Krasnovsky, A.A. (1983). Pathways of biological conversion of solar energy. In A.M. Braun (Ed.), Photochemical Conversions, Pressed Polytechniques Romandes, Lausanne, pp. 49-72.

Muallem, A., Bruce, D.L. and Hall, D.O. (1983). Photoproduction of H_2 and $NADPH_2$ by polyurethane immobilized cyanobacteria. Biotechnol. Lett. 5, 365-368.

Rao, K.K. and Hall, D.O. (1983). Photobiological production of fuels and chemicals. In A.M. Braun (Ed.), Photochemical Conversions, Presses Polytechniques Romandes, Lausanne, pp. 1-48.

Smith, G.D., Muallem, A. and Hall, D.O. (1982). Hydrogenase-catalyzed photoproduction of H_2 by photosystem I of the thermophilic blue-green algae M. laminosus and P. laminosum. Photobiochem. Photobiophys. 4, 307-319.

HYDROGEN CHLORIDE GAS PHASE HYDROLYSIS OF CELLULOSE FOR ETHANOL PRODUCTION

G.E. Ho

School of Environmental and Life Sciences
Murdoch University
Australia, 6150

ABSTRACT

The hydrolysis of cellulose extracted from wheat straw, newspaper, as well as whole wheat straw was studied using hydrogen chloride as a hydrolysing agent. The results of the experimental investigation show that alphacellulose, which was hydrolysed, was stoichiometrically converted to glucose. The hydrolysis of the alphacellulose and the production and decomposition of the glucose followed first order reaction kinetics.

KEYWORDS

Biomass; cellulose; wheat straw; newspaper; hydrolysis; hydrogen chloride; glucose; ethanol.

INTRODUCTION

A large quantity of biomass is produced annually in Australia. Stewart *et al* (1979) estimated that 24.6 million tonnes dry weight is produced from agriculture and forestry, with 15.8 million tonnes contributed by crop (cereals) residues. The latter represents a substantial potential for energy production from materials which are currently 'wasted'. Another potential source of energy in cities is wastepaper. About 1.7 million tonnes is discarded annually in Australia (Hinwood, 1976).

Western Australia in particular is well placed for utilizing crop residues (Ho and Barton, 1982). Cereal crops grown for grain produce 4.30 million tonnes of straw per annum. If oats and barley straw, both of which have a higher opportunity cost as stock feed than wheat straw, are disregarded, and assuming that 40% of the wheat straw would need to be retained in the paddock in the interests of good soil husbandry, then there would be a total of 2.02 million tonnes per annum potentially available for off-farm use. Solid waste disposed in the Perth Metropolitan Area contains about 48 kilo-tonnes per annum of waste paper, and 20 kilo-tonnes is potentially available for hydrolysis. The potential ethanol production from the above waste cellulose via acid hydrolysis followed by fermentation of the glucose produced is

604 million litres per annum. Only 24% of the potential would be needed to produce a 10% gasohol blend in all gasoline distributed in Western Australia.

Previous work (Higgins, 1978; Higgins and Ho, 1982) showed that hydrolysis using hydrogen chloride gas possessed several distinct advantages over other hydrolysis processes. The present project is part of an overall assessment of the technical and economic feasibility of producing ethanol from waste-paper and wheat straw. This paper reports the kinetics of the hydrogen chloride gas-phase hydrolysis process.

KINETICS OF HYDROLYSIS USING HCl GAS

Higgins (1978) found that the hydrolysis of alphacellulose to glucose followed a first order kinetics. The kinetics of sugar decomposition was not determined by Higgins and Ho (1982). The hydrolysis and subsequent sugar decomposition can be represented by

$$\text{cellulose} \xrightarrow{k_1} \text{sugar} \xrightarrow{k_2} \text{sugar decomposition products}$$

It can be expected, as in the hydrolysis using sulphuric acid, that the sugar decomposition would also follow first order kinetics. If the quantity of cellulose at any particular time t is denoted by A, and the quantity of sugars by B, the first order kinetics give

$$dA/dt = -k_1 A \qquad (1)$$

$$dB/dt = 1.11\, k_1 A - k_2 B \qquad (2)$$

where k_1 = first order reaction rate constant for cellulose hydrolysis

k_2 = first order reaction rate constant for sugar decomposition

and 1 kg of cellulose stoichiometrically produces 1.11 kg of glucose.

Intregration of equation (1) with an initial cellulose quantity A_0 gives

$$A = A_0 \exp(-k_1 t) \qquad (3)$$

which describes the exponential decline in the amount of cellulose as hydrolysis progresses. Integration of equation (2) with no sugar present initially results in

$$B = 1.11\, A_0 \{\exp(-k_2 t) - \exp(-k_1 t)\}\, k_1/(k_1 - k_2) \qquad (4)$$

MATERIALS AND METHODS

Determination of the Composition of Newspaper and Wheat Straw

Unprinted newspaper and wheat straw were analysed for their content of extractives, lignin, hemicelluloses and alphacellulose by the method of Green (1963). The alphacellulose left after the extraction of lignin and hemicelluloses was used in the hydrolysis experiments.

Hydrolysis of Alphacellulose Extracted from Newspaper and Wheat Straw

The hydrolysis reactor and the procedure described in Higgins and Ho (1982) was used. Besides monitoring the reduction in the weight of the alpha-cellulose, glucose production was determined using the 3,5 dinitrosalicylic acid (DNS) method.

Hydrolysis of Whole Wheat Straw

A jacketed cylindrical reactor similar in design to the hydrolysis reactor for extracted cellulose was used (Ho and Barton, 1982). Samples of 25g of whole wheat straw were hydrolysed each time. Three sets of experiments were conducted. The first set was similar to the hydrolysis of alphacellulose extracted from wheat straw in the smaller reactor. The second set investigated the effect of an increase in reaction temperature, while the third, the effect of terminating gas flow once hydrolysis had commenced. Glucose in the hydrolystate was analysed using a glucose specific enzyme (GOD-POD).

RESULTS AND DISCUSSION

Composition of Newspaper and Wheat Straw

The results of the analysis of newspaper and wheat straw are comparable to the results obtained previously (Table 1)

TABLE 1 Composition of Newspaper and Wheat Straw

Components	Newspaper		Wheat Straw	
	Present Work	Higgins (1978)	Present Work	Higgins (1978)
Extractives	0.7	3.4	4.9	5.0
Lignin	13.0	19.8	18.9	19.2
Hemicelluloses	22.3	20.8	35.2	34.4
Alphacellulose	63.0	56.1	41.1	41.3

Hydrolysis of Alphacellulose

Figure 1 shows the reductions in the weight of alphacellulose as a function of hydrolysis time, while Fig. 2 shows the amount of glucose formed.

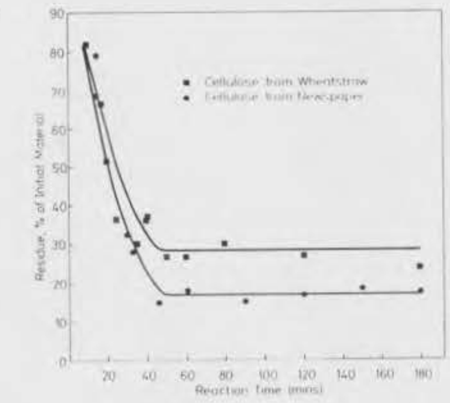
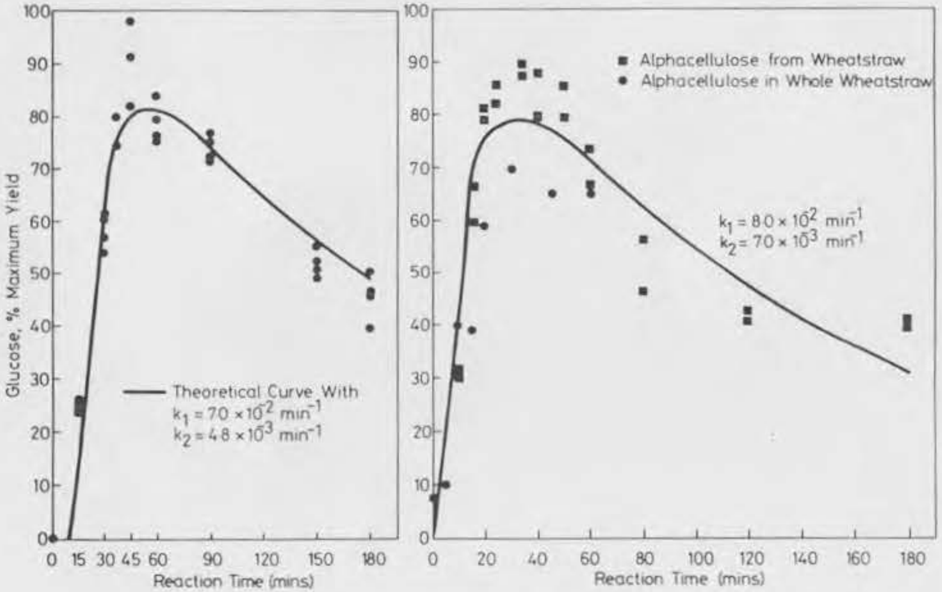


Fig. 1. Hydrolysis of alphacellulose

Beyond a reaction time of 45 minutes little further decrease in the weight of residue took place. This phenomenon was also observed by Higgins (1978), although he obtained lower values for the unhydrolysed portion (4% to 10%). There are two possible reasons for this apparent inert portion. The first is the presence of ash in the alphacellulose, undissolved lignin and substances resistant to HCl attack. The second is the possibility that some of the alphacellulose, in particular the amorphous portion, is decomposed too rapidly at the initial stages when hot spots could occur. Char is then produced which is resistant to HCl attack and is left as a residue.



(a) (b)

Fig. 2. Glucose from (a) Newspaper and (b) Wheat Straw

Considering only the alphacellulose that was hydrolysed, the reduction in the weight of alphacellulose and the formation and decomposition of the glucose produced can be described by first order reaction kinetics (Eqn. 4, Fig. 2).

Hydrolysis of Whole Wheat Straw

The hydrolysis of whole wheat straw was similar to the hydrolysis of alphacellulose. Considering only the alphacellulose that was hydrolysed the reaction kinetics is similar to the hydrolysis of alphacellulose extracted from the straw (Table 2 and Fig. 2). Only 50% of the alphacellulose in the straw was hydrolysed. Increasing reaction temperature or stopping gas flow once hydrolysis had commenced did not affect the reaction rates (Ho and Barton, 1982).

TABLE 2 Values of k_1 and k_2 for Alphacellulose in Different Subtrates

Alphacellulose Source	Temp. (°C)	k_1 (min^{-1})	k_2 (min^{-1})	Reference
From cardboard	20	1.7×10^{-2}	-	Higgins (1978)
From newspaper	50	7.0×10^{-2}	4.8×10^{-3}	Present work
From wheat straw	50	8.0×10^{-2}	7.0×10^{-3}	Present work
Whole wheat straw	50	8.0×10^{-2}	9.0×10^{-3}	Present work
Whole wheat straw	65	8.0×10^{-2}	8.0×10^{-3}	Present work

CONCLUSIONS

The hydrolysis of alphacellulose from newspaper and wheat straw, and the decomposition of the glucose produced followed first order kinetics, with

$$k_1 = (7.5 \pm 0.5) \times 10^{-2}\ min^{-1}$$
$$k_2 = (8 \pm 1) \times 10^{-2}\ min^{-1}$$

The rates mean that optimum section time would be about 30 minutes with only 20% of the glucose produced decomposed.

Work is in progress to increase the extent of cellulose hydrolysed.

ACKNOWLEDGEMENTS

The work reported in this paper was supported by the SOLAR ENERGY RESEARCH INSTITUTE OF WESTERN AUSTRALIA (Project 520/112). The experimental work was carried out by Mr. Philip Baxter, who was employed as a Graduate Research Assistant. Thanks are due to Mr. F.J. Higgins for supplying the wheat straw from his farm and for his continuing interest in the project; to Associate Professor A.F.M. Barton and Dr. T.H. Venkitachalam for ideas and inputs into the project.

REFERENCES

Green, J.W. (1963). Wood cellulose. In Whistler, R.I. (Ed.), Methods in Carbohydrate Chemistry. Vol. 3. Academic Press, p. 9.

Higgins, F.J. (1978). Energy recovery from cellulose wastes. Honours thesis. Murdoch University.

Higgins, F.J. and G.E. Ho (1982). Hydrolysis of Cellulose using HCl: A comparison between liquid phase and gaseous phase processes. Agricultural Wastes. Vol. 4, pp. 97-116.

Ho, G.E. and A.F.M. Barton (1982). Ethanol from Wastepaper and Crop Residues. Final report to SERIWA. Project 520/112. 49 pp.

Hinwood, D.B. (1977). Recycling in Perth - Current Economic Potential. Paper 15, Conference on Waste Management. Institution of Engineers, W.A. Branch, Perth.

Stewart, G.A., G. Gartside, R.M. Gifford, H.A. Nix, W.H.M. Rawlins and J.R. Siemon (1979). Liquid Fuel Production from Agriculture and Forestry in Australia. Search. Vol. 10, pp. 382-387.