Investigation of several surfactant use strategies to improve the hydrolysis of glucan in newspaper

L-P Vaurs¹, S Heaven² and Charles Banks²

¹ Faculty of Engineering, Prince of Songkla University, Hat Yai, Thailand
² Faculty of Engineering and the Environment, University of Southampton, Southampton, United Kingdom

E-mail: Leopaul.Vaurs@gmail.com

Abstract. Newspaper represent a large quantity of a relatively cheap and available source of lignocellulose. Newspaper could enzymatically be hydrolysed into fermentable sugars for further bioethanol or biochemical production. Low glucan conversions (20-50%) have been generally found in literature, thus this led to the investigations of multiple pre-treatments to improve sugars release. Surfactants such as sodium dodecyl sulphate (SDS), Tween 80 and polyethylene glycol represent a relatively low-cost pre-treatment to improve newspaper hydrolysability. Several surfactants use strategies were tested using the 3 products mentioned earlier. A simple mass, cost and energy model was developed to determine the optimum surfactant pre-treatment. SDS wash using 0.5% SDS based on total solids (TS) gave the most promising results: it released 82 kg of the cheapest produced sugars (0.7£ kg⁻¹ sugar).

1. Introduction

The past decade has seen the emergence of the circular bioeconomy concept where waste including unrecyclable newspaper is no longer a waste but rather a valuable material. Newspaper contain approximately 36-60, 8-26, 11-27 and 0-17% of glucan, other carbohydrates derived from hemicellulose (other-carbs), lignin and ash respectively (based on literature review from Vaurs [1]). Newspaper can only be recycled 5-7 recyclings after what paper fibres become too short and cannot further be used. Therefore, investigating new valorisation routes for unrecyclable newspapers is of interest. The high carbohydrate content of newspaper makes it a suitable feedstock for sugar production via enzymatic hydrolysis.

The potential of newspaper as a feedstock in a sugar biorefinery, however, is limited due to its poor enzymatic hydrolysis conversion [1, 2], with glucan conversions ranging from 20 to about 55%. Several pre-treatments have been tested such as steam explosion [3], alkali pre-treatment [2], ozone [4] or surfactants [5-11], etc. Surfactants have the advantage of requiring mild conditions which significantly reduce the energy demand of the pre-treatment step. They can reduce the negative impact of lignin on enzymes, increase enzyme activity and protect cellulolytic enzymes. Sodium dodecyl sulphate (SDS), Tween 80 (Tween) and polyethylene glycol (PEG) have been tested on newspaper hydrolysis leading to significant conversion improvement [5-11]. There is no study, however, comparing the impact of these 3 surfactants and investigating surfactant combinations as well as the economic benefits their use could bring on a sugar biorefinery based on newspaper.
In this study, different surfactants and several surfactant use strategies were investigated using experimental data from Vaurs [1]. A new cost and energy model were built to determine the optimum surfactant pre-treatment.

2. Methodology

2.1. Material and properties determination

Approximately 20 UK newspaper copies were purchased in local shops in 2015 and were shredded prior hydrolysis. Total solids (TS) and ash was evaluated following standard methods. Glucan and other-carbs were determined following a modified NREL procedure described in Vaurs [1]. The batch used in this study has the following composition glucan, other-carbs, lignin, ash, other equal to 38.4, 14.2, 23.4, 8.3, 15.7% respectively.

2.2. Hydrolysis

All materials were enzymatically hydrolysed at 5 % TS using 2 or 4 % commercial cellulase enzyme on a total solids (TS) basis (later simplified as % enzyme) for 72 h in a 50°C tumbler mixer. Sugars were measured at the end of the reaction by HPLC. Glucan conversions were calculated as described by Vaurs [1] and were normalised based on the non-treated newspaper glucan conversion (confidential results).

2.3. Pretreatment – surfactant application

Three different surfactants were tested in this work: SDS, Tween and PEG. They were applied in different strategies, dosages on a TS basis (later omitted to simplify the text) and their impacts on hydrolysis were assessed. In test 1, 0.25, 0.5, 1 and 5% PEG was added during hydrolysis at 4% enzyme. All other tests were performed at 2% enzyme and 0.5% surfactant added. In test 2a, the 3 surfactants were individually added in the reaction medium. A SDS and Tween combination added in the hydrolysis reaction medium was investigated (Test 2b). In test 3, the protocol based on the work of Xin et al. [9] was applied. The material was then either washed with deionized water (DI): SDS_W-W or not (SDS_W-NoW) at 5% TS. Attempt adding Tween on the unwashed material during hydrolysis was also carried out (SDS_W-NoW-Tween). Finally, a last test (Test 4) was performed where PEG was added before 4h before enzyme addition for hydrolysis.

2.4. Determination of the optimum surfactant use strategy

A mass, energy and cost balance were established on the process flow diagram shown in Figure 1 based on assumptions and data from Table 1. The objective was to determine the optimal surfactant treatment leading to the highest Key Performance Indicator (KPI, dimensionless) defined in equation 1 which was calculated based on 1,000 kg wet weight of newspaper (Wnewspaper).

\[
KPI = \frac{\text{Revenue} \times \text{Sugars}}{\text{Cost} \times W_{\text{newspaper}}} \times 1,000
\]  

Where Revenue (£) includes the revenue from electricity and heat production. Sugars corresponds to the amount of concentrated sugars obtained after nanofiltration (kg), and Cost is expressed in £.

In this simple model, water cost was not considered as it was assumed that it could be re-used in the process after being cleaned in the anaerobic digestion process (AD). AD is used to valorised lost solids and sugars through biogas production and further heat and electricity production.
Figure 1. Process flow diagram of the different surfactant scenarios. Dashes lines concern all scenario. Plain lines correspond to scenario involving SDS wash. Double lines are only for the SDS wash scenario followed by another washing with DI water. CHP = combined heat and power, in blue are all water flow.

Table 1. Assumptions and data used for modelling

| Description | Value | Unit   | Remark                                    |
|-------------|-------|--------|-------------------------------------------|
| Cost        |       |        |                                           |
| SDS         | 1,288 | £/tonne| Based on geometric mean from 15 prices   |
| Tween 80    | 1,271 | £/tonne| on Alibaba.com                             |
| PEG 6000    | 1,332 | £/tonne|                                           |
| Electricity | 0.13  | £/kWh  | UK Power website                          |
| Enzyme      | 3.128 | £/kg   | Estimated from Liu et al. [12]             |
### Energy requirement

| Process                                | Energy (kWh/tonne wet weight) | Note                                                                 |
|----------------------------------------|-------------------------------|----------------------------------------------------------------------|
| Washing process                        | 13.5                          | Assumed to be the same as a MSW pulper [1]                            |
| Shredder                               | 8.0                           |                                                                     |
| Screw press                            | 0.48                          |                                                                     |
| Mixing for enzymatic hydrolysis        | Min: 0.06, Max=1.5             | Geometric mean [13, 14]                                              |
| Nanofiltration                         | 5.3                           |                                                                     |
| Pumping                                | 0.03                          |                                                                     |

| Other                                   |                               |                                                                      |
|----------------------------------------|-------------------------------|----------------------------------------------------------------------|
| Final TS after press 1&2               | 20%                           |                                                                     |
| Removal after washing 1&2              | Solids=5.9, Glucan=1.4%, Other-Carbs=5.6%, Lignin=22.4%, Ash=72% | [1]                                                                |
| Nanofiltration product recovery        | 82.5%                         |                                                                     |
| Final TS after press 3&4               | 50%                           |                                                                     |

### Enzymatic hydrolysis

| Parameter                                             | Values | Source                           |
|-------------------------------------------------------|--------|----------------------------------|
| Conversion decrease due to solids content increase from 5 to 20% | 71%    | Estimation value [18]            |
| Duration                                              | 72 h   |                                   |
| Enzyme dosage                                         | 2%     | On a TS basis                     |
| Removal of non-carbohydrate compounds due to peel-off  | 20%    |                                   |

### Anaerobic digestion

| Parameter                                             | Values | Source                           |
|-------------------------------------------------------|--------|----------------------------------|
| Sugars to COD                                         | 1.06 g of COD/g compound | Stochiometric calculation |
| Lignin to COD                                         | 1.275 g of COD/g compound | [19]                    |
| COD removal                                           | 75%    |                                   |
| Methane yield                                         | 70%    |                                   |

### Energy generation

| Parameter                                             | Values | Source                           |
|-------------------------------------------------------|--------|----------------------------------|
| Methane energy content                                | 10 kWh/m³ |                                   |
| CHP                                                   | Electricity yield: 35%, Heat yield: 50% |                        |
| Carbohydrate energy content                           | 4.72 kWh/kg |                       |
| Lignin energy content                                 | 6.67 kWh/kg |                       |
| Ash energy content                                    | 0 kWh/kg  |                                   |

### Income generation

| Parameter                                             | Values | Source                           |
|-------------------------------------------------------|--------|----------------------------------|
| RHI**                                                 | Biogas=0.0297, Biomass=0.0311 | £/kWh OFGEM.gov website |
| FITs***                                               | Biogas=0.045 | £/kWh OFGEM.gov website |
| RO****                                                | 0.0186 £/kWh  |                                   |

Conversion rate $\text{\£} = 0.8$ the 2019-06-19.

*COD=Chemical Oxygen Demand, **RHI=Renewable Heat Insensitive, ***Feed-in-Tariffs, ****RO=Renewables Obligation
Table 2. Results from the modelling work aiming at determining the optimum surfactant use strategy

| KPI                        | Control | Peg 2 | Peg 4 | Tween | SDS  | SDS-W | SDS-NoW | SDS-Tween | SDS-NoW-Tween |
|----------------------------|---------|-------|-------|-------|------|-------|---------|-----------|---------------|
| Min                        | 74.9    | 79.6  | 49.2  | 84.3  | 82.1 | 79.0  | 87.8    | 73.0      | 73.1          |
| Max                        | 65.1    | 68.9  | 42.3  | 72.9  | 71.0 | 56.2  | 75.3    | 63.4      | 62.9          |
| Sugar produced (kg)        | -       | 63.5  | 76.6  | 89.9  | 81.5 | 77.4  | 82.0    | 76.7      | 73.9          |
| Revenue (£)                | Min     | 72.1  | 70.3  | 67.0  | 69.7 | 70.0  | 55.9    | 62.3      | 70.3          | 63.4          |
|                            | Max     | 62.7  | 60.9  | 57.6  | 60.3 | 60.6  | 49.5    | 53.4      | 60.9          | 54.5          |
| Cost (£)                   | Min     | 61.2  | 67.7  | 122.4 | 67.4 | 67.5  | 54.8    | 58.2      | 73.7          | 64.1          |
|                            | Max     | 61.2  | 67.7  | 122.4 | 67.4 | 67.5  | 68.2    | 58.2      | 73.7          | 64.1          |
| Sugar production cost (£ kg\(^{-1}\)) | Min | 1.0  | 0.9   | 1.4  | 0.8  | 0.9  | 0.7     | 0.7       | 1.0           | 0.9           |
|                            | Max     | 1.0  | 0.9   | 1.4  | 0.8  | 0.9  | 0.7     | 0.7       | 1.0           | 0.9           |
3. Results and Discussion

3.1. Impact of PEG dosage on glucan conversion (Test 1)

Different dose of PEG was added during the enzymatic hydrolysis of newspaper at 4% enzyme. PEG addition gradually increased the normalised glucan conversion which seemed to plateau at 140% at dosage higher than 0.5%. 0.5% surfactant was the dosage selected for further study. At similar PEG dosage, Kim et al. [7], found a normalised digestibility of 150-160 depending on the enzyme dosage. For further study, enzyme dosage was decreased from 4 to 2% [12].

3.2. Impact of different surfactant addition on glucan conversion (Test 2)

The use of all tested surfactants led to normalised glucan conversion increases in a 120-128% range (Figure 2). PEG led to higher glucan conversion improvement at 4% compared to 2% enzyme (PEG_2 and PEG_4 respectively) while the enzyme dosage reduction did not significantly affect the control (no surfactant, data not shown). This could be due to the impact of the PEG/cellulase ratio as discussed by Vaurs [1]. Tween gave the highest improvement (28% higher). Kim et al. [7] similarly found that Tween 80 was giving higher digestibility than PEG. SDS led to some improvement in glucan conversion even though it has been reported to negatively impact cellulase [9, 22-24]. SDS has been found to reduce enzyme-lignin interactions and the lignin content is high on the studied material [22]. As such, this beneficial effect could have compensated the adverse impact SDS has on enzyme. Adding SDS with Tween did not lead to further increase. Tween 80 and SDS are non-ionic and anionic surfactants respectively. Therefore, antagonist effects could have occurred, limiting the action of either enzyme or surfactants during the hydrolysis.

![Figure 2](image)

**Figure 2.** Normalised glucan conversion as a function of different surfactant addition. All surfactant dosages were 0.5%. Enzymatic hydrolysates carried out at 2% enzyme

3.3. Impact of different surfactant use strategies on glucan conversion (Test 3&4)

The impacts of all surfactant strategies around SDS wash are shown in Figure 3. SDS wash significantly increase the normalised glucan conversion which reached values higher than 141%. Washing the SDS pre-treated material gave higher glucan conversion but led to extra solids and carbohydrate loss (see Table 1). SDS can remove ink and other compounds which could be responsible for the glucan conversion improvement [9]. Adding Tween reduce the benefit of the SDS wash indicating again the incompatibility of those 2 surfactants. Adding PEG 4h before or in the same time as when adding the enzyme did not impact the conversion (~120% normalise glucan conversion).
Figure 3. Normalised glucan conversion as a function of different surfactant use strategies

3.4. Determination of the optimum surfactant use strategy
Results are shown in Table 2 where min. and. max depends on the enzymatic hydrolysis energy consumption for mixing considered (see Table 1). SDS_W-NoW has the highest KPI (75.3-87.8), sugar production (82 kg) and the lowest sugar production cost equal to 0.7 £ kg⁻¹. This remains however, much higher than sugar cane production cost [25]. The large difference between PEG0.2 and PEG0.5 KPI indicates the importance of minimising the use of enzyme to obtain feasible sugar-based biorefinery from lignocellulosic material. Note that this study did not consider the extra capital cost associated to the SDS washing process. It would have been interesting to investigate the repercussions this could have had on the importance of the SDS wash KPI and sugar production.

4. Conclusions
Different surfactants were investigated as a method of enhancing hydrolysis yields from newspaper. Washing with 0.5% SDS without further washing with DI water gave the highest KPI, amount of sugars and lowest sugar production cost equal to 75.3-87.8, 82 kg tonne⁻¹ and 0.7 £ kg⁻¹ respectively and reduced the sugar production cost was reduced by 30%. This is one step forward the validation of enzymatic hydrolysis as a new route to valorise unrecyclable newspaper. Further investigation should be undertaken, however, to understand the poor hydrolysability of newspaper.

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