*Biomass* 6 (1984) 183–191

# Hydrolysis of Biomass by Sulphur Dioxide

Morris Wayman, Andres Tallevi and Beatrice Winsborrow

Department of Chemical Engineering and Applied Chemistry, University of
Toronto, Toronto, Ontario, Canada M5S 1A4

(Received: 11 June, 1984)

## *ABSTRACT*

*Results of hydrolysis of several types of cellulosic biomass, namely pine sawmill residues, aspen poplar chips, sugarcane bagasse, wheat straw and corn cobs, are presented in which sulphur dioxide was the hydrolysis catalyst. Hemicellulose was first hydrolysed at 150°C, and following removal of hemicellulose sugars by water washing, residual cellulose was hydrolysed at 190°C, using* $SO_2$ *in both stages. Hemicellulose hydrolysis with* $SO_2$ *catalyst (prehydrolysis) was compared with steam hydrolysis in the absence of added catalyst (autohydrolysis) and poplar. In* $SO_2$ *hydrolysis of these five biomass species, recovery of hemicellulose sugars was essentially quantitative, while cellulose hydrolysis varied from 54·5% for wheat straw to 84·3% for pine. Some economic consequences of this process are discussed. Yields of ethanol, butanol and furfural from these raw materials were estimated.*

*Key words:* acid hydrolysis, cellulosics, wood, bagasse, straw, corn cobs, autohydrolysis, ethanol, butanol, furfural.

## INTRODUCTION

Presently operating fermentation fuel alcohol plants in Brazil and in the USA are based on sugar cane byproducts or on corn, which are both human food or animal feed, and there is widespread concern about driving automobiles on food- or feed-based fuel. This conflict is heightened by the need for relatively good land for these crops, resulting in competition for land. Inevitably, it is feared, such competition will

*Biomass* 0144-4565/84/$03.30 –

raise food costs, with harmful social consequences. As a result, much attention has been devoted to the much more difficult problem of converting cellulosics – wood, agricultural crop residues – to power alcohols.[1]

In Canada now there is enough waste wood and waste crop residual surplus to the needs of soils and animals, and in relatively concentrated locations to make about 6 billion litres/year of fermentation fuel ethanol, which is about 20% of Canadian gasoline consumption.[2] In addition, there is available abandoned farmland and other poor land on which to plant fast-growing hybrid trees and other energy crops sufficient to supply all of the rest of the motor fuel Canada requires. It would need only 5 million ha of relatively poor land to provide the cellulosic raw material for the full amount of motor fuel.

All presently operating commercial plants for producing fermentable sugars from wood have been based on hydrolysis by dilute sulphuric acid in percolation towers. Such processes have poor yields and many operating problems;[3] they give rise to humic substances which inhibit fermentation[4] and severe corrosion. Furthermore, the economics of such plants are questionable.[5]

A hopeful improvement appeared with the introduction of autohydrolysis as a pretreatment for cellulosics.[6] Autohydrolysis, that is steam cracking followed by rapid quenching, is highly effective for hydrolysis of hemicelluloses of deciduous woods, such as poplar, and of agricultural crop residues. In addition, much of the lignin becomes soluble in dilute alkali, or in organic solvents, and extraction of the lignin leaves a relatively pure cellulose, for hydrolysis or for other uses. The autohydrolysis-extraction-hydrolysis process[7] results in good yields of fermentable sugars and ethanol.[8] However, until now this process has not proved useful for coniferous woods such as pine, spruce or hemlock, which are the main residues of the forest industries. To improve the process by extending its raw material base to include the conifers, and to find a satisfactory alternative to sulphuric acid as hydrolysis catalyst, we have compared several acids as hydrolysis catalysts for production of fermentable sugars from cellulosics.[9] Of these, sulphur dioxide proved to be the most effective. Sulphur dioxide has a number of specific advantages as hydrolysis catalyst over $H_2SO_4$. Since $SO_2$ is a gas, it can be added either ahead of or with the steam; it is better distributed through the biomass than $H_2SO_4$, resulting in a more uniform reaction. Less $SO_2$ is used than $H_2SO_4$, and it costs less.

$SO_2$ has been made and used for many years in the pulp and paper industry in pressure vessels, and stainless steels are available which are satisfactorily resistant to attack by aqueous $SO_2$, while metallurgy for $H_2SO_4$ at these temperatures remains a serious problem. Lignin remains very light in colour in $SO_2$ hydrolysis, especially if sulphate or oxygen scavengers are present, whereas it turns black during sulphuric acid processing. Lignosulphonates made by the reaction of $SO_2$ during sulphite pulping of wood are the basis of a substantial chemical industry, including production of vanillin. Preliminary work here suggests that these lignins will prove to be quite suitable for chemical conversion.

## BIOMASS ANALYSES

The biomass species examined were: pine, mainly red pine with some white pine, as sawmill residues; aspen poplar chips about 3 × 12 × 20 mm; bagasse from a cane sugar mill in Louisiana; corn cobs from a large corn starch and alcohol plant; and wheat straw from a nearby farm. The summative analyses are given in Table 1.

**TABLE 1**
Summative Analysis of Cellulosics (% of dryweight)

| | *Red pine sawmill residue* | *Aspen chips* | *Bagasse Louisiana* | *Corn cobs* | *Wheat straw* |
|---|---|---|---|---|---|
| Polysaccharides | 68·0 | 67·7 | 59·9 | 76·3 | 73·0 |
| Klason lignin | 25·8 | 21·5 | 25·0 | 9·7 | 14·1 |
| Acid-soluble lignin | 1·2 | 5·4 | 1·6 | 3·2 | 2·0 |
| Extractives | 5·0 | 5·4 | 4·0 | 3·2 | 4·5 |
| Ash | – | – | 2·7 | 0·7 | 6·4 |
| Other | – | – | 6·8 | 6·9 | – |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |
| Polysaccharides | | | | | |
| Glucan | 50·7 | 42·2 | 34·9 | 32·0 | 37·5 |
| Non-glucan | 17·3 | 25·5 | 25·0 | 44·3 | 35·5 |

## COMPARISON OF AUTOHYDROLYSIS AND PREHYDROLYSIS WITH $SO_2$

Samples of the pine and the aspen woods were heated in small autoclaves in the presence of a small amount of water for autohydrolysis, or with very dilute $SO_2$ solution for prehydrolysis. The time and temperature of autohydrolysis were 15 min at 190°C and of prehydrolysis were 20 min at 150°C. The results are shown for pine in Table 2 and for aspen in Table 3. They confirm[5] that autohydrolysis is much more effective in hydrolysing aspen hemicellulose than it is pine hemicellulose. In the case of aspen, 88·4% of the theoretical yield of non-glucose sugars was obtained on autohydrolysis, whereas for pine only 59·2% of the hemicellulose non-glucose sugars was hydrolysed to soluble carbohydrates. A large proportion of these sugars occurred as oligomers rather than monomers, about 37% of the pine sugars and about 42% of the aspen sugars.

**TABLE 2**
Autohydrolysis and Prehydrolysis of Pine

| | *Glucose (%)* | *TRS (%)* | *Fibre residue* | *Alkali extract* |
|---|---|---|---|---|
| *Autohydrolysis (steam), 190°C, 15 min* | | | | |
| Monomer | 1·52 | 11·78 | 74·33 | 9·22 |
| Oligomer | 2·32 | 3·32 | | |
| Total | 3·84 | 15·10 | | |
| % of theory | | | | |
| Glucose | 6·9 | | | |
| Non-glucose | 59·2 | | | |
| *Prehydrolysis, 2% $SO_2$: wood, 150°C, 20 min* | | | | |
| Monomer | 5·29 | 20·55 | 69·06 | 4·91 |
| Oligomer | – | 4·32 | | |
| Total | 5·29 | 24·87 | | |
| % of theory | | | | |
| Glucose | 9·5 | | | |
| Non-glucose | 102·9 | | | |

**TABLE 3**
Autohydrolysis and Prehydrolysis of Aspen

| | *Glucose (%)* | *TRS (%)* | *Fibre residue* | *Alkali extract* |
|---|---|---|---|---|
| *Autohydrolysis (steam), 190°C, 15 min* | | | | |
| Monomer | 1·41 | 15·36 | 69·1 | 14·40 |
| Oligomer | 1·47 | 11·00 | | |
| Total | 2·88 | 26·36 | | |
| % of theory | | | | |
| Glucose | 6·2 | | | |
| Non-glucose | 88·4 | | | |
| *Prehydrolysis, 3% $SO_2$: wood, 150°C, 20 min* | | | | |
| Monomer | 2·56 | 29·07 | 67·1 | 7·86 |
| Oligomer | 0·81 | 1·62 | | |
| Total | 3·37 | 30·69 | | |
| % of theory | | | | |
| Glucose | 7·8 | | | |
| Non-glucose | 102·0 | | | |

In the presence of a small amount of $SO_2$ catalyst, 2% on pine wood (dry basis, 0·5% $SO_2$ solution) and 3% on aspen wood (dry basis, 0·75% $SO_2$ solution), hydrolysis of hemicellulose took place at much lower temperature (150°C instead of 190°C) and was complete. The sugars occurred mainly as monomers, only 5·3% of the aspen hemicellulose sugars being oligomers and 17% of the pine hemicellulose sugars.

It was noted that the solubility of the lignin in alkali was reduced on $SO_2$ prehydrolysis being about half that in autohydrolysis in both cases, presumably due to acid-catalysed polymerization.

## TWO STAGE $SO_2$ HYDROLYSIS

The procedure adopted for hydrolysis of these cellulosics was $SO_2$ prehydrolysis for 20 min at 150°C, the amount of $SO_2$ being 2–3% on fibre, in 0·5 or 0·75% $SO_2$ solution; the hemicellulose sugars were then washed from the fibrous residue with water and the alkali-soluble lignin with 2% NaOH; finally the fibrous residue was hydrolysed with 1% $SO_2$ on fibre (0·25% solution) at 190°C. The hydrolysis procedure was adapted to the particular small reactors used, such that temperature was raised during 16 min to 190°C and held there for 4 min, whereupon the reactor was cooled rapidly, and the glucose washed from the fibrous residue. This heating, cooling and washing was repeated a total of four times. This rather awkward procedure was adopted in order to minimize sugar destruction by the acid at the high temperature.

The results are shown in Table 4. As expected, hemicellulose hydrolysis was essentially complete in all cases. However, the amount of sugar recovered from the residual cellulose varied widely among these five species of biomass. The procedure was very good for pine wood, 84·3% of the theoretical yield of glucose being obtained. All other glucose yields were less than 70%, varying from 68·7% for aspen to only 54·5%

**TABLE 4**

Sugar Yields on Two-Stage $SO_2$ Hydrolysis of Cellulosics (% of dry raw material weight)

| | *Red Pine sawmill residue* | *Aspen chips* | *Bagasse Louisiana* | *Corn cobs* | *Wheat straw* |
|---|---|---|---|---|---|
| *Prehydrolysis* | | | | | |
| Glucose | 6·9 | 3·3 | 3·0 | 3·0 | 2·5 |
| Non-glucose sugars | 21·1 | 23·3 | 24·8 | 42·9 | 43·8 |
| *Hydrolysis* | | | | | |
| Glucose | 40·1 | 28·9 | 20·4 | 20·5 | 20·2 |
| Non-glucose sugars | 1·0 | 3·3 | 4·0 | 7·1 | 2·0 |
| *Total* | | | | | |
| Glucose | 47·0 | 32·2 | 23·4 | 23·5 | 22·7 |
| Non-glucose sugars | 20·1 | 26·6 | 28·8 | 50·0 | 45·8 |
| *% of theoretical yield* | | | | | |
| Glucose | 84·3 | 68·7 | 60·4 | 66·2 | 54·5 |
| Non-glucose sugars | 103·7 | 91·5 | 101·0 | 99·0 | 113·2 |

for wheat straw. Since in all cases the amount of fibrous residue at the end of the process was about what would be expected from the lignin content, the difference is due not to differences in rate of hydrolysis, but rather to differences in the rates of destruction of the glucose as formed; or perhaps a better formulation might be in our failure to preserve the glucose as formed. This procedure obviously requires improvement. However, it can be pointed out that the yield reported here for glucose from pine may be the highest yet obtained.

## ALCOHOLS AND FURFURAL FROM CELLULOSICS

Based on the yields of hexose and pentose sugars given in Table 4, yields of ethanol, butanol–acetone–ethanol and furfural have been estimated and are listed in Table 5. Ethanol yields are best with pine by some significant margin, based on fermentation of hexose sugars only (glucose and mannose) by ordinary yeast (*Saccharomyces cerevisiae*). No allowance has been made for possible fermentation of pentoses by *Pachysolen tannophilus*, or for conversion of pentose sugars to the pentulose form by isomerase and subsequent fermentation, two processes under investigation for fermentation of pentose sugars to ethanol.

Fermentation by *Clostridium acetobutylicum* to butanol–acetone–ethanol solvents would make use of both hexose and pentose sugars. Pine hydrolysates would give the highest yields of these solvents (fuels);

**TABLE 5**

Chemical Yields (litres $Mg^{-1}$ dry raw material) on Two-Stage $SO_2$ Hydrolysis of Cellulosics (estimated from sugar yields)

| | *Red pine sawmill residue* | *Aspen chips* | *Bagasse Louisiana* | *Corn cobs* | *Wheat straw* |
|---|---|---|---|---|---|
| Ethanol | 324 | 185 | 135 | 135 | 130 |
| Butanol-acetone-ethanol | 252 | 220 | 196 | 276 | 257 |
| Furfural | 28 | 73 | 80 | 138 | 126 |

however, yields from hydrolysates of the other species of biomass are estimated to be quite high, with corn cobs and wheat straw having an advantage compared to bagasse or aspen. Corn cobs and wheat straw are also the best sources of furfural, according to these estimates. The bagasse came out relatively poorly as a furfural source, which is surprising since there is a commercial operation producing furfural from sugarcane bagasse in southern Florida.

## ECONOMICS

Based on earlier economic studies,[5] it is possible to estimate capital and operating costs of plants to make ethanol based on these results with the pine sawmill residues. Considering a plant to make 240 000 litres day$^{-1}$ of anhydrous ethanol (84 million litres year$^{-1}$), investment is estimated at Cdn $31·2 million, or 37·1 ¢ litre$^{-1}$, before return on investment. Return on investment of 20% would amount to a further 7·4 ¢ litre$^{-1}$. This figure can be considered the approximate cost of gasoline at the refinery gate, so the two are competitive. Any reduction in wood costs would improve its competitive position, or perhaps permit a more attractive return on investment.

The above calculation includes no subsidy or tax concession, both of which are common in the fuel industry. Also, no allowance has been made in this calculation for the sale of lignin or other byproducts. Any substantial sale of lignin above its fuel value would materially improve the economics of processing pine wood to ethanol.

To comment briefly on the other biomass species considered here, none of them is as attractive as pine for ethanol production. This is primarily due to an unfavourable hexose/pentose balance. The finding of a successful process for fermentation of pentoses to ethanol would improve the economics materially for these other species. This is shown clearly in the estimates of butanol solvent production, where the advantage of pine over the other species is not so marked. Interest in butanol has increased quite markedly recently because of its use as a co-solvent in methanol–gasoline blends. In these fuels, the methanol is derived from natural gas, and up to now the butanol has been derived from petrochemical processes. However, newer processes[10] suggest that fermentation butanol may be competitive with petrochemical butanol.

## REFERENCES

1. *Proceedings, international symposium on ethanol from biomass*, Royal Society of Canada, Winnipeg (1982).
2. Hayes, R. D. (1982). Ref. 1, pp. 118-41; Clarke, M. R. & Sastry, C. B. R. (1982). Ref. 1, pp. 142-60.
3. Burton, R. J. (1982). Ref. 1, pp. 247-70.
4. Mackie, K., Deverell, K & Callander, I. (1982). Ref. 1, pp. 271-311.
5. Wayman, M. (1983). *Assessment of the New Zealand Forest Research Institute process for pine wood hydrolysis and fermentation to ethanol*, Report to Energy, Mines and Resources Canada.
6. Lora, J. H. & Wayman, M. (1978). *Tappi*, **61**(6), 46-50; Wayman, M. & Lora, J. H. (1983). Canadian Patent 1,147,105; Okamura, K. & Morikawa, H. (1983). In: *Recent technologies and prospects of wood chemicals*, ed. J. Nakano and T. Higuchi, CMC Report No. 40, Tokyo, CMC Publishers.
7. Wayman, M. (1980). *Proceedings IV intern. alcohol fuels techn. symp.*, Vol. I, pp. 79-84.
8. Wayman, M., Lora, J. H. & Gulbinas, E. (1978). In: *Chemistry for energy*, ACS Symposium Series Monograph No. 90, pp. 183-201.
9. Wayman, M. & Tallevi, A. (1983). ACS Annual Meeting, Washington, DC.
10. Wayman, M., Husted, G., Santangelo, J. & Levy, S. (1984). Paper to be presented at VI Intern. Alcohol Fuels Techn. Symp., Ottawa.