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The Development of a Process for the Hydrolysis of Lignocellulosic Waste [and Discussion]

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The development of a process for the hydrolysis of lignocellulosic waste

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The degradation of lignocellulose to provide feedstocks for fermentation and chemical use is the subject of increasing worldwide investigation. This paper outlines the current chemical and enzymic methods and discusses the problems presented to the process engineer. In view of these difficulties, the targets for a viable process are described. In the process, wheat straw is used as the feedstock and the removal of the hemicellulose is involved as a first step. In the second step, the majority of the lignin is removed, thereby yielding a cellulose-rich material for conversion to glucose in the final step. The paper concentrates on this last step, which is an acidic hydrolysis carried out in the presence of a metal halide. This combination leads to rapid dissolution of the solid, which is then susceptible to hydrolysis. The reaction conditions, acid recovery and separation of the glucose from inorganic material are described.

Introduction

The interest in upgrading and utilization of lignocellulosic wastes is not new, and history is scattered with industrial-scale processes for fractionation of lignocellulosics that have failed for both technical and commercial reasons. It is worthwhile noting that the only large-scale processes currently operating are those in countries that have an important strategic need and/or whose economies are centrally planned.

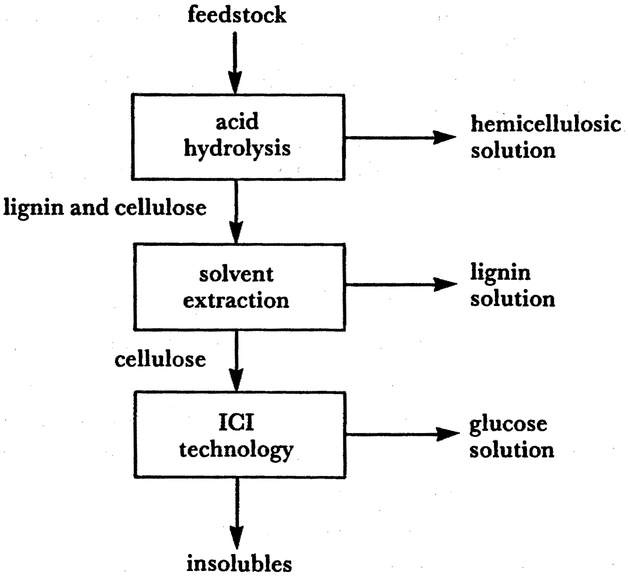
It is against this background that the development of a new process for the hydrolysis of lignocellulosic wastes will be discussed in this paper. The current chemical and enzymic methods for hydrolysis of cellulose will be reviewed, paying particular attention to the advantages and disadvantages of each. From this, a number of technical and economic targets will be identified and the development of a novel process for cellulose hydrolysis that will satisfy these targets will be described.

Overall process

Given that lignocellulose consists of three main components (hemicellulose, lignin and cellulose), it is worth giving a brief description of the possible treatment of the hemicellulose and lignin before discussing the main hydrolysis of cellulose.

Scheme 1 is a basic outline of a possible three-stage process for fractionation of lignocellulosics. It is generally recognized that, of the three major components, the removal of the hemicellulose is the easiest. This is largely because it is a substantially amorphous heteropolysaccharide made up of a relatively limited number of sugar residues. The proportions of these sugars are feedstock specific, and in most cases a simple acid or alkali extraction will effect substantial removal of the hemicellulose. To obtain as pure a glucose solution as possible, this extraction must occur before the cellulose hydrolysis. This is because the conditions for conversion of cellulose to glucose are generally more severe, and if the hemicellulosic fraction were not removed, a higher overall level of degradation would result.

The lignin removal constitutes a pulping operation and can be achieved by various means. Given that the prospect for a large market for such lignin may still be some way off, any process for conversion of cellulose to glucose should work either in the presence of, or in the absence of, lignin. However, the authors have developed a process for the extraction and production of a substantially pure lignin; i.e. a lignin that is essentially free of ash and carbohydrate and is acquired in a low molecular mass, reactive form. Given such a demand, lignin extraction would precede cellulose hydrolysis, as shown in scheme 1. It should be noted, however, that the hydrolysis process that is to be described is, in a technical sense, only marginally affected by the optional removal of the lignin.



SCHEME 1. A three-stage process for fermentation of lignocellulosics.

CURRENT CELLULOSE HYDROLYSIS PROCESSES

Having obtained a cellulose-rich feedstock, the conversion of cellulose to glucose can now be discussed. Processes to realize the potential value of cellulose can be classified into two broad categories, enzymic and chemical.

ENZYMIC PROCESSES

Table 1 summarizes the advantages and disadvantages of current enzymic processes. Certainly, enzymic hydrolysis has some advantages. It is specific, with glucose as the sole product. The reactions occur near ambient temperature, and no pressure vessels are required. However, the current disadvantages are serious. The reaction is slow and is measured in hours or even days. Pretreatment of the feedstock to enhance the conversion rate is desirable. Such treatments, which can be expensive, include solvent extraction, irradiation and steam explosion. Fur-

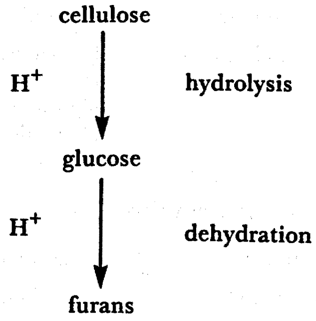
Table 1. Current enzymic processes: enzymic hydrolysis process characteristics

advantages	disadvantages
specific	very slow
low temperature	needs pretreatment
low pressure	expensive catalyst
	no enzyme recycling

thermore, the production of the enzymes is expensive and there is no enzyme recycle. The advantages and disadvantages, shown in table 1, should be borne in mind when comparing enzymic and acidic processes (especially the times for conversion and the cost of the enzyme production). In short, enzymic hydrolysis is currently slow and expensive.

Acidic processes

It has been known for a long time that cellulose and hemicellulose are hydrolysed by acid. However, the reaction is less specific and unwanted by-products, in particular the furans, can also accumulate. Scheme 2 shows a simple representation of the acidic reactions. The important feature to note from a process point of view is that the glucose is an intermediate product. The kinetics of this series, first-order reaction largely decide the reactor configuration and reaction time.



Scheme 2. A simple representation of acidic conditions showing the acidic reactions involved in cellulose hydrolysis.

Early commercial use of acid hydrolysis occurred in Germany in the 1920s, when they made fuel from glucose obtained from wood chips hydrolysed by sulphuric acid. This was the Scholler process, resulting in yields of about 50% with respect to the theoretical yield of fermentable sugars. It is worth noting that the remaining 50% was a mixture of partly hydrolysed oligosaccharides and furan derivatives. To use the sugar solution produced, the acid had to be neutralized, i.e. there was no acid recovery process. High pressure, about 20 atm,† and high temperature, 170 °C, were also used. After 1945 the process was no longer used because the strategic need had passed. Since the initial experience with the Scholler process, much effort has been put in to optimize the acidic hydrolysis of cellulose. Examples of these processes are shown in table 2. Although higher yields can be claimed for several of these processes, including anhydrous HCl and HF, the recovery and separation of the acid from the resulting sugar solution remains the major problem. Thus the main advantage of speed of reaction of acid

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† 1 atm ≈ 10^5 Pa.

hydrolysis is overshadowed not only by the formation of degradation products but by the high recovery cost of the acid.

Tables 3 and 4 summarize the case for acid hydrolysis. In the case of dilute-acid hydrolysis, the disadvantages clearly outweigh the advantages. The most notable problems are those of low yields and long reaction times. The case for concentrated acids can be similarly analysed. Although there is a significant improvement in glucose yield, there is now a serious problem with the catalyst cost and difficult recycle.

Thus, having studied enzymic and acidic hydrolysis processes, it can be seen that there is a need for substantial improvements in both cases before a viable process can be defined.

TABLE 2. DEVELOPMENT OF ACID HYDROLYSIS PROCESSES: A HISTORICAL VIEW OF CELLULOSE HYDROLYSIS

year	process	type	temperature
1923	Scholler	dilute H_2SO_4	170 °C
1937	Bergius	conc. HCl	ambient
1945	Madison	dilute H_2SO_4	180 °C
1960	Noguchi	gaseous HCl	ambient
1978	Grethlein	dilute H_2SO_4	240 °C
1981	Hoechst	anhydrous HF	40 °C

TABLE 3. THE CASE FOR DILUTE-ACID HYDROLYSIS: PROCESS CHARACTERISTICS

advantage	disadvantages
lower catalyst cost	low yields long time high temperature no catalyst recycling

TABLE 4. THE CASE FOR CONCENTRATED-ACID HYDROLYSIS: PROCESS CHARACTERISTICS

advantage	disadvantages
improved yield	high catalyst cost recycling problems long time high capital cost

A NOVEL PROCESS

ICI entered the search for a commercial cellulose hydrolysis process in 1979. During the course of biochemical research, on Teesside, it was considered that an inexpensive source of sugars would be attractive for several of the fermentation and microbiological processes that ICI had been investigating.

Thus, some targets were set to achieve a viable lignocellulosic fractionation process. Table 5

TABLE 5. TARGETS FOR ECONOMIC HYDROLYSIS BASED ON EXISTING-PROCESS SHORTCOMINGS

fast reaction rate	low by-product formation
high product yield	low reaction temperature
high product concentration	low reaction pressure
easy catalyst recycling	low catalyst cost

shows the targets that were based on the shortcomings of the previously described processes. Some, such as fast reaction rate, high yield and easy catalyst recycling were very important, but it was felt that if all the targets could be achieved it would result in an economically viable process.

After an initial assessment of enzymic hydrolysis, it was realized that current enzyme technology would not meet many of the requirements; therefore chemical alternatives were examined. With the help of Professor S. A. Barker and Dr P. J. Somers, of Birmingham University, several hydrolytic fractionation routes have been investigated.

The hydrolysis reaction

It has been known for many years that pure cellulose will swell in mixtures of organic reagents or in aqueous solutions of certain metal salts. The process of swelling, when carried out to the extreme, leads to complete dissolution. Concentrated acid will also dissolve cellulose via

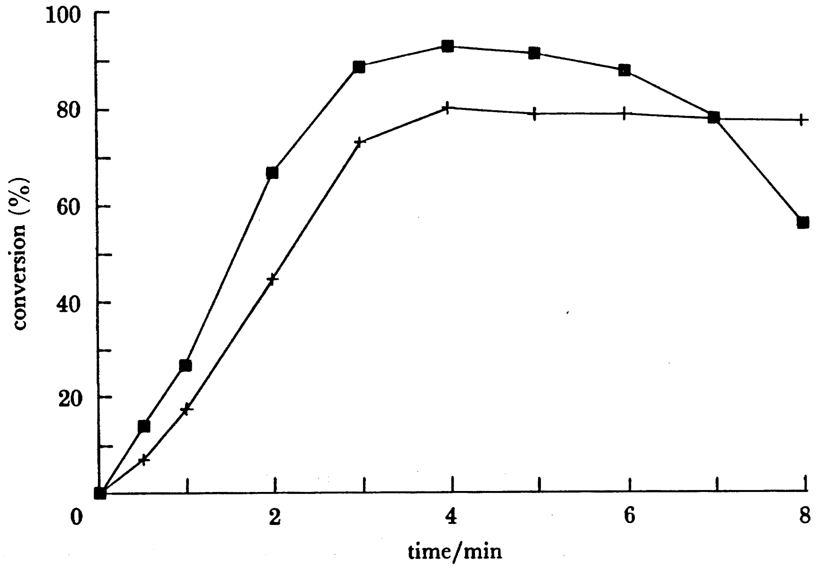

Figure 1. Reaction optimization studies of cellulose hydrolysis showing glucose conversion at 90 °C. Symbols: ■, 6 M LiCl, 7 M HCl; +, 1.64 M $CaCl_2$, 6 M HCl.

Table 6. Metal salts tested for effective performance in combination with HCl to hydrolyse cellulose

	most effective	
LiCl		$CaCl_2$
	less effective	
$ZnCl_2$	$MgCl_2$	$AlCl_3$
	least effective	
$FeCl_3$ KCl $CuCl_2$	$SnCl_4$ $MnCl_2$ $CoCl_2$	NaCl $NiCl_2$ $CdCl_2$

hydrolytic cleavage. What would happen if metal salts were used in combination with acids? The combination of metal salt to swell the cellulose and acid to promote hydrolysis might lead to a more rapid rate of reaction. Various combinations of acids and metal salts were tested for their ability to hydrolyse cellulose under mild conditions. Some metal chlorides were shown to be very active in promoting the hydrolysis of cellulose in the presence of hydrochloric acid.

The metal salts tested are shown in table 6. In each case, the metal salt was at saturating concentrations in the hydrochloric acid. The reaction temperature was 50 °C and the pressure, developed internally, was less than 4 bar.† Figure 1 shows some optimization studies with lithium chloride and calcium chloride at higher temperatures and 10% (by mass) pure cellulose as the substrate. As can be seen, the reaction was extremely rapid with relatively high yields. A choice now had to be made between the use of lithium chloride or calcium chloride. Because of the costs and relatively high concentrations of the metal halides required to hydrolyse the cellulose, a study of the recovery and recycle of these potential catalysts suggested that calcium chloride would be the better system to optimize.

Of course, pure cellulose could in no way be regarded as a viable substrate; so, by using the $CaCl_2$–HCl combination, a number of lignocellulosic materials have been tested. The results are shown in table 7. It is encouraging to note that conversions of greater than 85% are seen in all cases and for some, e.g. bagasse, newsprint, yields are close to maximum. In a U.K. context, the preferred feedstock was considered to be wheat straw. Patent applications covering processes with acids and metal salts have been filed. These have been published as Granted European Patent 44622B and Published European Patent Applications 91221A and 96497A.

TABLE 7. EFFECT OF CATALYST ON A RANGE OF SUBSTRATES: THE HYDROLYSIS OF LIGNOCELLULOSIC MATERIALS WITH THE ICI CATALYST

substrate	cellulose content (%)	conversion (%)
wheat straw	32	86
wood shavings	32	90
cardboard	55	89
newsprint	42	93
bagasse	44	98

CATALYST RECOVERY

The next important aspect is the recovery of the catalyst components. Herein lies the key to an economically viable process. The major problem with hydrochloric acid in the conventional concentrated-acid process is that it forms a constant-boiling azeotrope in water at a concentration of about 21% by mass (figure 2). This makes it difficult to recover the majority of the acid, as no distillation or evaporation process can reduce the HCl concentration in the liquid to below its azeotropic concentration.

However, it has been found that the presence of calcium chloride will shift the azeotropic concentration of HCl downwards until, above a certain level of $CaCl_2$, the azeotrope is broken completely. This is shown in figure 3. Extensive work on the $HCl–H_2O–CaCl_2$ system has led

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† 1 bar = 10^5 Pa.

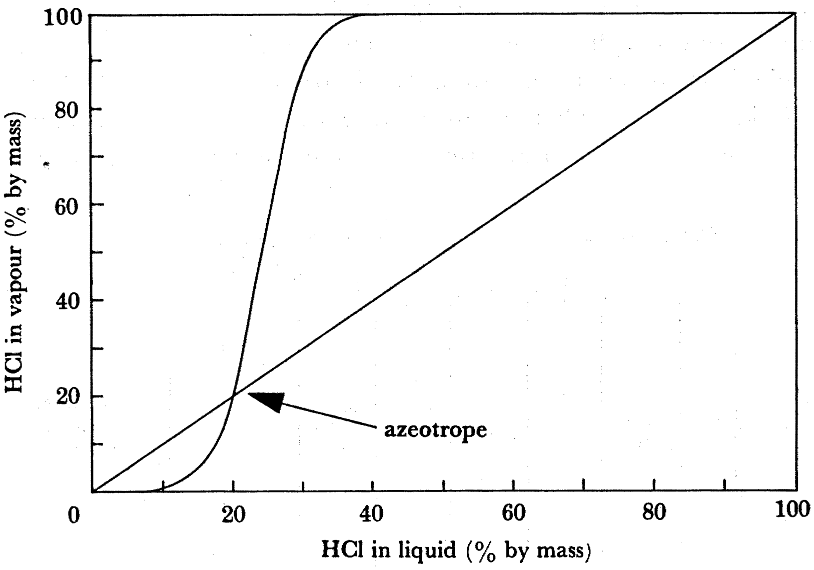


FIGURE 2. The azeotrope formed by HCl–water: the vapour–liquid equilibrium at 1 atm.

to a mathematical model that will predict the vapour–liquid–equilibrium HCl concentrations for any $CaCl_2$ concentration and operating pressure. The saturation temperature of the mixture can also be calculated. Thus, given this thermodynamic data, a process has been devised to permit virtually complete HCl recovery at low cost and, equally important, with minimum glucose degradation.

Having recovered the hydrochloric acid, a final problem remains: that of calcium chloride recovery and recycle. The calcium chloride can be removed from the glucose solution by a variety of processes with differing degrees of success. Such processes include solvent extraction, crystallization, ion-exchange and electrodialysis. The method described here is the membrane

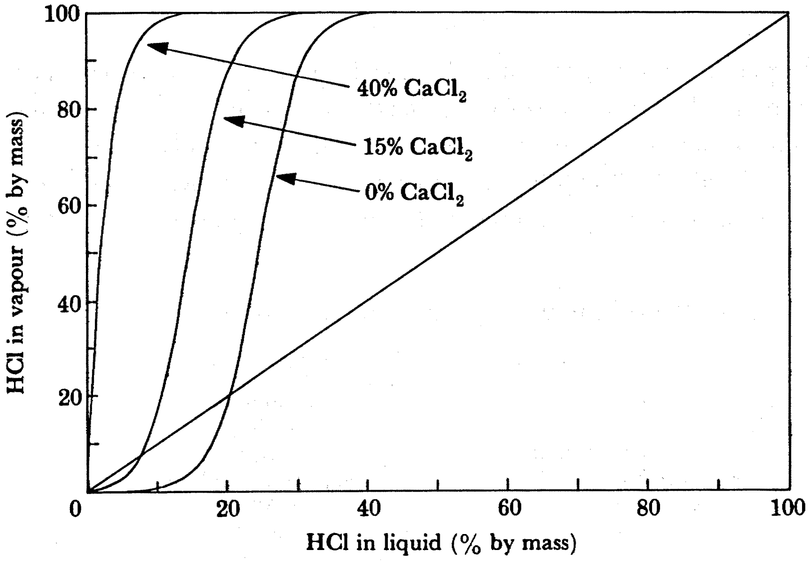


FIGURE 3. The effect of catalyst concentration on azeotrope. The vapour–liquid equilibrium with the effect of $CaCl_2$ on $HCl–H_2O$ azeotrope.

technique of electrodialysis (ED). A schematic diagram of the electrodialysis operation is shown in figure 4. Calcium chloride and glucose enter the unit in several streams separated, alternately, by cationic- and anionic-exchange membranes. An electric current is applied at right angles to the direction of fluid flow. The calcium ions migrate towards the cathode and the chloride ions migrate to the anode. Each ion passes through a membrane of opposite charge to itself but then can progress no further because it will not cross a membrane of like charge. In this way the calcium chloride can be separated from the glucose, which is not affected by the charge across the electrodialysis unit. This separation has been demonstrated on a pilot scale with a recovery of greater than 99% of the calcium chloride. Thus a stream that contains glucose and only trace amounts of furans, hydrochloric acid and calcium chloride is obtained.

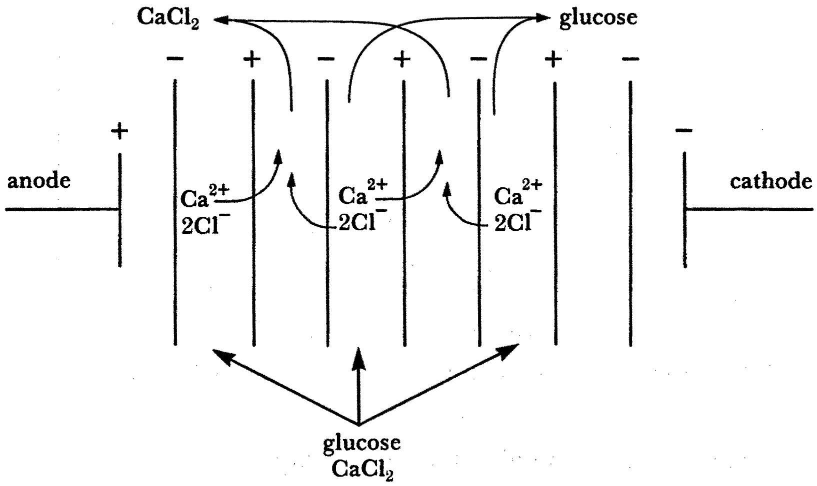


Figure 4. Schematic diagram of an electrodialysis unit.

Progress

The technical targets have been previously discussed (table 5). It is now worth checking what progress has been made. As can be seen from table 8, some success has been achieved with all of the targets set. The most noteworthy are the fast reaction, high yield and easy catalyst recycle.

Thus a calcium chloride–HCl catalyst system has been developed. The favoured reaction conditions are shown in table 9. In summary, the presence of the calcium chloride improves

Table 8. Process development: progress towards targets

target	achievement
fast reaction	5–20 min
high yield	> 85%
product concentration	> 15%
easy recycling	evaporation and ED
low by-products	< 5%
low temperature	<90 °C
low pressure	< 6 bar
low catalyst cost	calcium chloride and HCl

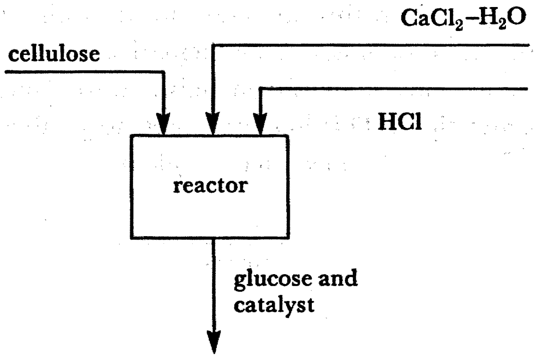
Table 9. Favoured reaction conditions for cellulose hydrolysis

substrate concentration (% by mass)	15–25
reaction medium (% by mass)	5–15 $CaCl_2$, 25–40 HCl
temperature/°C	60–90
pressure/bar	4–7
reaction time/min	10–20
yields (%)	> 85

the reaction conversion and selectivity. It also reduces the severity of the temperature–time conditions compared with those of conventional acidic hydrolysis. Secondly, it shifts the HCl–H_2O azeotrope, and allows complete recovery of the acid.

Process flowsheet

All the detailed information, previously described, was obtained initially in the laboratory. The next stage of development was the translation of conditions giving good yields on a 30 ml batch scale with 3 g of lignocellulose to a full-scale, continuous process. Thus a process flow diagram can be built up.



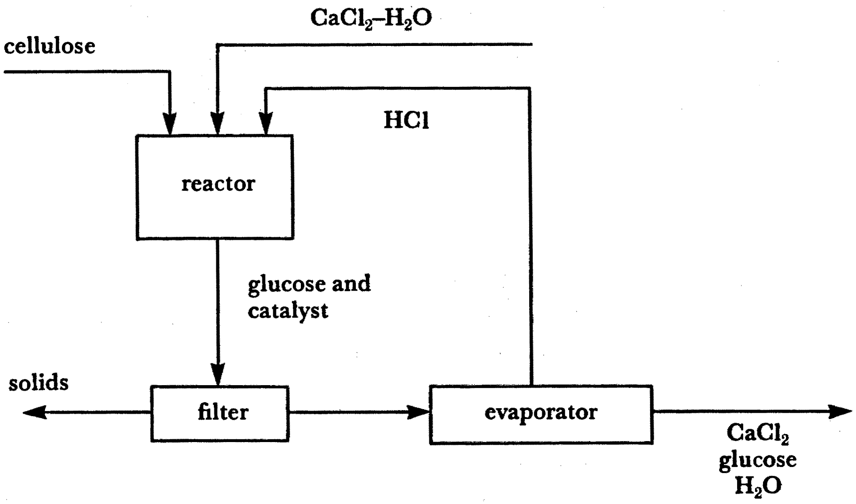
Scheme 3. The first stage in the cellulose to glucose process. ICI cellulose hydrolysis process: reactor.

The first stage in the cellulose to glucose process is the actual reaction. Scheme 3 serves to indicate the relative simplicity of this step. A few further points are worth noting:

(1) the detailed reactor design is consistent with a product that is intermediate in a series, first-order reaction;

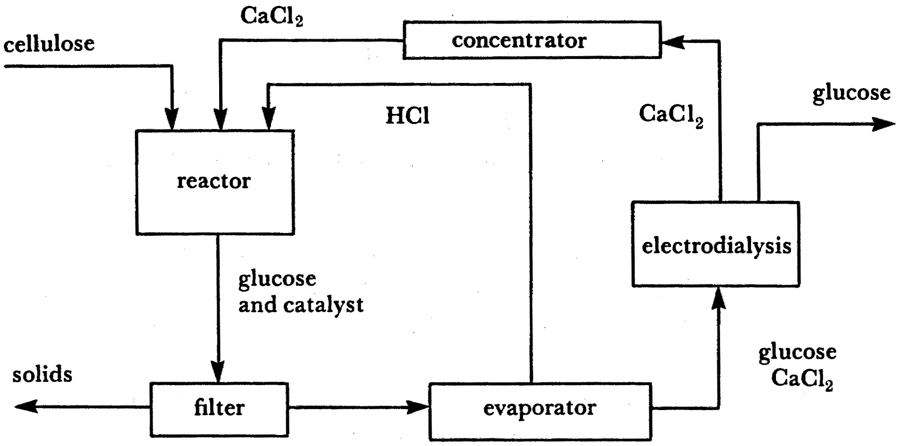
(2) as an indication of the intensity of the process, it should be noted that a reactor to process the cellulose from 50 kt a^{-1} of straw is only 3 m^3 in volume.

Scheme 4 depicts the reaction stage plus the addition of a filtration and acid-removal stage. It is after the reactor that attention has to be paid as to whether lignin has been extracted or not. The net effect of not removing the lignin is an increase in the size of the filter necessary for removal of the insolubles. As has been previously described, the HCl can be recovered by means of a simple evaporation stage. It should be noted that the low-temperature reaction lends itself to a large variety of inexpensive rubber or plastic linings for the reactor, followed by plastic pipework. The evaporator can make use of graphite for heat transfer, thereby minimizing chloride corrosion problems.



Scheme 4. Reaction plus filtration and acid recovery. ICI cellulose hydrolysis process: reactor and HCl recovery.

Scheme 5 shows a box diagram of the complete process with the addition of a calcium chloride recovery stage. The operation of electrodialysis for this purpose has been described previously. A lot of work has been completed on this operation to determine the values of parameters required to optimize the process economics. A mathematical model of an electrodialysis unit has been devised with resistance, current density, membrane area, membrane cost and calcium chloride and glucose concentrations. This has been used to predict the optimum operating conditions. Examination of scheme 5 shows that a calcium chloride concentration stage is required. This is because of the limits on electrodialysis operation and the reactor water-balance requirements.



Scheme 5. The complete process. ICI cellulose hydrolysis process.

Each of the forementioned stages has been demonstrated on a continuous basis, and a full engineering analysis, including cost estimation, has been developed. In conclusion, ICI has developed a process that can technically give high yields of glucose from a cellulose-containing feedstock and also one that satisfies conventional economic analysis and thereby provides a commercially viable process.

Discussion

P. B. Tinker (*Rothamsted Experimental Station, Harpenden, Hertfordshire, U.K.*). The characteristics of the process seem very impressive. If it is commercially successful, what fraction of the present straw surplus in the U.K. could be utilized in this way?

P. L. Ragg. It is likely that only a relatively small proportion of the current straw surplus could be utilized in this way; the quantity, of course, depends upon the demand for fermentation products derived from glucose. The technology cannot be viewed as a solution to the straw-burning problem, although it could undoubtedly make a significant contribution to this on a local basis.