Ethanol from Residues –

Paper Tubes and Textiles

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Waste Refinery

Etanol ur avfall – Pappersrullar och textilier

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Sammanfattning

Utgångspunkten för detta projekt har varit att undersöka möjligheten att producera etanol ur avfall. Projektet begränsades till att utvärdera avfallsfraktionerna pappersrullar och textilier.

Projektmålen var att undersöka följande:
(a) Är det möjligt att producera etanol ur de utvalda avfallsfraktionerna?
(b) Vilka problem kan uppkomma vid hydrolys och fermentation och hur kan dessa lösas?
(c) Vilket utbyte kan uppnås i praktiska försök (uttryckt som kg etanol per kg avfall)?

Försök har utförts i både laboratorieskala och i en pilotanläggning på 10 l. Svagsyrahydrolys har genomförts i både laboratorieskala (150 ml) och i pilotskala (10 l) medan enzytmatisk hydrolys och SSF (simultaneous saccharification and fermentation, dvs. samtidig försockring och fermentation) har genomförts endast i laboratorieskala. Två olika syror, fosforsyra och svavelsyra har också undersökts, inom ramen för projekt.

Resultaten från försöken visar att fosforsyra har den bästa effekten för att lösa upp den kristallina cellulosastrukturen och därmed frigöra glukos för vidare fermentation.

Vid försöken med pappersrullar har utbyten mellan 20-24 % baserat på torr råvara uppnåtts, medan vissa textilier (jeansmaterial) har resulterat i utbyten på 30-40% baserat på torr råvara.

Resultaten från försöken visar att utbyten på ca 25 till 30 l per 100 kg pappersrullar, och 35 till 50 l per 100 kg textilier uppnåddes.

Avfallsfraktionerna som studerats i detta projekt finns i hela Sverige, men lokala variationer i verksamheter påverkar andelen av de totala avfallen lokalt. Lokala mängder för Borås är 300 ton pappersrullar per år, och 17 000 ton textilier per år, varav ca 25 % bedöms som potentiellt tillgängligt för etanolframställning.

Några tydliga hämmande effekter av tillsatser i de studerade avfallsströmmarna kunde inte noteras. Exempelvis hämmar inte additivet polyvinylalkohol, PVA, som finns i pappersrullarna etanolproduktionen i någon större omfattning. Vid försöken med textilier visade jämförande tester med ren bomull även att färger och dylikt i textilier inte heller ger några störande effekter på fermentationen.

Vid pilotförsöken uppskattades optimal tid och temp för svagsyrahydrolys till ca 15 min och 180°C för försöken med textilier, och ca 15 min och 200°C för försöken med pappersrullar .

Nyckelord: Etanol, hydrolys, fermentation, avfall, papper, textil

Summary

The aim of this project was to investigate the possibilities to procude ethanol from waste fractions. In this project, the investigation was limited to paper tubes and textiles.

Project goals were to study:

(a) Is it possible to produce ethanol from the selected waste fractions?
(b) Which problems could arise in the hydrolysis and fermentation, and how could these be solved?
(c) What yields could be achieved in practice, expressed as kg ethanol per kg waste?

Tests have been made in both laboratory scale and in pilot scale (10 l). Weak acid hydrolysis was made in laboratory scale (150 ml) and in pilot scale (10 l), while enzymatic hydrolysis and SSF (simultaneous saccharification and fermentation), was made in laboratory scale only. Two different acids, phosphoric acid and sulphuric acid were used.

The results from the experiments show that phosphoric acid have the best effect on dissolving the crystalline cellulosic structure of the two acids tested. This results in higher glucose yields before fermentation.

The tests with paper tubes resulted in ethanol yields of 20-24 % based on dry raw material. Some textiles (jeans material) resulted in yields of 30-40% based on dry raw material.

The results from the experiments show that yields of 25-30 l ethanol per 100 kg paper tubes, and 35-50 l ethanol per 100 kg textiles were reached.

Waste fractions that were studied in this project are available in whole Sweden, but the relative share of the wastes depends on local conditions. In Borås, the amount of paper tubes is approximately 300 tons per year, and textiles amounts to about 17 000 tons per year. About 25 % of the textiles are considered to be available for ethanol production.

Any negative effects on the ethanol production from additives could not be noted in the experiments. For example, the additive poly-vinylic alcohol, PVA, which is present in the paper tubes, does not hamper the ethanol yield in any large proportion. During the experiments with textiles, comparative fermentation tests using pure cotton did not show any effect from dyes or other additives.

In the experiments with the pilot reactor, optimum reaction time and temperature were 15 minutes and 180°C for weak acid hydrolysis of textiles. Corresponding optimum conditions for the experiments on paper tubes were15 minutes and 200°C respectively.

Keywords: Ethanol, hydrolysis, fermentation, waste, paper, textiles

Preface

This project was financed by Waste Refinery.

Paper tubes were supplied by Nordens Pappersindustrier AB, and waste textiles were by the Sobacken waste management plant in Borås. Jeans material was kindly supplied by numerous people at SP, Technical Research Institute of Sweden and HB, University College of Borås.

The project group has included the following people:

Roger Nordman, SP, Project leader
Azam Jeihanipour, HB, Responsible for experiments on textile material
Anders Lorén, SP, Experiments on chemical characterization
Mohammad Taherzadeh, HB, Supervising experiments on textile material and paper tubes and scientific leader of the project
Farid Talebnia, HB, Responsible for experiments on paper tubes
Daniel Ryde, SP, Experiments on paper tubes and textiles in the pilot plant

In addition, a reference group for the project has consisted of:

Julia Fredäng, Dalkia FM AB
Catrin Lindblad, SP
Åke Nordberg, JTI
Andreas Ulveström, Borås Energi och Miljö AB

Thank you all for your contributions and for making this project possible!

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Nomenclature and abbreviations

DM	Dry Matter
FPU	Filter Paper Units
HMF	Hydroxy Methyl Furfural
HPLC	High Performance Liquid Chromatography
IU	International Units
PVA	Polyvinyl Alcohol
RI detector	Refractive Index
SSF	Simultaneous Saccharification and Fermentation

Utökad sammanfattning

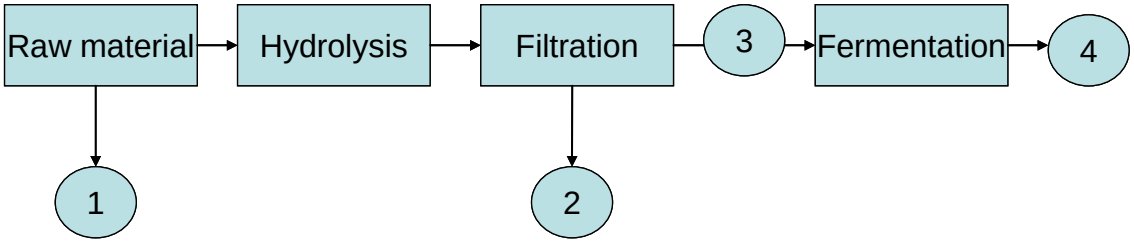
Utgångspunkten för detta projekt har varit att undersöka möjligheten att producera etanol ur avfall. I detta projekt utvärderades avfallsfraktionerna pappersrullar och textilier.
Avfallsfraktionerna som studerats i detta projekt finns i hela Sverige, men lokala variationer i verksamheter påverkar andelen av de totala avfallen lokalt. Lokala mängder för Borås är 300 ton pappersrullar per år, och 17 000 ton textilier per år. Dessa avfall bedömdes även som relativt lätta att få fram som rena fraktioner från avfallshanteringen, pappersrullarna kan samlas in från tillverkningen och ca 25 % av textilierna bedöms som potentiellt tillgängligt för etanolframställning. Även dessa skulle kunna samlas in separat vid källan.

Projektmålen var att undersöka följande:

- Är det möjligt att producera etanol ur de utvalda avfallsfraktionerna?
- Vilka problem kan uppkomma vid hydrolys och fermentation och hur kan dessa lösas?
- Vilket utbyte kan uppnås i praktiska försök (uttryckt som kg etanol per kg avfall)?

Även om avfallen är rena som fraktioner räknat, så finns det många ämnen som kan störa en etanoltillverkning som bygger på biologisk omvandling av cellulosa och stärkelse till glukos (socker) och sedan vidare till etanol.
I projektet har försök att omvandla avfall till etanol utförts i både laboratorieskala (150 ml) och i en pilotanläggning för hydrolys på 10 l. Denna pilotanläggning finns vid Borås Energis kraftvärmeanläggning. Genom att göra försöken i både både laboratorieskala och pilotskala kan man se om resultaten skiljer sig åt när man skalar upp produktionen.

Hydrolys av materialet sker för att kapa de långa cellulosakedjorna till kortare kedjor, samt för att frigöra glukos. För att detta skall ske kan man använda värme i form av ånga av högt tryck. För att ytterligare snabba upp processen kan man tillsätta någon form av katalysator. Både syror och baser kan fungera som katalysatorer, och den vanligaste man använder är utspädd svavelsyra (svagsyrahydrolys). Ett annat sätt att kapa cellulosakedjorna är genom att använda speciella enzym som gör detta. Dessa enzym förbrukas dock under processens gång. Svagsyrahydrolys har genomförts i både laboratorieskala (150 ml) och i pilotskala (10 l) medan enzymatisk hydrolys och SSF (simultaneous saccharification and fermentation, dvs. samtidig försockring och fermentation) har genomförts endast i laboratorieskala. Två olika syror, fosforsyra och svavelsyra har också undersökts, inom ramen för projekt. För ett av textilmaterialen som undersöktes användes även en bas som hydrolyskatalysator.



Vid försöken togs prov ut och analyserades i ett antal punkter, se bilden övan. I punkt 1 togs ett prov på råmaterialet som användes för att bestämma C, H, N och askhalt.

Filtratrejektet analyserades med avseende på C, H, N, askhalt, cellulosainnehåll och värmevärde. I punkt 3 analyserades sockerinnehållet, och i punkt 4 etanolhalten.

Förbehandling
Vid pilotförsöken fylldes reaktorn med ca 1 l vatten och 10 % material. Vid förbehandlingen varierades syrakoncentration, uppehållstid och temperaturen i hydrolysreaktorn. Detta gjordes för att hitta den kombination som gav högst utbyte av glukos.

Vid pilotförsöken uppskattades optimal tid och temperatur för svagsyrahydrolys till ca 15 min och 180°C för försöken med textilier, och ca 15 min och 200°C för försöken med pappersrullar. I laboratorieförsök utfördes även försök med enzymatisk hydrolys och SSF, samtidig förbehandling och fermentation. Enzymatisk hydrolys har fördelen att ske vid lägre temperatur, ca 45°C, men kräver mycket längre uppehållstid än syrahydrolys.

Resultaten från försöken visar att fosforsyra har den bästa effekten för att lösa upp den kristallina cellulosastrukturen och därmed frigöra glukos för vidare fermentation.

Glukos var den största reaktionsprodukten vid hydrolys av pappersrullarna, men även xylos förekom. Obehandlat prov inte nådde mer än ca 15 g/l glukos efter 72 timmar. Behandlade prov gav bättre utbyte, och de prov som behandlats med fosforsyra nådde 93% av teoretiskt möjligt utbyte efter 72 timmar. De prov som utfördes som SSF visar att etanolhalten ökar med ökande satsning av enzym. Då två olika satsningsnivåer har undersökts kan man inte säga från dessa försök vad som är optimal satsning, men detta blir i slutändan en ekonomisk optimering. Försöken visar dock även att den högre satsningen ger ett snabbare förlopp.

Fermentation
Fermentationen (jäsningen) utfördes i alla försök med jästsvampen *S. cerevisiae,* som är vanlig bagerijäst. Denna kan inte omvandla xylos till etanol, så i alla försök har utbytet beräknats från glukoshalten. Med jästkulturer som klarar att omvandla xylos till etanol skulle utbytet kunna ökas ytterligare.

Vid försöken med pappersrullar har utbyten mellan 20-24 % baserat på torr råvara uppnåtts (Tabell 1), medan vissa textilier (jeansmaterial) har uppnått utbyten på 30-40% baserat på torr råvara (Tabell 2).

Tabell 1. Utbyte av glukos från enzymatisk hydrolys och etanolutbyte från SSF av Avicel, obehandlad och behandlade prover av pappersrullar. Alla utbyten är beräknade på torrvikten av råvaran.

SAMPLES	Enz. hydrolysis	SSF-15 FPU/g DM	SSF-30 FPU/g DM
	YGlu(%)	YEth (g/g DM)	YEth (g/g DM)
Untreated (Unt.)	29	0.14	0.18
H_2SO_4-treated (SP)	39	0.17	0.20
H_3PO_4-treated (PP)	54	0.19	0.24

Tabell 2. Utbyte av etanol från SSF av olika förbehandlade och obehandlade textilprover

SAMPLES	SSF – 3% solid	SSF – 5% solid
	YEth (g/g fibres)	YEth (g/g fibres)
Phosphoric acid treated jeans	0.38	0.30
Dilute sulf. acid treated jeans	0.30	-
Untreated jeans	0.27	-
Phosphoric acid treated viscose	0.39	-
Untreated viscose	0.50	0.48
Phosphoric acid treated cotton	0.35	-

Resultaten från försöken visar att utbyten på ca 25 till 30 l etanol per 100 kg pappersrullar, och 35 till 50 l etanol per 100 kg textilier kan uppnås.
Textilier av viskos visade sig kunna fermenteras över 87% av teoretiskt utbyte utan förbehandling.

Störande ämnen
Några tydliga hämmande effekter av tillsatser i de studerade avfallsströmmarna kunde inte noteras. Exempelvis hämmar inte additivet polyvinylalkohol, PVA, som finns i pappersrullarna etanolproduktionen i någon större omfattning. Vid försöken med textilier visade jämförande tester med ren bomull även att färger och dylikt i textilier inte heller ger några störande effekter på fermentationen.

Rekommendationer för fortsatt arbete
För att bättre kunna bestämma potentialen för att tillverka etanol ur avfallsfraktioner bör en mer utförlig analys av avfallsflödena göras. Karakterisering av avfallsmaterial borde även ge beslutsunderlag för om man skall satsa på etanol eller till exempel biogastillverkning.

Hydrolys- och fermatnationsstegen behöver optimeras genom att justera processparametrar.

Fler avfallsfraktioner skulle behova studeras för att visa på potentialen för ytterligare fraktioner för etanolproduktion.

Restfraktionen från hydrolyssteget är relativt stor. Denna fraktion skulle kunna brännas eller utgöra råvara för biogasproduktion. En studie skulle kunna utreda vilket alternativ som är mest fördelaktigt.

Fermentationstiden måste förkortas för att processen skall kunna bli industriellt konkurrenskraftig.

1 Introduction

1.1 Problem description

As a fuel for transport, ethanol is in a fast-growing market, with the EU having set goals of 20 % of transport fuels being provided by renewables by 2020. The fuels that are competitive today are biodiesel, biogas and ethanol. Ethanol is predominantly made from sugar cane in Brazil, corn in the US and grains in Sweden (local production). All these raw materials result in what is known as first-generation ethanol. Over the last few years, there has been a growing debate on whether ethanol from crops is justified from a resource point of view, with many millions of people starving. Research in Sweden is today therefore mainly focused on what is known as second-generation ethanol, made from lignocellulosic materials, such as forest chips and residuals. The ongoing debate in the EU on a renewable energy supply of 20 % in electricity production has also made wood-based ethanol production a hot topic.

In this light, ethanol production from waste fractions and residues appears as a promising alternative. There are several types of waste materials that can potentially be used for ethanol production, but their heterogeneity make them technically difficult to be processed. Industrial residues that are more homogeneous were therefore chosen in this project. This choice has some direct advantages:

- The raw material has a negative cost (residue owners pay to dispose of them)
- The residue streams are relatively homogenous
- The residues streams are relatively large.

With this background, this project focus on:

1. What residues and waste materials that can be efficiently processed to ethanol are available?
2. What conversion ratios could be achieved, depending on the choice of conversion technology?
3. Is there enough material available to make this processing interesting in full-scale operation?

The first two questions were investigated through laboratory and pilot experiments. The last question was answered (for the Borås region) through an estimation of the waste streams passing the Sobacken waste treatment plant.

1.2 Aim and scope

The technology for ethanol production from specific types of lignocellulosic materials such as forest chips and wheat straw is already well-investigated by different research groups [1, 2]. However, wastes comprise a wide range of materials, where different material fractions have specific characteristics and therefore require individual research. Our previous results on ethanol production from orange peel showed two specific problems for this material, compared to forest chips: (a) the presence of limonene as an antimicrobial oil in the peel, which deactivates the fermenting organisms, (b) difficulties in the hydrolysis and fermentation of pectin. We therefore expected other problems, characteristic of the

particular materials, when investigating new categories of wastes. The specific goal of this project was to investigate:

a. The possibility of producing ethanol from selected waste materials,
b. Problems with ethanol production from selected wastes, and finding possible solutions to overcome these problems,
c. Yield from the fermentation of the selected wastes (theoretically and practically) in kg of ethanol per kg of the selected wastes.

In addition, the chemical properties of the remaining materials were investigated, to indicate final treatment/processing of them (for example incineration or biogas.).

The measurable goal to achieve (if no specific problems appeared during the research work) was to obtain:

1. 50 l ethanol per 100 kg of the sum of sugars, starch, cellulose and hemicellulose content of the wastes, in enzymatic processes
2. 40 l ethanol per 100 kg of the sum of sugars, starch, cellulose and hemicellulose content of the wastes, in dilute-acid processes

Target groups for this research are policy makers, residues and waste producers, plant owners, researchers and manufacturers of equipment.

1.3 Delimitations

A number of different residues suitable for conversion to ethanol were identified by the project, and are further discussed in the background section. However, only two fractions *viz.* paper tubes and textiles, were investigated in more detail. The fractions studied could possibly also be converted to biogas, but this option was not studied in this project.

All results are based on laboratory and pilot-scale trials. Further research is needed in order to quantify the conversion efficiency in full-scale production. The techno-economic potential has not been analysed in this work, but the process could be greatly helped by the negative cost of the raw material.

2 Background

Ethanol has a significant share of the fuel market [3]. It is now the largest biofuel product in the world, with a total annual production of about 50 billion litres, with the transport fuel market standing for more than 75 % of the total consumption [3]. Ethanol can be produced from a number of raw materials, each with different problems. The present status of the processes is shown in Table 3.

Table 3. Current status of ethanol production technologies.
Tabell 3. Nuvarande status för olika etanolproduktionstekniker.

Raw material main component	Type of raw material	Current status
Sugars	Sugar cane, molasses, sugar beet	Industrial processes
Starch	Grains	Industrial processes
Cellulose	Wood chips, straw	Pilot plants
Wastes including all of the above	Different residues	Lab-scale research

Ethanol performs well as a fuel in cars, either in a neat form or in a mixture with gasoline [4]. Ethanol is available on the Swedish fuel market as 85 % blend (E85) and 5 % mixed with gasoline. Sugar sources, such as sugar cane, and starch sources (grains), such as corn and wheat, have been the dominant raw materials for ethanol production. In addition, huge amounts of cheap lignocelluloses, such as forest residuals and crop wastes, encouraged different countries to consider lignocelluloses as a potential raw material for ethanol production in the future. Sweden and Canada are pioneers in using forest residuals for this purpose. The current work takes the next step in using waste materials for ethanol production. The following physical/chemical/biological reactions are usually considered in conversion of waste materials to ethanol:

$$\text{Wastes} \xrightarrow[\text{Delignification}]{\text{Pretreatment}} \text{Treated wastes} \xrightarrow[\text{Hydrolysis}]{\text{Acid/Enzymatic}}$$

$$\text{Carbohydrates} \xrightarrow{\text{Fermentation}} \text{Ethanol Solution} \xrightarrow[\text{Dehydrration}]{\text{Distillation}} \text{Purified Ethanol}$$

Ethanol production from cellulose is not a new field, and almost all its aspects are known to the research community [1, 2]. However, no research on ethanol production from paper tubes or textiles was found in the literature. The main task of this project was to investigate the effects of other chemicals (adhesives, dyes, etc.) on different parts of the ethanol process, including pre-treatment, hydrolysis (by acid and enzymes) and fermentation.

Waste raw materials

Four different waste materials were identified as interesting options for further investigation in this project. The general criteria for choosing them were that they should be available in large amounts, and that they should have a certain amount of material that can serve as the feedstock for ethanol production. The four materials identified for this project are listed and described below. In this project, however, only two residues - paper tubes and waste textiles - were studied experimentally.

Paper tubes

The residue from paper tubes is a raw material considered for production of ethanol in this project. This material is a waste product, amounting to about 300 tons/year[1], from paper tube production at Nordens Pappersindustri AB. There are several types of paper tubes, depending on the papers used, adhesives, processing conditions and the specifications of the final product. The main materials of the residues from these tubes are cellulose and adhesives. The adhesives are sodium silicate (water-glass) and Polyvinyl Alcohol (PVA). We expected no major problem from water-glass or PVA during pretreatment and hydrolysis, but the effect of PVA as an inhibitor in the fermentation step has been investigated. The residues available from Nordens Pappersindustri AB contain over 90 % recycled paper and about 8-10 % adhesives. Preliminary results on the analysis of this residue showed cellulose content of more than 50 %. However, more analyses were carried out before reporting this number more accurately.

Waste textiles

Waste textiles are a large source of waste materials, with about 17 000 tons/year collected in the waste collecting station in Borås (Sobacken), with an estimated extraction potential of about 25 % of this waste[2]. These materials are currently incinerated, but they cause troubles in the pretreatment by slowing rotating equipment and in the incinerator by acting as a fuse by which fire could burn backwards.

Textiles are typically made of (a) natural materials including, cotton, flax, wool, hemp, ramie, silk, or (b) synthetic fibres such as lyocell, polyester, viscose, Nylon, aramid or acrylics. In addition, down, fur, leather, and less common clothing materials such as paper, jute, rubber, PVC, PET, polyethylene fibres, rayon, bamboo, soy, glass fibres, basalt fibres, etc. may be encountered among the materials used in textiles. The different materials can be divided into four different categories; (a) animal textiles, (b) plant textiles, (c) mineral textiles and (d) synthetic textiles. Among these categories, the plant textiles (cotton) can theoretically be treated for ethanol production. Cotton fibers are the seed hairs of the plant *Gossypium*. Cotton is typically composed of 88–96% cellulose, the remainder being protein, pectin materials and wax. It is therefore comparable with straw and other types of lignocellulosic materials, which have already been investigated. In the global market, cotton - with an annual production of over 23 million tons [5] - represents about one third of the global market of textile fibers [6]. Polyesters make up roughly another third of the textiles market, with the remaining one third being produced from other types of natural or synthetic materials. This project did not obtain detailed statistics on the composition of the waste textiles collected in Borås.

Wallpapers

At least 750 tons/year of wallpaper are available as a residue in the Sjuhärad region[3]. The composition of this material depends on the type of the wallpaper. However, we can generally classify the material into three groups: (a) the carrier, (b) colour, and (c) surface treatment. The compositions of three different wallpapers showed a wide range of the

[1] C. Rydström. Personal communication.
[2] A. Johnsson, Personal communication.
[3] A. Johnsson, Personal communication.

materials used in their manufacture. Cellulosic materials were dominant in the carriers, and composed 11 % to 80 % of the total weight of the wallpapers. The other components, including synthetic polymers, inorganic materials and pigments are not likely to be converted to ethanol, and can be considered as solid residuals after the hydrolysis process.

Manures

Livestock manure is a readily available source of waste in Sweden and many other countries. In addition to carbon, the manures contain a variety of elements such as N, P and K. Different types of manures are available in the Borås region. Horse manure, which is available in our vicinity, to the extent of about 3000 - 5000 tonnes per year, could be one interesting option to study. The amount of bedding material (e.g. sawdust and straw) makes up a large proportion of horse manure, which makes it especially interesting for ethanol production.

Chen et al. [8] analyzed the composition of some manures in terms of total fibres, cellulose and hemicellulose. They reported 31-53 % of the dry matter of the manures to be fibres. Fibre provides a considerable resource for cellulose and hemicellulose which can be degraded to monosaccharides and then used as feedstocks to produce bio-ethanol. The dry matter contained 8-27 % cellulose, 12-22 % hemicellulose [8].

3 Materials and methods

Among the identified materials described in the Background, paper tubes and textiles were selected for further investigation in this project.

3.1 Materials

3.1.1 Paper tubes

The paper tubes used in the current work were reject materials from the products of Nordens Pappersindustri AB (Sandared, Sweden). Photographs of the material are shown in Appendix A.

3.1.2 Textile materials

The materials used in this work were pure cotton (obtained from local shops in Borås), jeans textile (donated by the project team), a viscose-type textile, a white residual textile from furniture manufacture, a red filter textile and a polyester-based textile obtained from Sobacken in Borås. Photographs of the materials are shown in Appendix A. Pure cellulose (Avicel, Fluka 11365) was used as a reference material.

3.1.3 Enzymes and yeast strains

3.1.3.1 Hydrolysis enzymes

Two enzymes, cellulase (SIGMA, C2730) and β –glucosidase (SIGMA, G0395), were used for enzymatic hydrolyses and SSF experiments. The activity of cellulase was measured as 140 FPU/ml of enzyme solution. The activity of β-glucosidase was reported by the supplier as 5.2 IU/mg solid.

3.1.3.2 Yeast strain and medium

A laboratory strain of baker's yeast *S. cerevisiae* CBS 8066, obtained from Centraalbureau voor Schimmelcultures (Delft, the Netherlands), was used in all experiments with the paper tubes. The strain was maintained on agar plates made from yeast extract 10 g/l, soy peptone 20 g/l, and agar 20 g/l with D-glucose 20 g/l as an additional carbon source. The experiments were carried out using a defined synthetic medium as described by Taherzadeh *et al.* [14], where 50 g/l glucose or the hydrolysed wastes were used as carbon and energy sources.

Another strain used for the textile wastes was a flocculating yeast strain of *S. cerevisiae*, CCUG 53310 (Culture Collection University of Göteborg). This was maintained on agar plates made of yeast extract 10 g/l, soy peptone 20 g/l, and agar 20 g/l, with D-glucose 20 g/l as an additional carbon source.

3.2 Analytical methods

Total dry content of the paper tubes was determined by drying at 110 °C for 48 h.

The carbohydrates content in paper tubes and the cellulose contents of the textiles were determined in accordance with the method "Determination of carbohydrates in biomass by

high performance liquid chromatography. LAP-002 NREL" provided by National Renewable Energy Laboratory, USA [12].

Cellulase activity was determined with a method provided by NREL, "Measurement of cellulase activities. LAP-006 NREL" [13].

All experiments were performed at least in duplicate, and results are presented as averages.

3.3 Equipment

The paper samples were shredded and then knife-milled with a food grinder (DeLonghi S.p.A, 31100 Treviso, Italy) to less than 1 mm in average diameter before further treatment.

Laboratory scale hydrolyses were performed using sealed tubular micro-reactors (150 ml volume). The reactors are constructed from SS-316, due to its strength at elevated temperatures and corrosion resistance.

A 10-l pilot hydrolysis reactor was used for pretreatment of paper tube samples. The heating steam (60 bar) was provided from the combined heat and power plant in Borås.

An ion-exchange Aminex HPX-87P column (Bio-Rad, USA) was used at 85 °C for measuring glucose and xylose concentrations. Ultra-pure water was used as eluent at a flow rate of 0.6 ml/min.

Concentrations of ethanol, furfural and HMF were determined by an Aminex HPX-87H column (Bio-Rad, USA) at 60 °C, using 5mM H_2SO_4 at a flow rate of 0.6 ml/min. A refractive index (RI) detector (Waters 2414, Milipore, Milford, USA) and UV absorbance detector at 210 nm (Waters 2487) were used in series. Furfural and HMF concentrations were analyzed from UV chromatograms, while the rest of the chemicals were quantified with a refractive index (RI) detector.

4 Experimental procedures

All materials were hydrolysed in both laboratory and pilot-scale hydrolysis plants. The resulting substrates (in both cases) were then fermented in bioreactors in the laboratory of Högskolan i Borås (University of Borås).

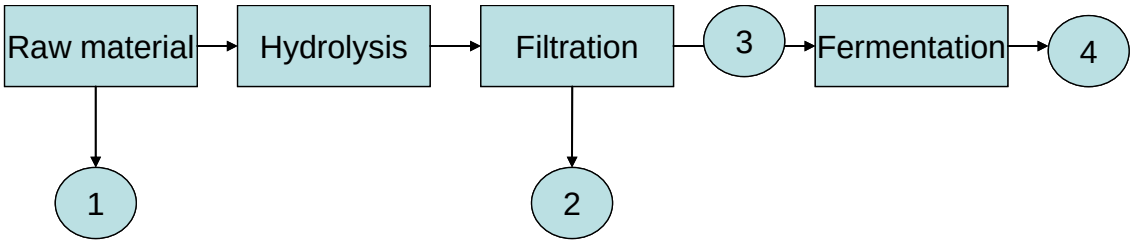


Figure 1. Process with sample points indicated by circles.
Figur 1. Process med provpunkter indikerade med cirklar.

Samples were withdrawn at sample points 1-4 as shown in Figure 1 above and analysed. Analyses were performed to determine:

- **Sample point 1**: Total cellulose content, CHN (Carbon:Hydrogen:Nitrogen) and ash content,
- **Sample point 2**: Solid phases from filtration, cellulose content (total cellulose), CHN, ash and net calorific value,
- **Sample point 3**: Permeate from filtration, sugar content,
- **Sample point 4**: Ethanol content

4.1 Chemical characterization

The two main waste fractions studied, textiles and paper, consists to a large percentage of cellulose and cellulose/lignin/binder respectively. Chemical characterization was performed to quantitatively describe these materials. Characterization was made on both raw materials (Sample Point 1 in Figure 1) and after hydrolysis (Sample Point 2 in Figure 1).

The textile samples from Sobacken were characterized in order to determine the polymer type. Since only cellulose-based materials can be hydrolysed and fermented into ethanol, this information was also used to evaluate the ethanol production potential of the waste materials.

Identification of polymer type in some of the textiles was performed using an infra-red spectrometer coupled to an attenuated total reflection (ATR) module. The spectra were evaluated manually by using reference spectra from a database (Hummel Polymer and Additives).

Determination of carbon, hydrogen and nitrogen were performed using a CHN analyser. CHN data are reported on dry basis, and hydrogen is corrected for the moisture content. Determination of moisture and ash content were performed using a thermo-gravimetric analyser. The samples were stored under ambient conditions, which affect the moisture content. Ash data are reported on a dry basis.

Determinations of net calorific values were performed using a bomb calorimeter. Data are reported on a dry basis, but without correction for sulphur.
Determination of the extractives, cellulose and lignin content were performed using wet chemistry in accordance with ASTM D1105 (water/ethanol/toluene extraction principle) and ASTM D1106 (H_2SO_4 principle) standards. Data are reported on a dry basis, and the cellulose content represents total cellulose content (including hemicellulose).

4.2 Paper tubes

Residues from paper tubes were hydrolysed and fermented in accordance with the process paths shown in Figure 2. They were:

- Enzymatic hydrolysis, with or without pretreatment. Pretreatment consisted of either dilute acid or concentrated phosphoric acid pretreatment.
- Simultaneous saccharification and fermentation (SSF), with or without pre-treatment. Pretreatment consisted of either dilute acid or concentrated phosphoric acid pretreatment.

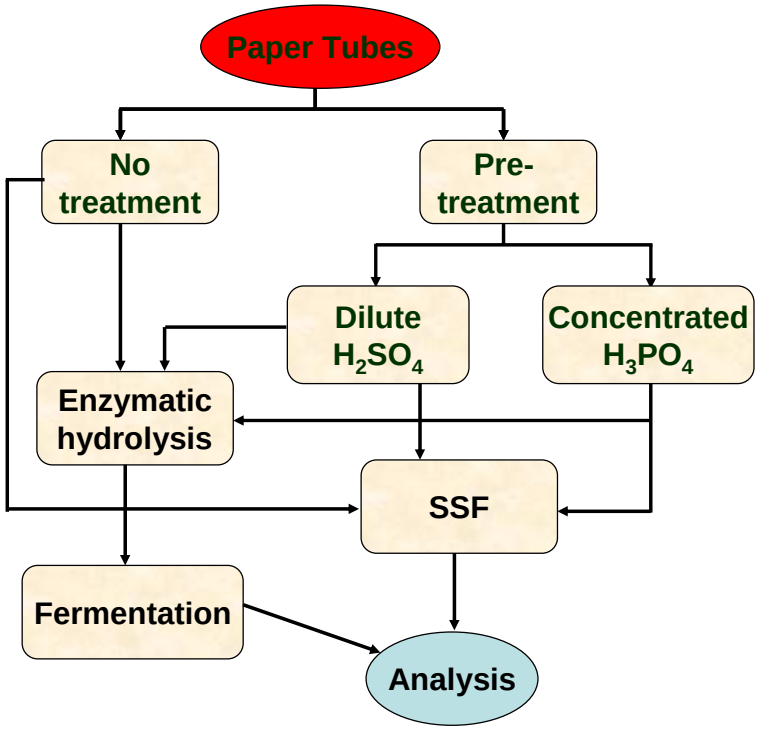


Figure 2. Diagram showing process paths for production of ethanol from paper tubes.
Figur 2. Schema som visar processvägar för produktion av etanol ur pappersrullar.

4.2.1 Pretreatments of paper tubes

4.1.2.1 Pretreatment with dilute sulphur acid (H_2SO_4) at high temperature

In pilot plant tests, steam was directly injected to the pilot plant reactor, which had previously been filled with 1 litre paper/water slurry containing 10 % solid fraction (Figure 3). The reaction variables of temperature, dwell time and acid concentration were varied between 180-200 °C, 10-15 min and 0.5-2 % respectively. The materials were then

discharged explosively to an expansion tank to cool down for further processing, including enzymatic hydrolysis and SSF experiments.

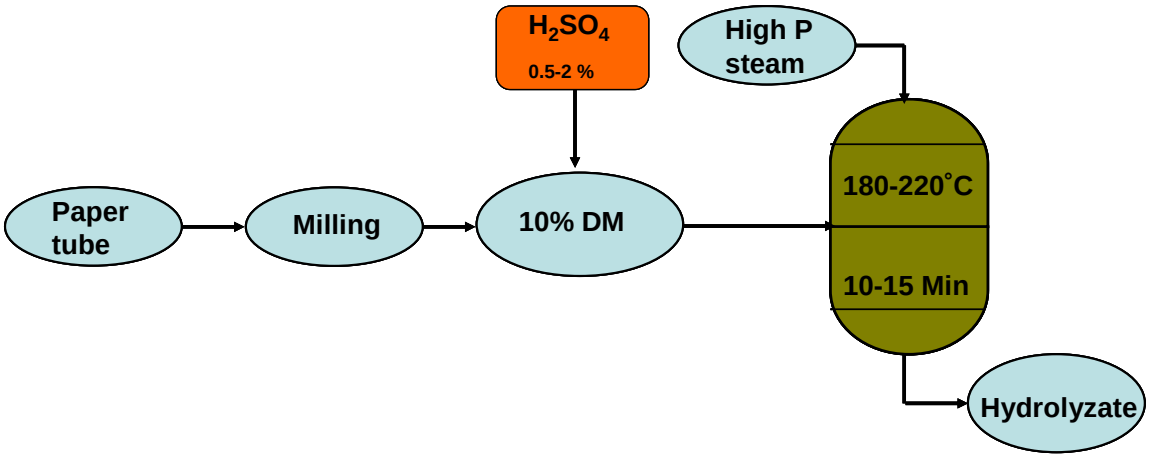


Figure 3. Diagram of acid pre-treatment and hydrolysis using H_2SO_4.
Figur 3. Schema för förbehandling och hydrolys med svavelsyra.

4.1.2.2 Pretreatment with concentrated phosphoric acid (H_3PO_4)

In laboratory-scale tests, 5 g of ground paper tube sample (based on the dry matter) were pretreated with concentrated phosphoric acid, as schematically shown in Figure 4. The samples were treated with 50 ml of H_3PO_4 (85 %) at 50 °C for 1 hour in 100 ml flasks on the rotary shaker bath with a speed of 130 rpm. The treatment was terminated by addition of acetone to the solution, followed by mixing. The mixture was then centrifuged at 4000 rpm for ten minutes, and the precipitate was suspended in acetone and centrifuged. This procedure was repeated three times. The same procedure was then repeated with distilled water. The resulting solid materials were further processed by acid or enzymatic hydrolysis and fermentation.

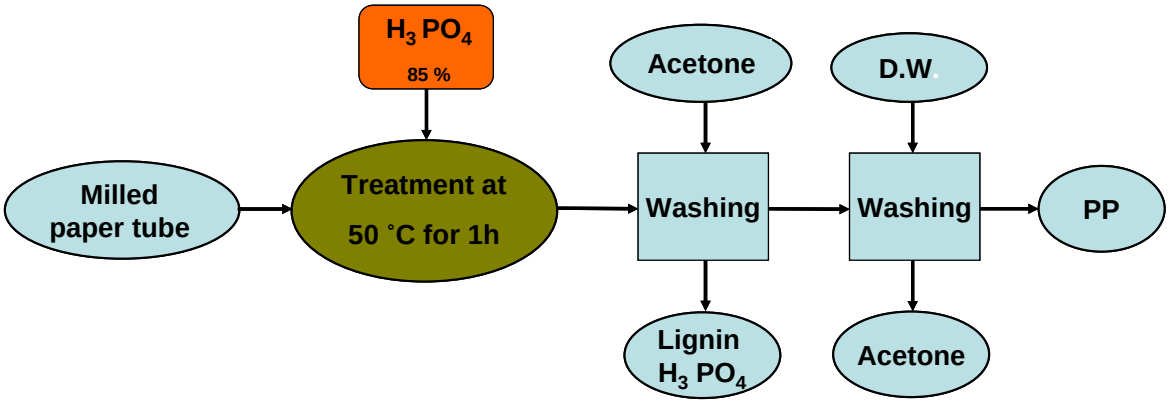


Figure 4. Diagram of acid pre-treatment and hydrolysis of paper tube material by using phosphoric acid (H_3PO_4).
Figur 4. Schema för förbehandling och hydrolys med fosforsyra (H_3PO_4).

4.2.2 Enzymatic and acid hydrolysis

Various samples of paper tubes, both treated and untreated, along with pure cellulose (Avicel), were added into 250 ml conical flasks containing 50 mM sodium citrate buffer at pH 4.8 to obtain 100 ml of milled-paper/water slurry with solid fractions of 5 %. Cellulase and β-glucosidase enzymes were added as 30 FPU and 10 IU per gram of dry matter (g DM) respectively. The slurries were then hydrolysed by the enzymes at 45 °C and 130 rpm for 72 hours in a shaker bath. For the acid hydrolyses, the samples were suspended in distilled water to obtain 100 ml of ground paper/water. The acid concentration was adjusted as 0, 1, and 2% (w/v) respectively. The slurries were then transferred to micro-reactors and heated in an oil bath at various temperatures of 180-220 °C, with residence times between 10-20 min.

4.2.3 Simultaneous Saccharification and Fermentation (SSF)

SSF was performed under anaerobic conditions in a medium similar to synthetic defined medium for yeast cultivation, with the exception that a citrate buffer (50 mM and pH 4.8) was used instead of distilled water. In this set of experiments, untreated and pretreated samples of paper tubes were added to the 250 ml flasks along with a pure cellulose sample (Avicel) with a solid concentration of 5 %. All flasks were autoclaved before the enzymes and yeast *S. cerevisiae* were aseptically added to each flask. The final volume in each flask was 100 ml. All the SSF experiments were performed at 37 °C. The cellulose enzyme loading was 15 or 30 FPU/g DM of sample, while β-glucosidase was added as 10 IU/g DM of sample in all experiments. Pure nitrogen gas was sparged into the media at the beginning of the fermentation and during the sampling to maintain the anaerobic condition. All the experiments were performed in duplicate and reported as an average value.

4.2.4 Toxicity Test of Poly Vinyl Alcohol (PVA)

Poly Vinyl Alcohol, PVA, is used as an adhesive in production of paper tubes. An experiment was carried out to examine the toxicity or inhibition effects of this component on baker's yeast. The yeast *S. cerevisiae* was aerobically cultivated in a defined medium containing 10 (g/l) PVA and the result was compared with that from PVA-free medium.

4.3 Textile materials

Textiles were hydrolysed and fermented according to the process paths shown in Figure 5. They were:

- Enzymatic hydrolysis with or without pre-treatment. Pretreatment consisted of either dilute acid or concentrated phosphoric acid pre-treatment. In the case of textile containing polyester, pre-treatment with alkali followed by fermentation was also carried out.
- Simultaneous saccharification and fermentation (SSF), with or without pre-treatment. Pretreatment consisted of either dilute acid or concentrated phosphoric acid pre-treatment.

Treatment with enzymes resulted in only low yields; and so the textiles were pretreated with an additional step using alkali or concentrated sulphuric acid. These process paths are briefly discussed in this section.

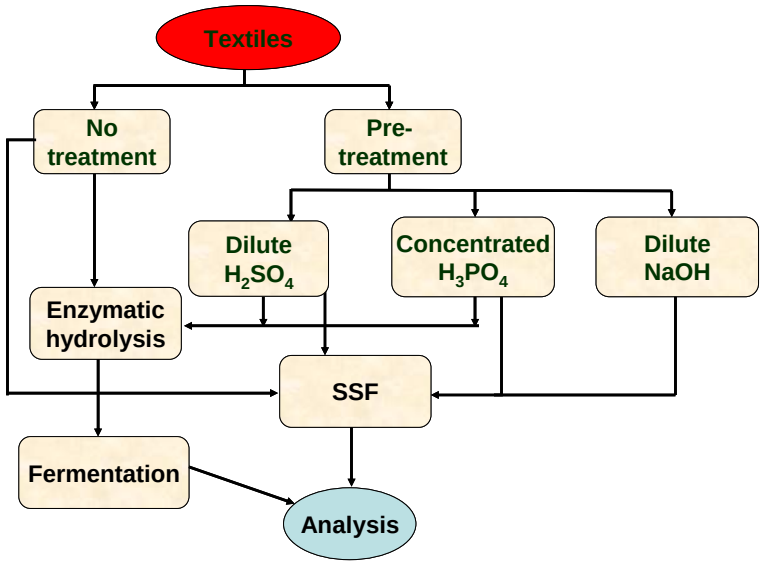


Figure 5. *Diagram showing process paths for production of ethanol from textiles.*
Figur 5. *Schema som visar processvägar för produktion av etanol ur textilier.*

4.3.1 Dilute sulphuric acid hydrolysis

Dilute acid hydrolyses were performed using micro-reactors (150 ml volume). The reactor was loaded with 10 g of solid substrate and 100 ml of an acid solution with a concentration of 0.5 % (w/v) to achieve a solid to liquid ratio of 1:10. The reaction temperatures were controlled in an oil bath that was designed to control the temperature up to 250 °C. When the hydrolysis was completed, the reactor was cooled in an ice bath.

4.3.2 Alkali hydrolysis of polyester textiles

Polyester textiles were hydrolysed using micro-reactors loaded with 10 g of the textiles and 100 ml of a 1 % sodium hydroxide solution. The reaction temperatures were controlled in the oil bath at 240 °C. The hydrolysis experiments were carried out for 30 minutes, followed by cooling the reactors in an ice bath.

4.3.3 Pretreatments of cotton textiles

4.2.3.1 Pretreatment with dilute sulphur acid (H_2SO_4) at high temperature

The jeans textiles were shredded and then ground by a grinder at SP before dilute-acid hydrolysis. In the pilot plant tests, saturated steam was directly injected to the reactor previously loaded with one (1) litre of textile/water slurry containing 10 % solid fraction. The reaction variables of temperature, dwell time and acid concentration were selected as 230 °C, 15 min and 0.5 % respectively. The hydrolysed material was then explosively discharged to an expansion tank, where it was cooled down. It was then filtered and the dried solid materials were used in SSF experiments.

4.2.3.2 Pretreatment with concentrated phosphoric acid (H_3PO_4)

Concentrated phosphoric acid hydrolysis was carried out by mixing 100 ml of 83-85 % phosphoric acid solution with 10 gram of the textiles in a 500 ml bottle, at 50 °C in an oven for 5 h (cf. Figure 4). The solution was mixed every 30 min with a homogenizer. The solution was then filtered and 200 ml of pre-cooled acetone was added to the filtrate to

precipitate the dissolved cellulose. The precipitated solid was then centrifuged, washed with distilled water 10 times, dried at 30 °C and used in SSF experiments.

4.3.4 Simultaneous Saccharification and Fermentation (SSF)

4.2.4.1 Inoculum preparation

The inoculums used for fermentation were prepared using a defined synthetic medium according to Taherzadeh *et al.* [14], in which 50 g/l glucose was used as a carbon and energy source. Volumes of 100 ml medium were autoclaved at 121 °C and inoculated in 250 ml cotton-plugged Erlenmeyer flasks before they were incubated for 24 h at 32 °C and shaken at 140 rpm. At the end of the incubation, the contents of the flasks were aseptically centrifuged and used for SSF. This resulted in inoculation of SSF by 1.0 ± 0.3 g biomass (based on the dry biomass) of *S. cerevisiae* in 100 ml working volume in all the SSF experiments.

4.2.4.2 Simultaneous saccharification and fermentation (SSF)

Ground pretreated or untreated materials were added to 250 ml conical flasks containing 100 ml sodium acetate buffer (50 mM and pH 4.8) with the desired solid fraction. They were then autoclaved and enzyme was added to each flask aseptically. The enzyme loading was 30 FPU cellulase and 30 IU β-glucosidase per gram of cellulose in all experiments. After 48 h cultivation at 45 °C, 10 ml media containing (g/l): yeast extract, 50; $(NH_4)_2SO_4$ 75, KH_2PO_4 35, $MgSO_4.7H_2O$ 7.5, $CaCl_2.2H_2O$ 10, and 1.0 ± 0.3 g (based on the dry biomass) of inoculum *S. cerevisiae,* were added to each flask. The temperature was then adjusted to 37 °C. During hydrolysis at 45 °C the flasks were sealed with cotton plugs, except during the fermentation, where an anaerobic conditions setup was applied. In this setup, a loop-trap containing water allowed the gas to exit but prevented the entrance of air.

The setup also included a needle for sample removal and nitrogen gas sparging to the flasks. Pure nitrogen gas was sparged into the medium at the beginning of the fermentation. During the saccharification and fermentation, the liquid samples from flasks were withdrawn and stored in a freezer.

5 Results

5.1 Chemical characterisation

Identification of the polymers in the textiles show that the white, red and blue samples, sample A, and the filter material, contain some PET material which cannot be hydrolysed into glucose. It would probably be possible to hydrolyse the modified cellulose in the filter material.

Table 4. Identification of the polymers used in several waste textiles sampled at Sobacken.
Tabell 4. Identifiering av polymertyp i några textila avfall. Prov tagna från Sobacken.

Sample description	Polymer type
Sample A	Polyethyleneterephthalate
Filter material	Polyethyleneterephthalate and modified cellulose
White sample	Polyacrylonitril and polyester
Red sample	Cellulose
Blue sample	Polyethyleneterephthalate

Table 5. Carbon, hydrogen, nitrogen and water content in the raw/hydrolysed jeans and paper samples, see Figure 1.
Tabell 5. Kol, väte, kväve och fukthalt i urspungliga/hydrolyserade jeans och pappersmaterial, se Figur 1.

Sample description	C (%)	H (%)	N (%)	Moisture (%)
Jeans (untreated)	45.2	5.9	0.4	4
Jeans (filtrate after hydrolysis)	45.1	5.3	0.2	5
Paper (untreated)	42.6	5.0	0.1	5
Paper (filtrate after hydrolysis)	42.4	4.6	0.1	5

Table 6. Ash, extractives, lignin and total cellulose content in the raw/hydrolysed jeans and paper samples, see Figure 1.
Tabell 6. Askhalt, extraktivämnen, lignin och totalcellulosa i ursprungs- och hydrolyserat jeans och pappersmaterial, se Figur 1.

Sample description	Ash (%)	Extractives (%)	Lignin (%)	Cellulose (%)
Jeans (untreated)	1	-	0	100
Jeans (filtrate after hydrolysis)	1	-	33	67
Paper (untreated)	10	N.D.	7	84
Paper (filtrate after hydrolysis)	10	N.D.	11	80

N.D. None detected

Since no extractives were found in the paper samples, and the ash content is high (10 %), it is probable that the binder in the paper is based on silicate and not on PVA.

Table 7. Net calorific value for the filtrate after hydrolysis, see Figure 1.
Tabell 7. Effektivt värmevärde för filtraten efter hydrolys, se Figur 1.

Sample description	Net calorific value (MJ/kg)
Jeans (filtrate after treatment)	16.9
Paper (filtrate after treatment)	15.5

5.2 Paper tubes

5.2.1 Enzymatic hydrolysis

The carbohydrates content of the paper tubes was determined and the results showed that glucose is the main product of hydrolysed samples, along with minor amount of xylose. Glucose and xylose accounted for 58 (± 2) % and 7 (± 0.7) % of paper tube dry matter respectively. This means that the cellulose content of paper tubes is about 52 (± 2) %. The enzymatic hydrolysis of both treated and untreated samples were carried out under conditions described in 4.2.2. The profile of glucose production for different samples is shown in Figure 6. The rate of reaction for untreated sample was low, and after 72 h only 50 (± 1) % of the theoretical yield of glucose was achieved. Pre-treatment of samples in the steam-explosion reactor increased the rate of enzymatic hydrolysis and led to 67 (± 1) % of theoretical yields for glucose production after 72 h. The best result for enzymatic hydrolysis was from the H_3PO_4-treated sample where the initial rate of reaction was significantly higher than other samples. After 21 h of reaction, the respective glucose concentrations for untreated, H_2SO_4-treated (SP) and H_3PO_4-treated (PP) samples were 8.67, 11.31 and 21.97 (g/l), equal to 30, 39 and 76% of theoretical value. After 72 h, H_3PO_4-treated (PP) samples yielded 93 (± 1) % of theoretical value. The corresponding value for pure cellulose was 72 (± 2) %.

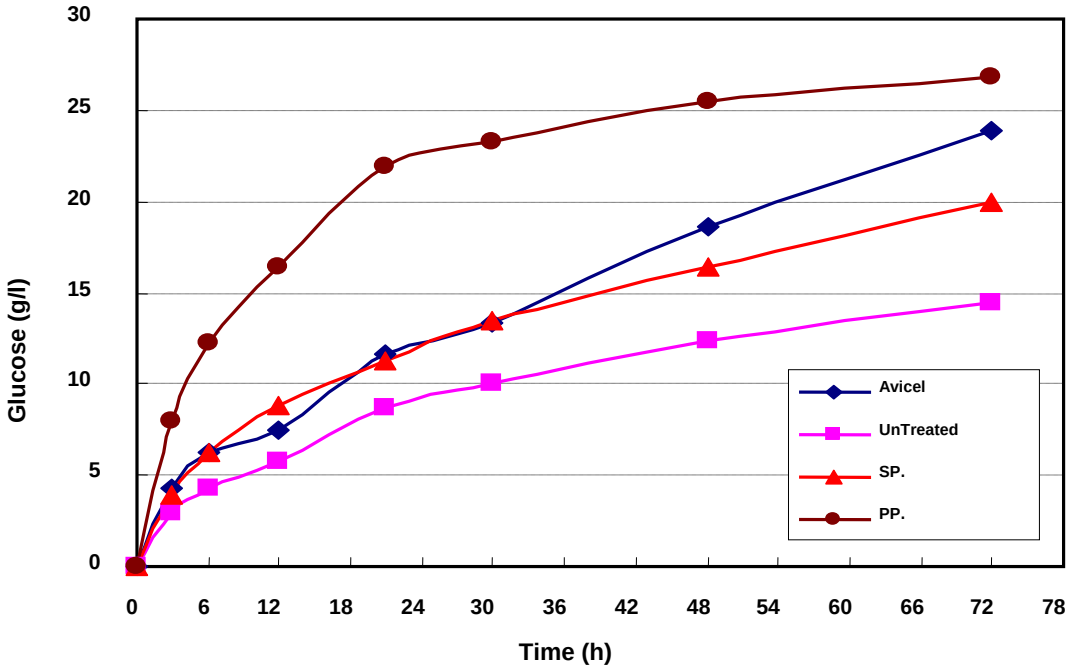


Figure 6. Profiles of glucose production during enzymatic hydrolysis of Avicel and untreated and treated samples of paper tube. Cellulase and β-glucosidase loading were 30FPU and 10IU /g DM respectively. SP stands for H_2SO_4-treated and PP stands for H3PO4-treated samples.
Figur 6. Profiler för glukosprouktion under enymatisk hydrolys av Avicel och obehandlade och behandlade prov av pappersrullar. Cellulas and β-glucosidase satsningar var 30FPU och 10IU/g DM, respektive. Beteckningen SP betyder att provet behandlats med H_2SO_4 och PP betyder behandling med H_3PO_4.

5.2.2 SSF experiments using *S. cerevisiae*

Simultaneous saccharification and fermentation (SSF) of pre-treated and untreated paper tube samples was investigated, and the results were compared with those of pure cellulose (Avicel) as a reference. The anaerobic experiments were carried out under conditions as previously described, and the most important results including the profiles of glucose consumption and ethanol production are summarized in Figure 7. The effect of cellulase enzyme loading was investigated by performing two sets of experiments, where 15 and 30 FPU/g DM was added into the medium. Due to the action of hydrolytic enzymes, the concentration of glucose in the medium in all cases was increased in the early stage of the experiments (within the first 3-6 h). The concentration then declined due to assimilation of glucose by the yeast cells. Overall, a higher cellulose enzyme loading resulted in increased maximum ethanol concentration and enhanced the rate of ethanol production. However, this increase was significantly greater for H_3PO_4-treated (PP) samples. Two-fold increase in loading of cellulase enzyme resulted in 28, 20 and 25 % higher ethanol concentration for untreated, H_2SO_4-treated (SP) and H_3PO_4-treated (PP) samples respectively (Figure 7). When the loading of cellulose enzyme was increased, the production rate and concentration of cellulose, cellobiose and ethanol for the H_3PO_4-treated (PP) sample was substantially higher than the other samples. This fact suggests that this sample is highly susceptible to

enzymatic attack. Pretreatment with H_3PO_4 is therefore the most efficient method used in this work in making the crystalline cellulose accessible to the enzymes.

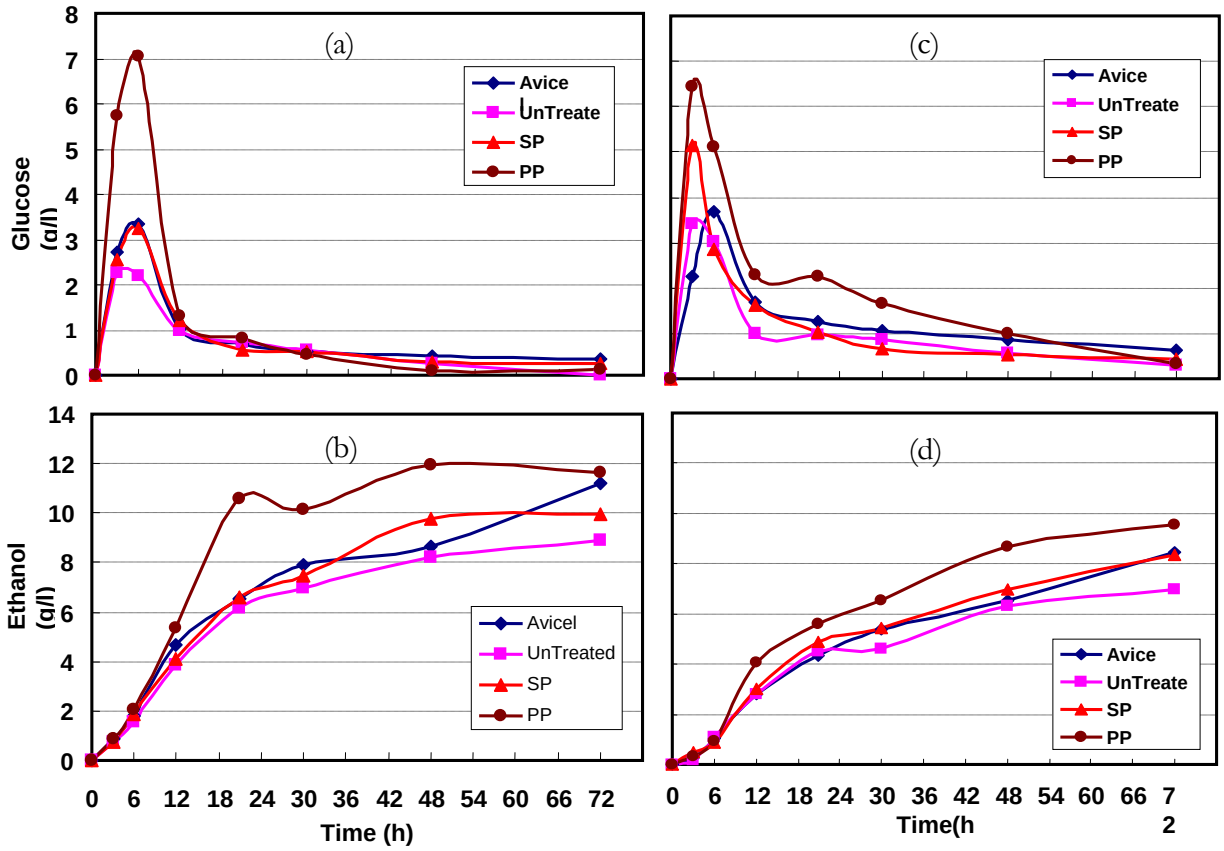


Figure 7. Profiles of glucose (a,c) and ethanol (b,d) concentration during SSF experiments using S. cerevisiae. (a), (b), (c) and (d) represent the following conditions: (a) and (b) with cellulose loading of 30 FPU/g DM, (c) and (d) with cellulose loading of 15 FPU/g DM.
Figur 7. Profiler för glukos- (a,c) respektive etanol- (b,d) koncentration under SSF experiment med S. cerevisiae. (a), (b), (c) och (d) representerar följande förhållanden: (a) och (b) med cellulosa-satsning 30 FPU/g DM, (c) och (d) med cellulosa-satsning 15 FPU/g DM.

The concentration profiles of cellobiose with cellulose loading as 30 FPU/g DM for various samples, shown in Figure 8, are very similar to the profiles of glucose. Both of these sugars are intermediate chemicals in the sequential reactions from cellulose to ethanol. Inspection the profile of these two sugars indicates that, except in the early stage of SSF experiments, where the concentration of glucose is high, the rate of enzymatic hydrolysis controls the overall rate of the reaction.

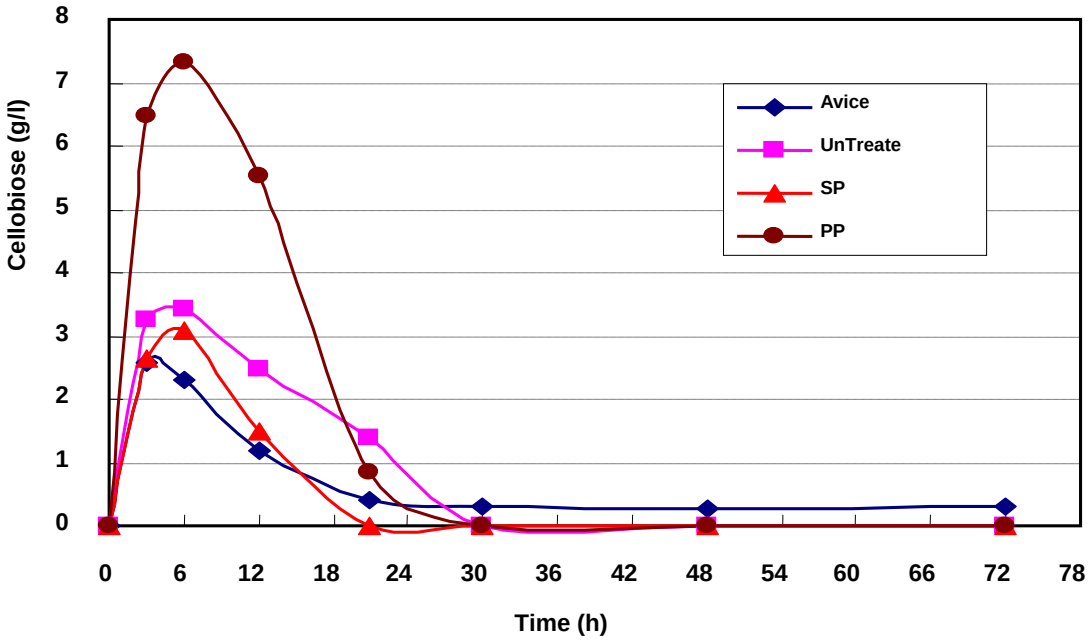


Figure 8. Profiles of cellobiose concentration during SSF of Avicel and untreated and treated samples of paper tube. Cellulase and β-glucosidase loading were 30FPU and 10IU /g DM respectively.
Figur 8. Profiler för cellobias-koncentration under SSF av Avicel och obehandlade och behandlade prov av pappersrullar. Cellulas och β-glucosidas satsningar var 30FPU och 10IU/g DM, respektive.

5.2.3 Dilute-acid hydrolysis

Preliminary experiments on dilute-acid hydrolysis of untreated samples of paper tubes showed that the materials are very resistant and the yield of glucose is very low. The samples of paper tubes that gave the best results in enzymatic hydrolysis and SSF experiments were therefore subjected to dilute-acid hydrolysis using H_2SO_4. A set of hydrolysis tests was carried out at various temperatures, acid concentrations and dwell times. The most important results of dilute-acid hydrolysis are summarized in Table 8. The highest yield of glucose, 57% of the theoretical yield, was obtained at 1 % acid, hydrolysed at 180 °C for 15 min. Hydrolysis at higher temperatures showed a negative effect on liberation of glucose and xylose due to enhancement of decomposition reactions and conversion of sugar to furfural and HMF.

Table 8. Key results from dilute-acid hydrolysis of H_3PO_4 treated (PP) samples
Tabell 8. Nyckelresultat från svagsyrahydrolys av H_3PO_4-behandlade (PP) prov.

Spec.(Time-T-Acid) (min / °C / %)	Glucose (g/l)	Furfural (g/l)	HMF (g/l)	Xylose (g/l)	YGlu (%)
20 / 200 / 1	7.90	0.53	0.88	0.42	28
10 / 220 / 0.5	11.95	0.63	1.45	0.47	42
15 / 180 / 2	15.69	0.26	0.71	1.02	55
15 / 180 / 1	16.22	0.24	0.61	1.15	57

5.2.4 Effect of polyvinyl alcohol (PVA)

Approximately 10 % of the paper tubes consist of either sodium silicate or PVA. PVA is an organic substance that could hamper fermentation, and so the effect of this adhesive on yeast cultivation was investigated. The profiles of glucose consumption and ethanol production in fermentation with or without the presence of PVA are shown in Figure 9.

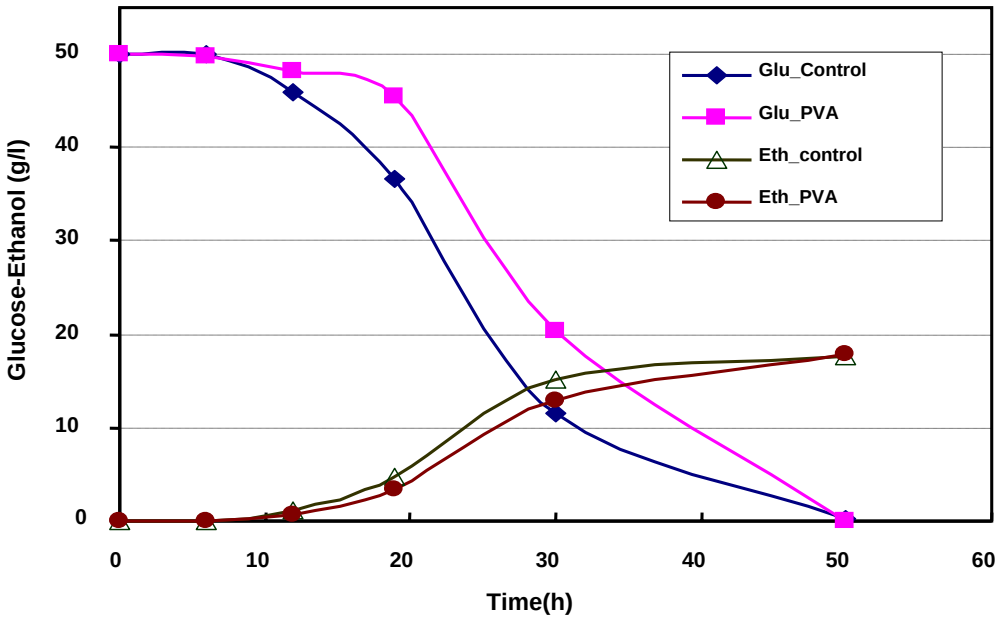


Figure 9. Profiles of ethanol production and glucose consumption in batch cultivation of yeast S.cerevisiae in synthetic defined medium with and without the presence of PVA.

Figur 9. Profiler över etanolproduktion och glukoskonsumption i batchodling av S.cerevisiae i syntetiskt definierat medium, med och utan tillsats av PVA.

The experiments showed no affect of the PVA additives on the ethanol yields. The only notable affect was an extension of the lag phase in the growth of yeast cells. This can be overcome by adaptation of cells, or increased cell concentration in the medium.

5.3 Textile materials

5.3.1 Cellulose content of raw materials

The cellulose content of textiles was determined using concentrated sulphuric acid, and the results are presented in Table 9. The cellulose content of the white and red samples (white sample is a residue from furniture manufacturing, and red sample is a textile filter, see also Section 3.2) was negligible, while the jeans and viscose were approximately pure cotton (cellulose). Since the goal of this work was ethanol production, which is possible from cellulosic material, the experiments were continued with jeans and viscose materials.

Table 9. Cellulose content of various textiles samples, measured by the NREL method
Tabell 9. Cellulosainnehåll i olika textilprov, uppmätt med NREL-metoden.

Sample	Cellulose content (%)
Jeans	97
Cotton	99
Viscose	99
White sample	0
Red sample	0

5.3.2 Dilute sulphuric acid hydrolysis

Pure cotton material was chosen as a reference sample of cellulosic textiles to study the effect of time and temperature on dilute acid hydrolysis. The results are shown in Tabell 8Table 8. By increasing the temperature to 220 °C, glucose yield reached about 18 % of the theoretical yield, and were the best results obtained in this process. Several hypothesized boundary layer resistances such as structured water viscosity and re-hydrogen bonding of released glucose have been suggested as the diffusion resistance for released glucose to the bulk medium, which might be the reason for this low yield in dilute-acid hydrolysis of the cotton. On the other hand, the cotton has a higher crystallinity than the cellulose present in lignocellulose materials, and it is more difficult to break down its structure by dilute acid hydrolysis.

Table 10. Effect of time and temperature on glucose yield in dilute sulphuric acid hydrolysis of cotton (acid concentration = 0.5 % (w/v), acid: solid (v: w) = 4:1)
Tabell 10. Effekt av tid och temperatur på glukosutbyte vid svagsyrahydrolys av bomull (syrakoncentration= 0.5 % (w/v), syra: fastmaterial (v: w) = 4:1)

Temp. (°C)	Time (min)	Glucose conc. (g/l)	Glucose yield (%)
220	10	40.65	18.29
210	10	35.26	15.87
200	15	39.10	17.60
200	10	30.16	13.57
190	10	12.77	5.75
180	15	17.50	7.87
170	15	11.07	4.98

5.3.3 Effect of various pretreatment on enzymatic hydrolysis

The current leading lignocelluose pretreatments - for example, dilute acid, ammonia fibre explosion, lime and steam explosion - cannot efficiently disrupt orderly hydrogen bonds among glucan chains in crystalline cellulose and result in slow hydrolysis rates and low cellulose digestibility. Pretreatment with concentrated phosphoric acid results in breaking down hydrogen bonds between cellulose chains in microfibrils, and the regenerated amorphous cellulose has a high reactivity. This process consists of two steps. In the first

step, concentrated H_3PO_4 is used to dissolve cellulose fibrils and break up orderly hydrogen bonds among cellulose chains. In the second step, acetone is added to precipitate the dissolved cellulose. On the other hand, synthetic fibres might not be soluble in these conditions, and it is possible to separate cellulosic part of textiles.

Dilute acid steam explosion and pretreatment with concentrated H_3PO_4 have been chosen in this work to study the effect of pretreatment on enzymatic hydrolysis and ethanol production of cellulosic textiles. The results of enzymatic hydrolysis and ethanol production of both treated and untreated samples, carried out under conditions as previously described, are shown in Figure 10. The solids percentage in these experiments was 3 %. It can be seen from the figure that after 48 h of enzymatic hydrolysis without fermentation, H_3PO_4-treated and dilute acid-treated jeans samples have higher yields than untreated jeans.

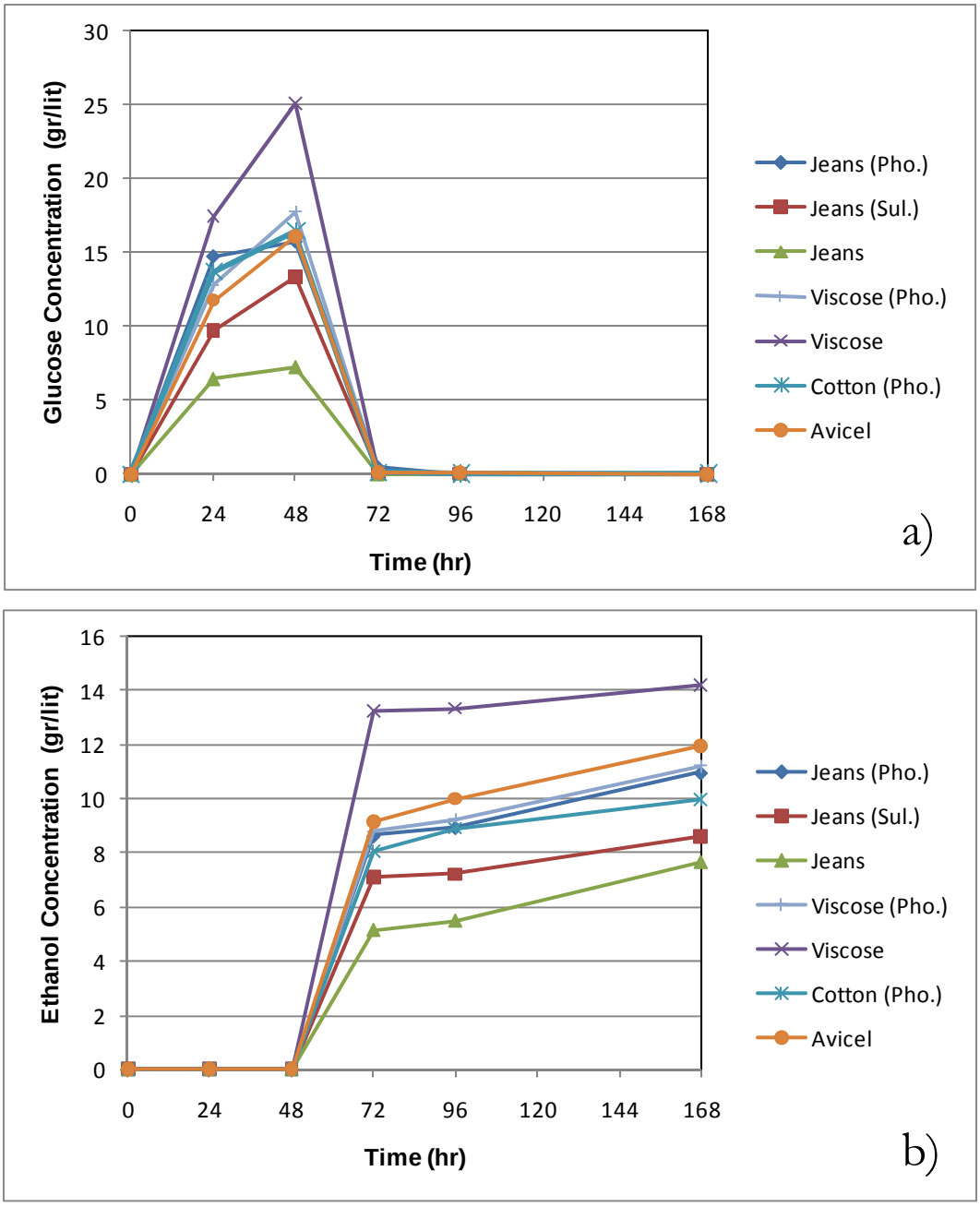


Figure 10. a. Glucose and b. ethanol concentration during SSF of various pre-treated jeans textiles, (enzyme loading= 30 FPU cellulase and 30 IU β-glucosidase per g cellulose, solid percent= 3 %).
Figur 10. a. Glukos- och b. etanolkoncentration under SSF av olika förbehandlade jeanstextilier, (enzymsatsning = 30 FPU cellulas och 30 IU β-glucosidas per g cellulosa, fastandel = 3%).

However, on the 5th day of the SSF, the concentration of ethanol from untreated and dilute-acid-treated jeans is around 8 g/l, and significantly lower than that for the H_3PO_4-treated sample. This means that dilute-acid treatment could increase the rate of digestibility of cellulose but cannot increase the yield of hydrolysis.

The profiles in Figure 10 shows that the rate of enzymatic hydrolysis and ethanol production for pretreated jeans, cotton and viscose samples with H_3PO_4 are approximately the same. By the 5th day of the SSF process, the untreated jeans have the lower ethanol yield (0.24 g/g DM), and untreated viscose has the higher yield (0.45 g/g DM) (Figure 10).

The effect of treatment with H_3PO_4 on viscose textiles was opposite to the effect of that on jeans. H_3PO_4 treatment in this case decreased the yield of glucose from 0.75 to 0.53, and the yield of ethanol on the 5th day of fermentation decreased from 0.45 to 0.35 (Figure 11). Viscose textiles did not need to be pretreated by enzymatic hydrolysis, and with no pretreatment it was possible to obtain about 87.7 % of the theoretical ethanol yield (Figure 11). Viscose is formed by dissolving raw cellulose in carbon disulphide and sodium hydroxide to produce a highly viscous liquid. Continuous cellulose filaments are then precipitated by extrusion of this fluid into sulphuric acid followed by zinc sulphate. During this process the crystallinity and degree of polymerization of the cellulose is decreased, and these are the goals of treatment of the cellulosic materials before enzymatic hydrolysis.

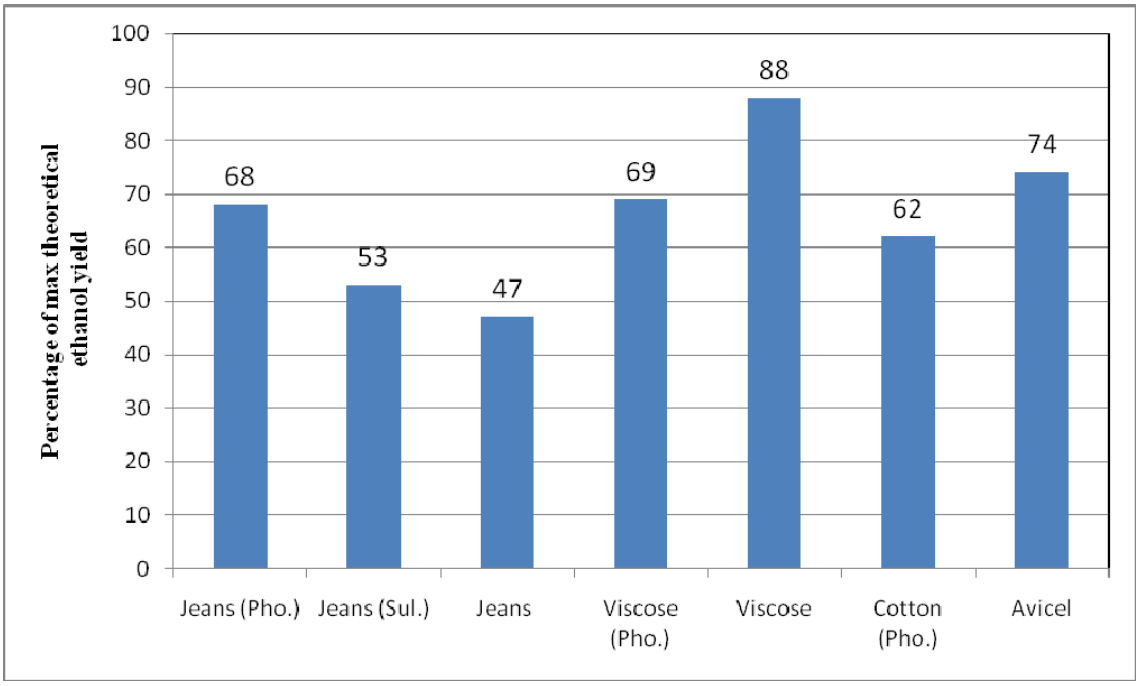


Figure 11. Percentage of maximum theoretical ethanol yield in simultaneous saccharification and fermentation (SSF) of various pre-treated and untreated textiles. (Percentage of maximum theoretical ethanol yield = [max produced ethanol (g/l)]/[0.51×1.111×dry weight of substrate (g/l)]×100).
Figur 11. Andel av maximal teoretiskt etanolutbyte vid SSF av olika obehandlade och förbehandlade textilier. (Andel av maximalt teoretiskt etanolutbyte = [max producerad etanol (g/l)]/[0.51×1.111×torrvikt av substrat (g/l)]×100)

The effect of increasing solids percentages in SSF process was studied. The results are shown in Table 11. Increasing the solids content from 3 % to 5 % reduced the yield of ethanol from untreated viscose from 0.45 to 0.43 g/g DM, while that from H_3PO_4- treated jeans was decreased from 0.35 to 0.27 g/g DM.

Table 11. Glucose and ethanol concentration during SSF of pre-treated jeans and untreated viscose with higher solid percent, (enzyme loading= 30 FPU cellulase and 30 IU β-glucosidase per g cellulose, solid percent= 5%)
Tabell 11. Glukos- och etanolkoncentration under SSF av förbehandlat jeanstyg och obehandlad viskos vid högre andel fast material , (enzyme-satsning= 30 FPU cellulase och 30 IU β-glucosidas per g cellulosa, fast-andel = 5%)

Sample	Time (h)	Concentration (g/l)		Yield (g/g)		% of theoretical ethanol yield
		Glucose	Ethanol	Glucose	Ethanol	
Untreated viscose	0	0.00	-	0.00	-	-
	24	31.56	-	0.57	-	-
	48	31.90	-	0.57	-	-
	72	0.15	17.48	-	0.33	64.85
	96	0.16	21.86	-	0.41	81.10
	168	0.00	22.77	-	0.43	84.48
H3PO4-treated jeans	0	0.00	-	0.00	-	-
	24	27.20	-	0.49	-	-
	48	34.32	-	0.62	-	-
	72	0.30	12.73	-	0.24	47.24
	96	0.03	13.06	-	0.25	48.45
	168	0.01	14.30	-	0.27	53.03

5.3.4 Alkali hydrolysis of polyester textiles

Some preliminary experiments on polyester fibres were carried out. The results show that it is possible to hydrolyse polyester fibres with dilute sodium hydroxide solution at high temperature. The reaction variables of temperature, dwell time and base concentration were selected as 240 °C, 30 min and 1 % respectively. In this condition, about 60 % of initial fibres were dissolved, and the remaining solid was a fine powder. Analysis of the hydrolysed solution with HPLC shows an unidentified component in the solution (Figure 12), which needs further investigation.

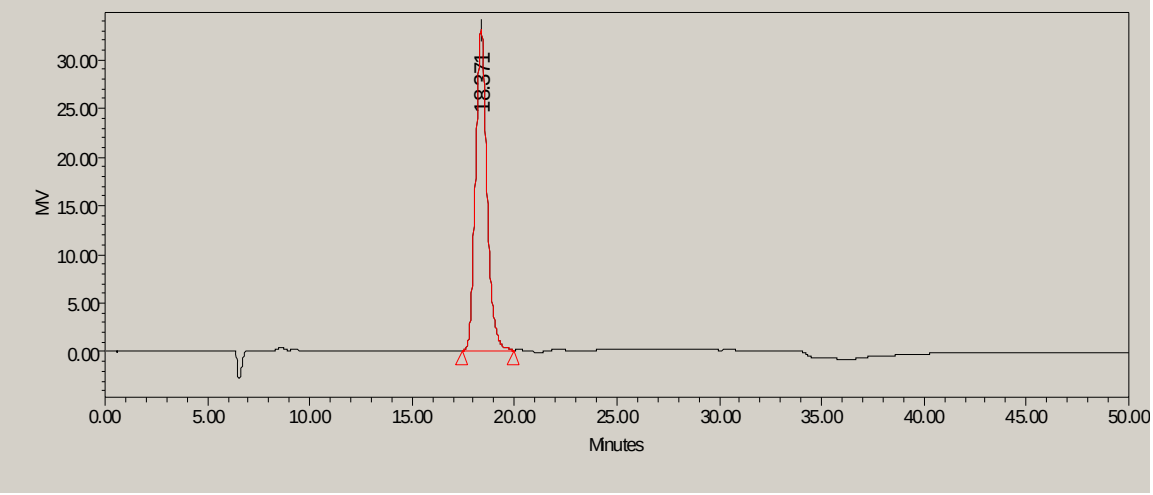


Figure 12. HPLC analysis with RI detector on the liquid resulting from alkali hydrolysis of polyester textiles.

Figur 12. HPLC-analys med RI-detektor av vätskan från alkalisk hydrolys av polyestertextil.

6 Discussion

6.1 Paper tubes

The analysed samples of paper tubes were composed of approximately 65 % glucose and xylose as two monomeric sugars present in the samples. These two sugars can be used by appropriate microorganisms and converted into ethanol. In the current work, however, xylose could not be consumed by the applied yeast and so all calculation was based on the theoretical value of glucose. Based on the results obtained during the current work, waste paper tube is shown to be a potential raw material for production of ethanol. The most important results from enzymatic hydrolysis and SSF experiments are summarised in Table 12. Pretreatment of samples, as well as increased cellulase loading, improves the yield of ethanol. The best result was found with the H_3PO_4-treated samples (PP), with a cellulase load of 30 FPU/g DM resulting in 0.42 (g/g glucose) of ethanol yield, equal to 82 % of theoretical value.

Table 12. Yields of glucose from enzymatic hydrolysis and ethanol from SSF of Avicel, untreated and treated samples of paper tubes.
Tabell 12. Utbyte från enzymatisk hydrolys och etanol från SSF av Avicel, obehandlad och behandlade prover av pappersrullar.

SAMPLES	Enzymatic hydrolysis	SSF-15 FPU/g DM glucose	SSF-30 FPU/g DM glucose
	YGlu (%)	YEth (g/g)	YEth (g/g)
Pure cellulose (Avicel)	72	0.19	0.34
Untreated (Unt.)	50	0.24	0.31
H_2SO_4-treated (SP.)	67	0.29	0.35
H_3PO_4-treated (PP.)	93	0.34	0.42

It is sometimes more convenient to present the results based on the dry matter of the sample: for example, how much glucose could be attained from 100 g of paper tube sample. Such results can be found in Table 13. Within the experiment time applied in this work, the maximum attainable glucose from 100 g paper tube sample was 54 g, obtained from H_3PO_4 pre-treated sample. The corresponding values for untreated and H_2SO_4 pretreated samples (SP) were 29 and 39 g respectively. The maximum ethanol produced from 100 g of waste paper tube sample was 24 g, which was achieved through phosphorus acid pre-treated sample with 30 FPU/g DM loading in the SSF process.

Table 13. Yields of glucose from enzymatic hydrolysis and ethanol from SSF of Avicel, untreated and treated samples of paper tubes. All yields were calculated based on the dry matter of the raw material.
Tabell 13. Utbyte av glukos från enzymatisk hydrolys och etanolutbyte från SSF av Avicel, obehandlad och behandlade prover av pappersrullar. Alla utbyten är beräknade på torrvikten av råvaran.

SAMPLES	Enz. hydrolysis	SSF-15 FPU/g DM	SSF-30 FPU/g DM
	YGlu(%)	YEth (g/g DM)	YEth (g/g DM)
Untreated (Unt.)	29	0.14	0.18
H_2SO_4-treated (SP)	39	0.17	0.20
H_3PO_4-treated (PP)	54	0.19	0.24

6.2 Textiles

There are two groups of cellulosic textiles from which it is possible to produce ethanol: those based on cotton fibres, and those based on synthetic fibres. In this work, jeans textile was chosen as a cotton sample and viscose textile as a synthetic sample. The summaries of final results are shown in Table 14.

Because of the high crystalline structure of cotton, dilute-acid hydrolysis is not a good choice for hydrolysis of cotton. With enzymatic hydrolysis of this kind of cellulose material, without any pre-treatment, it is possible to obtain 27 gram of ethanol per 100 gram of cotton. The best result for this material was 38 gram of ethanol. That is the result of pre-treatment by concentrated phosphoric acid.

Viscose fibres were found to be a suitable material for ethanol production, delivering 50 gram of ethanol from 100 gram of viscose fibre without any pretreatment. No significant change in the results was obtained when the solid content increased to 5 %.

It is important to note that the glucose resulting from saccharification was successfully converted to ethanol by *S. cerevisiae*, and that pigments and other impurities in the textile did not affect the hydrolysis and fermentation process.

The preliminary experiments on polyester fibres show that it is possible to hydrolyse this kind of materials.

Table 14. Yield of ethanol from simultaneous saccharification and fermentation (SSF) of various pre-treated and non-treated textiles.
Tabell 14. Utbyte av etanol från SSF av olika förbehandlade och obehandlade textilprover

SAMPLES	SSF – 3% solid	SSF – 5% solid
	YEth (g/g fibres)	YEth (g/g fibres)
Phosphoric acid treated jeans	0.38	0.30
Dilute sulf. acid treated jeans	0.30	-
Untreated jeans	0.27	-
Phosphoric acid treated viscose	0.39	-
Untreated viscose	0.50	0.48
Phosphoric acid treated cotton	0.35	-

7 Conclusions

It has been shown in this project that:

- Both textiles and paper tubes of the qualities used in this project can be hydrolysed and fermented into ethanol.
- The conversion ratio is about 20-25 % based on dry material for the paper tubes, and 30-40 % for the some of the textiles (jeans) in the textiles group.
- No unwanted side reactions (production of inhibitors) occurred that affected the yields significantly.
- Optimum reaction times and temperatures for the dilute-acid hydrolyses step are in the range 15 min and 180-200 °C respectively in the pilot tests.

The tests have shown that it is possible to use both paper tubes and cotton textiles for ethanol production.

Residues from the fermentation could possibly be dewatered and used for further energy recovery either by combustion or by an anaerobic biogas process.

8 Recommendations and use

The laboratory-scale results showed that, depending on the raw material, between 20-40 % ethanol by weight (based on the raw material) could be produced from the wastes.

Large-scale experiment should be carried out to study the performance in a further scaled-up process.

In order to find the true potential for textile material as a raw material for ethanol production, a thorough investigation should be made to establish the amount of waste textiles available in the society, as well as the content of different textiles within the material flow.

Optimisation of the hydrolysis and fermentation steps could proceed by tuning process parameters.

More waste fractions should be studied for their potential as raw material for ethanol production.

There is a quite large fraction of organic residues left after hydrolysis and ethanol fermentation. Work is needed to investigate how these residues could be used for (for example) biogas production.

In order to make the fermentation step industrially viable, the fermentation time must be reduced. Högskolan in Borås is making interesting tests that could improve the fermentation time, by using encapsulated yeast strains.

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Appendix A. Photos of materials and procedures

A.1 Paper tubes

Figure 13. Photos showing the variety of paper tube waste. The paper tubes are manufactured in dimensions of 8-411 mm diameter and with varying thickness. Generally, they consist of about 10% glue (PVA or Sodium Silicate and clay), and 90% recycled paper.
Figur 13. Foton som visar pappersrullar av olika dimensioner. Rullarna tillverkas i diametrar mellan 8 – 411 mm, och med varierande tjocklek. Generellt innehåller rullarna 10% lim och 90% återvunnet papper.

A.2 Textiles

Figure 14. 1. The raw material is prepared by cutting it into small fragments.
Figur 14. 1. Råvaran prepareras genom att klippas till små fragment.

Figure 15. 2. Concentrated phosphoric acid (85 % H_3PO_4) is added. The mixture is homogenised every 30 min for 4 hours. Temperature is 50 °C.
Figur 15. 2. Koncentrerad fofsforsyra adderas och provet homogeniseras var 30:e minut under 4 timmar vid 50°C.

Figure 16. 3. Filtration of the mixture
Figur 16. 3. Filtrering av blandningen.

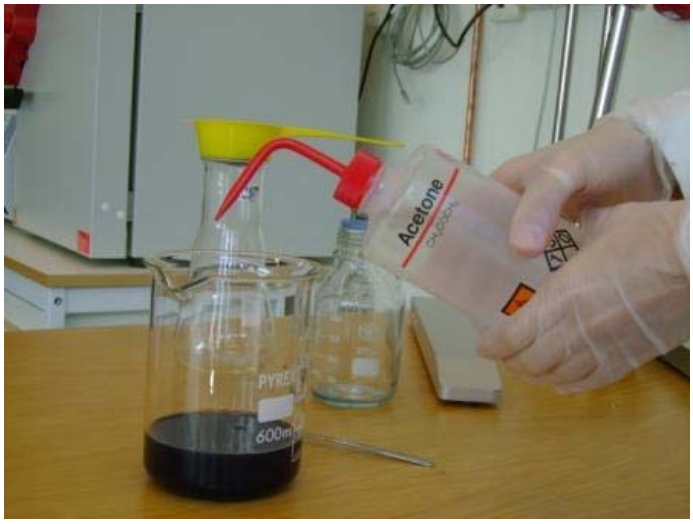

Figure 17. 4. Acetone is added to precipitate the cellulose in the solution.
Figur 17. 4. Aceton tillsätts för att fälla ut cellulosan I lösningen.

Figure 18. 5. Settling of the precipitate.
Figur 18. 5. Fällningen separeras.

Figure 19. 6. Filtration.
Figur 19. 6. Filtrering.

Figure 20. 7. Washing the celloulose.
Figur 20. 7. Tvättning av cellulosan.

Figure 21. 8. Washed cellulose.
Figur 21. 8. Tvättad cellulosa.

Figure 22. "White sample", a kind of rextile used in furniture manufacturing.
Figur 22. Vitt prov, en sorts textil som används vid möbeltillverkning.

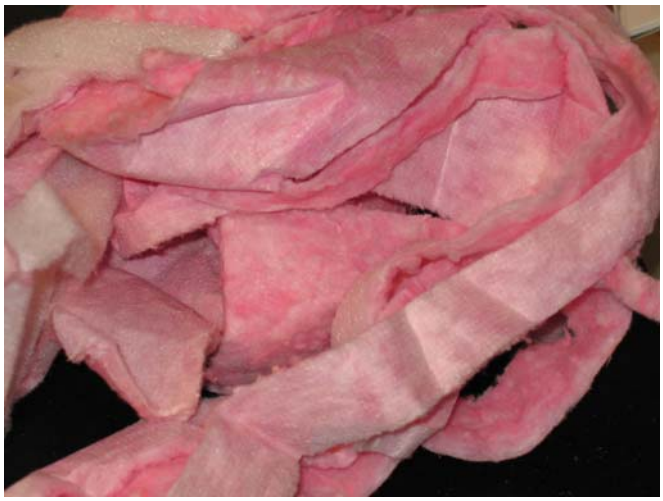

Figure 23. "Red sample", a sort of textile filter media.
Figur 23. Rött prov, ett sorts filtermedium.

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