cellulose for hydrolysis. Hydrolysis, often also called saccharification, refers to the process of breaking the glycosidic bonds that link the monomers in cellulose and hemicellulose. This process is crucial as it produces the hexose and pentose sugars necessary for fermentation. Some pre-treatment methods hydrolyse the biomass to such an extent that a subsequent hydrolysis step is not required.

Since many pre-treatment, delignification and hydrolysis methods are available, as well as many combinations of these methods, which have differing economics and associated environmental impact, determining the optimal flowsheet for processing sugarcane bagasse is a complicated task. Computer modelling can be used to help understand these interactions and make more informed decisions. By using optimisation software in combination with these models the process flowsheet can be optimised in terms of unit choices and flowrates. More than one objective can be investigated, such as an economic and an environmental objective, to solve the problem with a more holistic view.

2. Methodology

The following pre-treatment methods were selected for modelling in this study: steam explosion (un-catalysed and acid-catalysed) and acid pre-hydrolysis. The pre-treatment was followed by an optional delignification unit which uses NaOH to remove lignin. Hydrolysis could use either acid or enzymes. Figure 2 below shows the superstructure used in this paper.

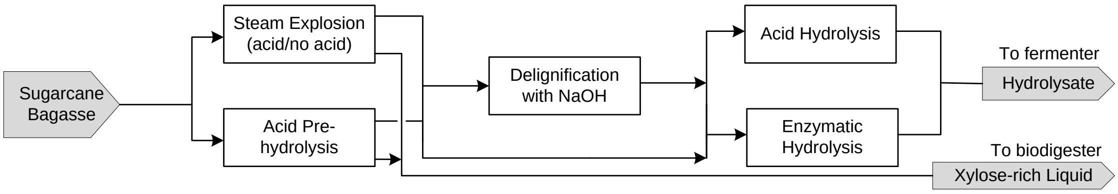

Figure 2: Block flow diagram superstructure for pre-treatment of sugarcane bagasse for the production of bio-ethanol and bio-methane

In order to perform a true simultaneous optimisation of the pre-treatment flowsheet the superstructure shown in Figure 2 above needs to be programmed using optimisation software, such as GAMS (GAMS, 2013), so that all possible options can be compared simultaneously in terms of both economic and environmental objectives. For a network involving many choices of unit operations, and thus many binary variables, a sophisticated optimisation procedure is needed. To use this approach, GAMS models with fixed topologies would be solved individually as mixed integer non-linear programs (MINLPs) and used to initialise the overall superstructure MINLP which would then be solved using MipSyn (Kravanja, 2010). However, solving the initial fixed flowsheets was time consuming and the overall superstructure in MipSyn could not be completed. As a result, a more sequential approach was used for the flowsheet optimisation, and is presented in this paper.

The sequential method involved decomposing the superstructure (Figure 2) into eight separate flowsheets which represent all the possible flowsheets embedded in the superstructure.

These flowsheets are:

- Steam explosion followed by acid hydrolysis (SA);
- Steam explosion, delignification followed by acid hydrolysis (SDA);
- Steam explosion followed by enzymatic hydrolysis (SE);
- Steam explosion, delignification followed by enzymatic hydrolysis (SDE);
- Acid pre-hydrolysis followed by acid hydrolysis (AA);
- Acid pre-hydrolysis, delignification followed by acid hydrolysis (ADA);

- Acid pre-hydrolysis followed by enzymatic hydrolysis (AE);
- Acid pre-hydrolysis, delignification followed by enzymatic hydrolysis (ADE).

Note that acid pre-hydrolysis and acid hydrolysis are separated because they require different acid strengths and different reactor conditions.

Each of these flowsheets is a possible pre-treatment route for producing bio-ethanol from sugarcane bagasse. Flowsheets including steam explosion, acid pre-hydrolysis or acid hydrolysis contain binary variables relating to various reactor choices. The enzymatic hydrolysis model had no discrete choices in the model and thus contained no binary variable however, all the eight possible flowsheets are MINLPs rather than NLPs (non-linear programs). In this paper, both the economic and environmental implications of each possible flowsheet were determined and compared. The models developed were programmed in GAMS V24.2.1 and the MINLP solver used was DICOPT, CONOPT was used as the NLP solver and CPLEX was the MIP (Mixed Integer Program) solver.

The following methodology was used in this paper:

1. The set of eight flowsheets were solved as MINLP models to maximise total profit. The environmental impact (EI) associated with the total profit obtained was then calculated for each flowsheet.
2. From this analysis it was discovered that delignification flowsheets were unprofitable and NaOH recycling was investigated using a sensitivity analysis. From literature, a NaOH recycle cost of 25 % of the annual NaOH cost seemed feasible and was used for further investigations.
3. A sensitivity analysis was also performed with regards to the amount of lignin solubilised by acid in hydrolysis however this had a small effect on the overall solution and thus no changes were made regarding the acid soluble lignin constant.
4. After this, step 1 was repeated with a fixed NaOH recycle cost of 25 %.
5. Each fixed flowsheet MINLP was then solved to minimise the total environmental impact. The profit associated with the total environmental impact was then calculated.

Profit and environmental impacts from steps 4 and 5 were then plotted on a graph. This was the procedure for generating the overall solution space seen in Figure 3.

2.1 Steam Explosion

The GAMS model of the steam explosion unit was based on an Aspen simulation by CTBE (Brazilian Bio-ethanol Science and Technology Laboratory) (Bonomi et al., 2011) which was based on the work of Rocha et al. (2012). Binary variables were used to select whether the unit was un-catalysed or sulphuric acid-catalysed.

2.2 Acid Pre-hydrolysis

Kinetics were available for describing the acid pre-hydrolysis reactions for hemicellulose and cellulose, and the formation of acetic acid and furfural from Aguilar et al. (2002). The work of Lavarack et al. (2002) was used to describe the solubilisation of lignin by sulphuric acid. The kinetic equations were programmed in MATLAB and black box datasets describing the reactor operation for 13 different operating regimes were constructed. These datasets were then used in the GAMS model and binary variables were used to select a dataset. The work of Aguilar et al. (2002) did not include Arrhenius relationships for all the kinetic parameters and thus these had to be looked up for each of the temperatures (100 °C, 122 °C and 128 °C) and acid weight percent (2 %, 4 % and 6 %) that were used in the paper of Lavarack et al. (2002). Logical programming is easier in MATLAB as GAMS requires the use of disjunctive programming and thus MATLAB was used to construct the datasets.

2.3 Delignification

The work of Rezende et al. (2011) was used to develop a linear relationship for the solubilisation of cellulose, hemicellulose and lignin with the weight percentage of NaOH used. This was then used in the GAMS model for the delignification unit. The detoxifying effects of adding NaOH were not included in this paper. The precipitation of any residual sulphuric acid from pre-treatment was however included in this unit.

2.4 Acid Hydrolysis

The work of Gurgel and Marabezi (2012) was used to develop Arrhenius relationships for the hydrolysis of cellulose using sulphuric acid. These relationships were used directly in GAMS so that acid weight percent and temperature could be variables. Conversion factors were used for the other components. The work of Xiang et al. (2003) was used to derive a linear relationship to alter the glucose yield depending on the amount of lignin removed.

2.5 Enzymatic Hydrolysis

The GAMS model for enzymatic hydrolysis, like the steam explosion model, was based on an Aspen simulation by CTBE (Bonomi et al., 2011). The work of Rezende et al. (2011) was used to develop a linear relationship describing the change in the increase of the released glucose concentration with the percentage of lignin removed.

2.6 Objective Functions

The economic objective function shown in Eq(1) calculates the annual profit [millions of ZAR/year] based on the revenues from glucose and methane, the annualised capital costs and the raw material costs. The objective function is non-linear as some of the terms, such as purchased cost of equipment, are non-linear. In some models, those with steam explosion or acid hydrolysis, the objective function contains binary variables associated with steam choice ($z_{unit,st}$).

$$Profit = [Revenue] - \{Purchased\ Cost\ of\ Equipment\} - (Cost\ of\ Raw\ Materials) \tag{1}$$

The environmental objective function uses environmental impacts which were determined using SimaPro V7.3.3 by Product Ecology Consultants (PRé Consultants) using EDIP/UMIP 97 V2.05 with World normalisation factors and the Ecoinvent V2.2 database. Some components were taken from the South African Liquid Fuels Database developed by the University of Cape Town and The Green House. The weighting factors used were taken from Stranddorf et al. (2005). Where available global values were used and EU-15 values were used when global values were not available. The environmental impact of each component in the environmental analysis, g, can be calculated in each impact category, c, as follows:

$$EI_{c,g} = EIData_{c,g} \times F_g \times 0.8 \tag{2}$$

Where: $EIData_{c,g}$ is the data calculated using SimaPro [kg^{-1}], F_g is the flowrate of the component g [kg/y], where 0.8 is the percentage operating time in a year. Steam components will be multiplied by the appropriate binary variable to ensure that the impact is only calculated if that utility is selected.

The environmental objective function multiplies $EI_{c,}$ by a weighting factor, WF_c, which is summed over the impact categories c and components g to get the total environmental impact per year (TotEI):

$$TotEI = \sum_g \left(\sum_c WF_c . EI_{c,g} \right) \tag{3}$$

3. Results and Discussion

3.1 Sensitivity to NaOH Recycle Cost

Initially the models did not consider the recycling of NaOH which caused the delignification models to be unprofitable. A sensitivity analysis was used to investigate the relationship between profitability and NaOH cost and was incorporated by adding a variable, NaOHRecycCost. A sensitivity analysis was used to investigate the relationship between profitability and NaOH cost (NaOHRecycCost). This sensitivity determined the profitability of the flowsheets with respects to the cost of recycling NaOH. It was found that the SDE flowsheet was profitable when NaOHRecycCost is less than 0.74. This means that if the annual recovery cost of NaOH (including annualised capital costs, energy costs and NaOH make-up costs) is less than 74 % of the total cost per annum of NaOH required by the plant with no recycling, the plant will be profitable. For the other flowsheets this crucial NaOHRecycCost value was lower: 26 % for SDA and 27 % for ADE. For ADA the profit was negative for all values of NaOHRecycCost below 0.05 % so ADA is not profitable unless there is no cost involved with recycling NaOH. This is due to the large amounts of acid entrained in the solids after acid pre-treatment which forms a precipitate with NaOH and thus more NaOH needs to be added to achieve the same weight percent. This suggests that delignification should only be considered after steam explosion pre-treatment and is most viable when enzymatic hydrolysis is used.

3.2 Multi-Objective Evaluation

The profit and environmental impact were calculated when the models were optimised using each objective function. These were then plotted on a graph as is shown in Figure 3 below. Figure 3 shows the solution space for the flowsheets although it is not strictly a Pareto curve as this was not constructed using a simultaneous approach. Delignification models include 25 % of the total NaOH cost and environmental impact. Some models with complete recycle of NaOH were included on the graph as ‘SDE-R’. Cases where only methane was produced from steam explosion or acid pre-hydrolysis are shown as ‘S’ or ‘A’.

Two methods of enzyme production were investigated in this work, scenario H1 which uses 183 MJ/kg enzyme and scenario H2 which uses significantly less energy than scenario H1, 82.4 MJ/kg enzyme (Harding, 2008). The use of scenario H2 rather than scenario H1 of Harding (2008) for enzyme production can be seen on Figure 3 as the points that contain ‘H2’. Figure 3 below shows how much larger the environmental impact of models using enzymatic hydrolysis for models using scenario H1 is, even though on-site enzyme production was considered. By using scenario H2, the EI of enzymes decreased significantly and enabled the enzymatic hydrolysis models to be competitive with the acid hydrolysis models from an environmental perspective. Often the two optimum points for enzymatic models are close together because the enzyme flowrate cannot be reduced significantly and the profit and EI cannot change significantly.

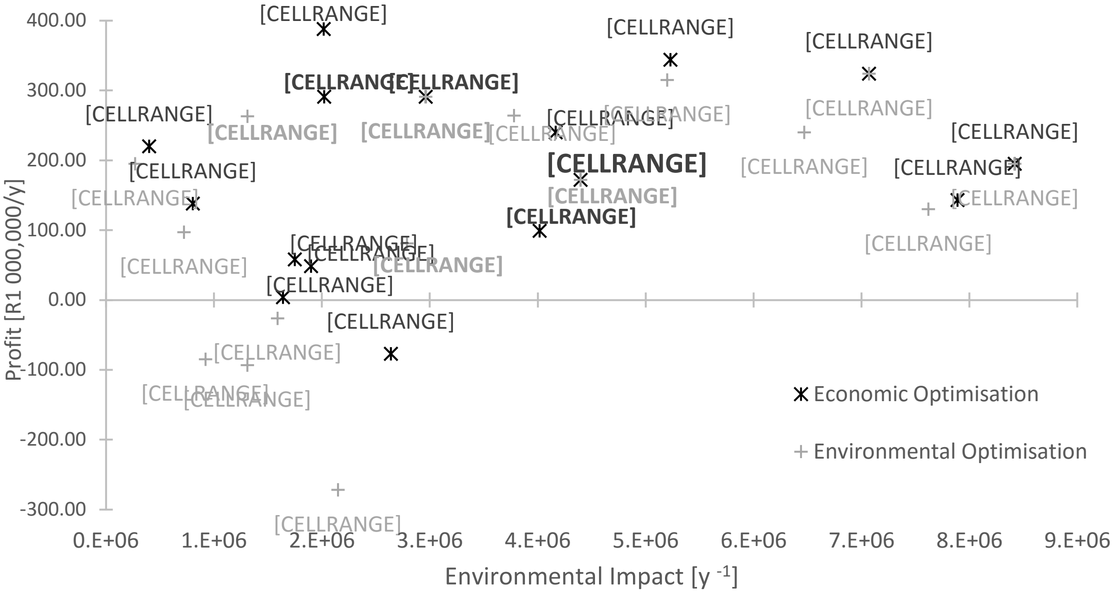

Figure 3: Solution space for pre-treatment flowsheets considering two enzyme production methods

Adding delignification to acid hydrolysis models (SA and AA, to SDA and ADA) reduced the profit and increased the environmental impact, the points move down and right on Figure 3. For enzymatic hydrolysis models (SE and AE, to SDE and ADE), adding delignification reduced the environmental impact due to a decrease in the enzyme flowrate. If all NaOH is recycled delignification has the potential to increase the profit of SE and AE as can be seen by points SDE-R and ADE-R on Figure 3. Depending on the costs and efficiency of recycling NaOH, delignification should only be considered for steam explosion with enzymatic hydrolysis (SE) as delignification could reduce the environmental impact to levels similar to that of acid hydrolysis models.

Points S and A have no revenue from glucose but only produce methane. Adding acid hydrolysis (AA) to acid pre-treatment (A) causes an increase in environmental impact and a decrease in profit. If acid pre-treatment is used for glucose production, it should be in combination with enzymatic hydrolysis rather than acid hydrolysis. The S model is preferable to the A model for a methane only scenario as the EI is less and profit is greater. When both EI and profit are considered, the SA model has a low EI and reasonable profit and is recommended for the production of methane and glucose.

4. Conclusions

The environmental impact of enzymes with on-site production was large however this could be reduced significantly depending on the electricity consumption of enzyme production. Bagasse could be used to produce bio-methane using steam explosion (S) as this has a low environmental impact (805,000 /y) and is profitable (138 × 10^6 ZAR /y). Steam explosion followed by acid hydrolysis (SA) could be used to produce both bio-methane and glucose for bio-ethanol production and is more profitable than bio-methane only scenario (220 × 10^6 ZAR /y) and has a lower environmental impact (400,000 /y). If the focus is to produce high glucose flowrates, steam explosion with enzymatic hydrolysis (SE) would be recommended. The model is profitable (324 × 10^6 ZAR /y) however the environmental impact could be quite large (7,070,000 /y) if a lot of electricity is used in enzyme production. The environmental impact of this method may be lower (2,960,000 /y) if the enzymes are produced in a more energy efficient manner however this is still larger than steam explosion with acid hydrolysis. Adding delignification to the enzymatic hydrolysis models can reduce the EI by 4 % - 68 %, depending on the efficiency of NaOH recycling, and can also increase the glucose flowrate by 49 % - 107 %. Delignification should only be considered for steam explosion with enzymatic hydrolysis (SE) as it has the potential to increase the profit beyond that of SE while decreasing the environmental impact to a level similar to the acid hydrolysis models. The acid hydrolysis model with the highest glucose flowrate is steam explosion with acid hydrolysis (SA) however the glucose flowrate is 62 % lower than in steam explosion with enzymatic hydrolysis.

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