

f3 2016:02

# FLEXIBILITY IN ETHANOL BASED LIGNOCELLULOSE BIOREFINERIES: A KNOWLEDGE SYNTHESIS

Report from an f3 project

February 2016



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### PREFACE

This report is the result of a collaborative project within the Swedish Knowledge Centre for Renewable Transportation Fuels (f3). f3 is a networking organization, which focuses on development of environmentally, economically and socially sustainable renewable fuels, and

- Provides a broad, scientifically based and trustworthy source of knowledge for industry, governments and public authorities,
- Carries through system oriented research related to the entire renewable fuels value chain,
- Acts as national platform stimulating interaction nationally and internationally.

f3 partners include Sweden's most active universities and research institutes within the field, as well as a broad range of industry companies with high relevance. f3 has no political agenda and does not conduct lobbying activities for specific fuels or systems, nor for the f3 partners' respective areas of interest.

The f3 centre is financed jointly by the centre partners, the Swedish Energy Agency and the region of Västra Götaland. f3 also receives funding from Vinnova (Sweden's innovation agency) as a Swedish advocacy platform towards Horizon 2020. Chalmers Industriteknik (CIT) functions as the host of the f3 organization (see <a href="https://www.f3centre.se">www.f3centre.se</a>).

#### This report shoud be cited as:

Fornell, R., Willquist, K., Alriksson, B. & Kalmendal, R. (2016) *Flexibility in ethanol based lignocellulose biorefineries: A knowledge synthesis.* Report No 2016:02, f3 The Swedish Knowledge Centre for Renewable Transportation Fuels, Sweden. Available at <u>www.f3centre.se</u>.

### SUMMARY

This report is a knowledge synthesis addressing flexibility in ethanol based biorefinery processes using lignocellulosic feedstocks from the Swedish forestry and agricultural sectors. The flexibility of biorefinery operations is important as it determines their capacity to respond to fluctuations in feedstock supply and market demands. Here, the flexibility of feedstocks, processes, volumes and products, referred to as manufacturing flexibility, is reviewed. Particular emphasis has been given feedstock and product flexibility.

In Sweden, the forestry feedstocks spruce, pine and birch stemwood are more abundant and display less variation in chemical composition and supply over the year compared to the common agricultural feedstocks, thus facilitating flexibility in their use. Similarities in chemical composition between wheat straw, maize stover and reed canary grass make these raw materials possibly interchangeable, but differences in their local availability may limit alternating uses.

Preprocessing and pretreatment of feedstocks largely influence the prerequisites for manufacturing flexibility in subsequent process steps. A high degree of manufacturing flexibility is achievable using appropriate designs of thermochemical pretreatments. The pulping pretreatment method may increase product flexibility due to the possibilities to fractionate the biomass. Promising alternative pretreatment methods exist, but few have been realized commercially.

Other means to increase manufacturing flexibility in biorefineries include the design of hydrolysis and fermentation mode, the choice of microorganisms, and process configuration. Today, although lignocellulosic feedstocks are used in large scale second generation ethanol plants, the potential of manufacturing flexibility has not been fully exploited.

Increasing the product flexibility of a biorefinery is one means of reducing the risks associated with uncertainties in the future biofuel demand. Biofuels other than ethanol are e.g. butanol, hydrogen and biogas. The production of butanol allows for a larger fraction of the biomass to be conversed, but requires a different process design from that of ethanol and further development of some technical aspects. Microbial hydrogen production displays similar advantages and disadvantages to those of butanol, but further research is needed prior to commercialization. Integration of biogas production with that of ethanol from lignocellulosic materials may increase the flexibility of feed-stocks, volumes and products, more or less irrespective of which process design is chosen.

A number of non-fuel products can be generated in a flexible biorefinery and there is future market potential in e.g. polyhydroxyalkanoates, lactic acid and other organic acids. Further, single cell proteins may be produced with a number of microorganisms, using lignocellulosic sugars, simple nutrients and equipment similar to that of second generation ethanol plants.

It is concluded that a vast number of options to increase manufacturing flexibility in biorefinery operations exist. Although the present report does not include assessments of these options from a techno-economical perspective, it is indispensable that such analyses are made in conjunction with a scrutiny of the effects on the production as a whole, and the interdependency of the different processing steps in relation to the prerequisites of each biorefinery facility.

Abbreviations used	
ABE	Acetone, butanol and ethanol (fermentation)
BALI	Borregaard Advanced Lignin
COD	Chemical oxygen demand
DM	Dry matter
GRAS	Generally regards as safe
PLA	Polylactic acid
TRL	Technology readiness level
USAB	Upflow anaerobic blanket

### SAMMANFATTNING

Den här rapporten är en kunskapssyntes av forskning och erfarenheter kring flexibilitet i bioraffinaderiprocesser baserade på etanolproduktion från svenska skogs- och lantbruksråvaror med högt innehåll av lignocellulosa. En hög flexibilitet ger utrymme att kontinuerligt anpassa processen till fluktuationer i tillgång på råvaror och efterfrågan av produkter på marknaden. Rapporten belyser olika aspekter av flexibilitet med avseende på råvaror, produktionsprocesser, produktionsvolym och produkter; här sammanfattat som tillverkningsflexibilitet. Särskilt fokus har lagts vid råvaru- och produktflexibilitet.

I Sverige är volymerna av massaved från gran, tall och björk, större och varierar mindre över tid samt i kemisk sammansättning, jämfört med vanliga jordbruksråvaror. Dessa faktorer ökar möjligheterna till tillverkningsflexibilitet i bioraffinariderier med skogsråvara. Likheter i kemisk sammansättning mellan vetehalm, rörflen och skörderester från majs gör dessa råvaror potentiellt utbytbara, men den geografiska spridningen i landet kan utgöra ett praktiskt hinder.

Tekniken vid mottagning och förbehandling av råvaror har stor inverkan på förutsättningarna för tillverkningsflexibilitet senare i processen. Termokemiska förbehandlingsmetoder anpassade till aktuella råvaror och processer ger en hög grad av tillverkningsflexibilitet. Möjligheter att fraktionera biomassan genom massakokning kan påverka produktflexibiliteten positivt. Lovande alternativa förbehandlingsmetoder finns, men få har hittills fått kommersiell spridning.

Olika aspekter av tillverkningsflexibilitet kan bland annat tillämpas på val av hydrolysmetod, jäsningsteknik, mikroorganismer och processutförande. Medan det idag produceras andra generationens etanol med råvaror rika på lignocellulosa i stor skala, är potentialen med ökad tillverkningsflexibilitet relativt outnyttjad.

Att öka flexibiliteten i vilka produkter som produceras är ett sätt att minska riskerna kopplade till osäkerheter kring efterfrågan av biobränslen i framtiden. Exempel på alternativa biobränslen till etanol är butanol, vätgas och biogas. Produktion av butanol möjliggör omvandling av en större del av biomassan till biobränsle, men processen kräver en särskild design samt ytterligare utveckling av vissa tekniska aspekter. Mikrobiell vätgasproduktion uppvisar för- och nackdelar liknande de kopplade till butanolproduktion, och mer forskning behövs innan tekniken kan bli kommersiellt gångbar. Mer eller mindre oberoende vilka processer som används i en etanolfabrik, kan tillverkningsflexibiliteten öka om biogasproduktion integreras i processflödet.

Utöver biobränslen kan ett flexibelt bioraffinaderi generera ett antal produkter med framtida marknadspotential. Exempelvis kan polyhydroxyalkanoat, mjölksyra och andra organiska syror tillverkas med ett antal mikroorganismer. Flera mikroorganismer kan även odlas för att producera protein med hjälp av socker framställt ur råvaror rika på lignocellulosa, enkla näringsämnen och processutrustning liknande den som används i andra generationens etanolfabriker.

Sammantaget är möjligheterna att öka tillverkningsflexibiliteten i bioraffinaderier många. Även om denna rapport inte inkluderar tekno-ekonomiska analyser, är dessa nödvändiga tillsammans med en genomgripande förståelse för, och anläggningsspecifika analyser av, hur de olika stegen i processen påverkar varandra och produktionen som helhet.

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## 1 INTRODUCTION

#### 1.1 WHAT IS A BIOREFINERY?

The term 'biorefinery' is a relatively new, and the interpretations thereof vary slightly. According to the International Energy Agency (IEA Bioenergy Task 42 Biorefinery Report) a biorefinery can be defined as:

"...the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)."

While the IEA definition is very general, there are several different ways to classify biorefineries in more detail. Sandén & Pettersson (2014) state that:

"Biorefineries is a concept that represents a broad class of processes that refine different forms of biomass into one or many products or services."

A general distinction is commonly made between thermochemical (e.g. gasification, pyrolysis) and biochemical (e.g. fermentation) conversion processes. Biorefineries utilizing thermochemical reactions are able to process the biomass in its entirety, but only the sugars present in the biomass are used in the fermentation reactions. Other constituents of the biomass, such as lignin, typically need to be processed for the process to be profitable.

#### 1.2 WHAT IS FLEXIBILITY?

Flexibility may generally be used to describe an entity's susceptibility to modification. Thus, the flexibility in manufacturing may be used to describe the degrees of adaptability of the machines, processes, products, operations, routings, volumes, expansions, and production of question (Browne et al. 1984). Based on reviews in the PhD-thesis by Mansoornejad (2012) and the book by Stuart & El-Halwagi (2012), feedstock flexibility represents an important factor to the success of biorefinery operations. Following the discussions in the work by the aforementioned authors, and the classification made by Browne et al. (1984), the four most important types of flexibility all fit under the concept of manufacturing flexibility (Figure 1). Whereas the flexibility of feedstocks, products and volumes relates to the capacity to manipulate what products are manufactured from what type of raw materials, and in what amounts, the flexibility of the process relates to the ability to operate at different physical conditions (e.g. pH, temperature, moisture) and using different aspects of flexibility in manufacturing processes, readers are referred to Mansoornejad (2012) and Stuart & El-Halwagi (2012).

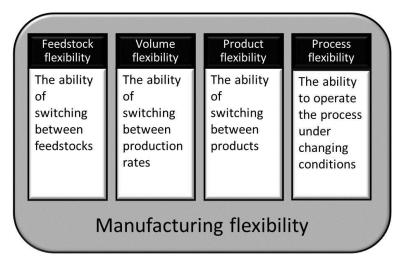


Figure 1. The four different aspects of manufacturing flexibility addressed in this report. Adapted from discussions in Mansoornejad (2012), and Stuart & El-Halwagi (2012)

#### 1.3 WHY IS FLEXIBILITY IMPORTANT?

In order minimize operational risks and maximize profit opportunities, industrial operations must respond to changes in feedstock supply and product demand. As changes in the use of feedstocks and production outputs affect the entire value chain, it is necessary to apply a supply chain-based approach. A schematic illustration of supply chains in generic processes is shown in Figure 2.



Figure 2. Supply chain of generic processes. Based on descriptions in You & Wang (2011) and Mansoornejad et al. (2013).

In supply chains of manufacturing processes, the flexibility of the processing plant is of particular importance. Practical examples wherein profits are highly dependent on optimization of the supply chain are oil refineries and corn wet milling industries (Lynd et al. 2005b). Here, the production margin is maximized by using product value and the costs of feedstock and externally produced process energy as variables. Optimal operating scenarios are identified based on the flexibility of product, volume and feedstock at a given time and within the constraints of the plant (equipment, capacity, contractual obligations etc.). The supply chain approach is highly relevant to biorefinery operations, particularly as the markets of the associated feedstocks and products are less mature compared to those of oil refineries and corn wet milling industries. In other words, to compensate for risks associated with higher feedstock prices or lower product prices, manufacturing flexibility is essential. Only a few studies have previously assessed supply chain optimization and flexibility in biorefineries. A concept denoted "Forest Biorefinery" was developed in Canada, reflecting the transformation of the Canadian pulp and paper sector to biorefinery process operations (Mansoornejad 2012; Stuart & El-Halwagi 2012; Mansoornejad et al. 2013). These studies suggest that volume and product flexibility are paramount dimensions to the future viability of biorefineries based on feedstock from the wood industry.

#### 1.4 FRAMING THE STUDY

This report addresses flexibility in biorefinery processes based on lignocellulosic feedstocks from the forestry and agricultural sectors in Sweden. While the concept of flexibility introduces an immense number of options theoretically possible in biorefinery processes, certain practical limits apply, such as investment costs, ethics (e.g. whether feedstocks are suitable for food production) and feasibility (e.g. whether technologies are commercially available). To increase the applicability of this study to current Swedish conditions, the discussions in this report were made with the following restrictions:

- 1) Processes are based on a facility for production of ethanol from lignocellulosic biomass.
- 2) Feedstocks have no, or limited, use in conventional food production (e.g. animal feed).
- 3) Methods described are at least validated in lab, i.e. technology readiness level (TRL) 4.
- 4) Products are based on conversion of sugars, i.e. via the "sugar platform".

From this framework, the main questions addressed in this report are:

- What are the supply and composition of lignocellulosic feedstocks present in Sweden?
- What products can be generated from these feedstocks in biorefinery processes?
- What are the preferred process pathways and what process steps can be manipulated to increase a biorefinery's ability to adapt to changes in feedstock supply and market demands?

Because feedstock and product flexibility is vital to the prospect of utilizing biorefinery process equipment for multiple purposes (e.g. hydrothermal reactors used for pretreatment of different feedstocks and bioreactors used in the fermentation of sugars into different products), the focus of this study has primarily been devoted to different aspects of feedstock and product flexibility.

A schematic illustration of an ethanol production process corresponding to these restrictions is given in Figure 3.

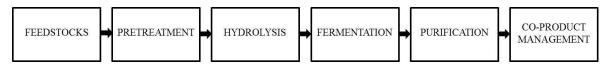


Figure 3. Schematic illustration of a production process line suitable for ethanol production.

# 2 FEEDSTOCKS

The total land area of Sweden (40.7 million hectares) is dominated by productive forest land (57%), while agricultural land used for crops and grazing of animals is comparatively small (8%). Currently, forestry feedstocks are primarily consumed in the pulp and paper industry (57%) and saw mills (41%), whereas arable land is primarily used in the production of green fodder (45%) and cereals (38%) whereof the largest shares are used in animal feed (Official Statistics of Sweden, 2014a).

#### 2.1 ANNUAL SUPPLIES AND GEOGRAPHIC DISTRIBUTION

Both forestry and agricultural feedstocks are abundant in Sweden, some of which can be considered promising substrates for biorefinery processes. Geographical distributions, variations in composition and availability are however important aspects to the prospect of sourcing and utilizing feedstocks in large scale operations. While agricultural feedstocks are geographically dispersed and vary in supply within and between years, forestry feedstocks are abundant throughout the entire Sweden and the supply is characterized by relatively small within- and between year fluctuations.

As feedstock for biorefineries, substrates rich in fibres are often termed lignocellulosic feedstocks. In this context, the fibrous fractions are often described in terms of their cellulose, hemicellulose and lignin constituents. When fermentation of lignocellulosic feedstocks is addressed, the building blocks forming the fibrous polymers are sometimes referred to C5 (pentoses) and C6 (hexoses), reflecting the number of carbon (C) atoms of the monomer sugars.

Generally, the largest volumes of lignocellulosic agricultural feedstocks in Sweden are represented by green fodder and wheat straw. Other lignocellulosic agricultural feedstocks potentially suitable for biorefinerery processes are maize stover, reed canary grass and wheat bran. The major forestry feedstocks are, in general, lignocellulosic by nature. The standing wood in Sweden is primarily composed of the softwood speices Norway spruce (42%), Scots pine (39%) and the hardwood species birch (12%) (Official Statistics of Sweden, 2014a). The reminding 7% of standing wood in Sweden will not be discussed in this report.

Gross estimations of national annual supplies of lignocellulosic feedstocks in Sweden are illustrated in Figure 4 below. More detailed figures of forestry and agricultural feedstock supplies, and their literature sources, are found in Table 5 and Table 7 in the Appendix, respectively.

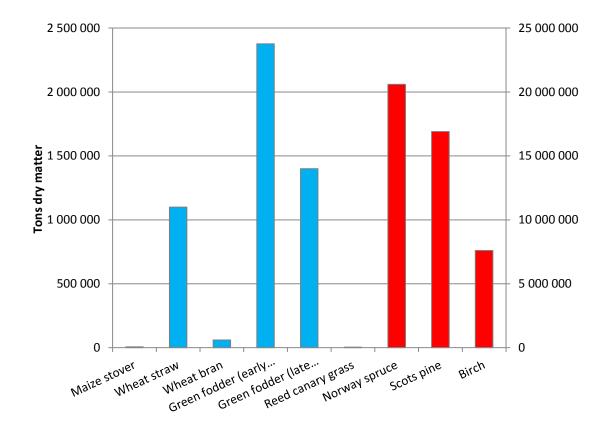


Figure 4. Gross estimations of national annual supplies (tons dm) of lignocellulosic feedstocks in Sweden. Different scales apply for agricultural (blue bars, left y-axis) and forestry materials (red bars, right y-axis).

#### 2.1.1. Supplies and distributions of agricultural feedstocks

The agricultural land in Sweden has traditionally been divided into areas with common agricultural conditions. A geographic illustration of these areas and how they are grouped in the following is illustrated in the Appendix, Figure 8. In general, the areas South, Mid and North of Sweden correspond roughly to the regions Götaland, Svealand and Norrland.

In 2013, the gross annual supplies of lignocellulosic feedstocks of agricultural origin were in the order of 5 000 000 tons dm. Here, the supply of feedstocks were in falling order: green fodder (early harvest; mid-June) > green fodder (late harvest; mid-July) > wheat straw > wheat bran > maize stover > reed canary grass. To estimate the annual supplies of wheat straw and maize stover feedstock to kernel ratios of 0.6:1 (Nilsson & Bernesson, 2009) and 1:1 (Roth, 2015), respectively, were used.

In 2013, the major share (66%) of the lignocellulosic feedstocks considered here was produced in the South of Sweden. This is primarily attributed to that the Southern region generated the largest volumes of wheat straw (78%) and green fodder (63%), nationally. There are no public data on the geographical distribution of wheat bran used in animal feed, but based on the location of cereal mills it can be approximated that the largest shares are found in the South and Mid region of Sweden. Maize stover was primarily produced in the South, while reed canary grass was primarily

produced in the North of Sweden. However, a lack of detailed statistical data reduces the precision of geographical distribution of reed canary grass.

It should be noted that figures of annual supply presented in Figure 4 above and Table 5 and Table 7 in the Appendix are merely indicative as they represent the state of 2013, and does not take year-to-year variations into account. For example, unfavourable sowing conditions in fall 2012 led to a 33% reduction in harvested volumes of winter wheat in 2013 compared to the average harvests of 2007-2012. On a 20 year s basis, a wheat straw supply of approximately 1 500 000 tons per year can be assumed realistic (Official Statistics of Sweden, 2014b).

While gross volumes of agricultural feedstocks may justify a techno-economical evaluation of their use in biorefineries, current uses limit the available (net) volumes. Nilsson & Bernesson (2009) estimated that animal feed and bedding consumes 65% of the annual supply of straw in Sweden. The remaining 35% were primarily found in the South; production areas 1, 3, 4 and 5 (see Figure 8, Appendix for illustration). Wheat bran and green fodder currently enter the animal feed chain. As their uses largely depends on world market feedstuff prices, and in the case of green fodder; within-and between-year-variations in nutritional quality, net volumes available for biorefinery purposes are difficult to predict. Today, the feedstocks of maize stover and reed canary grass are used for energy purposes.

Although not within the scope of this study, evaluating the potential of lignocellulose based biorefineries should address implications of withdrawing agricultural land or feedstocks from their current uses. For example, removing straw from cultivated land may increase greenhouse gas (GHG) emissions due to increased needs for fertilizers and losses of soil organic carbon as CO<sub>2</sub> (Cherubini & Ulgiati, 2010). Similarly, removing wheat bran or green fodder from the animal feed chain and maize stover or reed canary grass from the energy chain will increase the demand for alternative raw materials.

It is worthwhile considering that not all arable land in Sweden is used for agricultural production. Börjesson (2007) stated that a major share of the agricultural land in fallow was non-mandatory and primarily situated in Mid-Sweden. However, fallow land decreased between 2005 and 2013 by 51%, and amounted to 6% of the total arable land in 2013 (Official Statistics of Sweden, 2014b). The production potential of fallow land may be of relevance to future biorefinery feedstock sourcing.

#### Seasonal variation in supply of agricultural feedstocks

Agricultural feedstocks vary by season in supply. This feature of lignocellulosic feedstocks of agricultural origin highlights the importance of feedstock flexibility in biorefineries. Feedstocks are generally abundant at the time of harvest, in general being spring for reed canary grass, summer for green fodder and autumn for maize stover and wheat straw. Wheat bran supply is not related to times of harvest, but rather depends on times at which cereal mills are run. A theoretical distribution of supply over the year is illustrated in Figure 5, but as indicated, supplies of green fodder and wheat straw are in the magnitude of x1000 compared to other agricultural feedstocks.

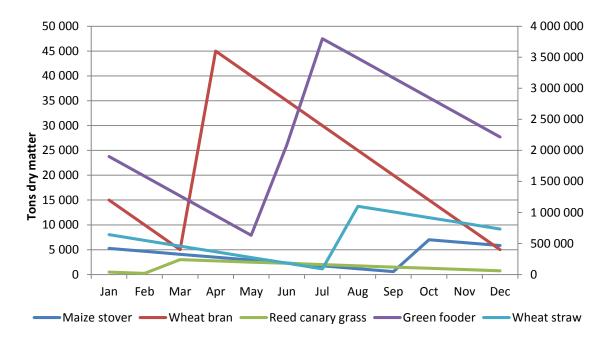


Figure 5. Theoretical distribution of seasonal variation in supply (tons dm) of agricultural feedstocks in Sweden. Different scales are used for maize stover, wheat bran and reed canary grass (left y-axis) and green fodder and wheat straw (right y-axis).

#### 2.1.2. Supplies and distributions of forestry feedstocks

Productive forest land is divided into somewhat different geographical areas than agricultural land. The definitions of South (Götaland), Mid (Svealand), Southern North (Södra Norrland) and Northern North (Norra Norrland) of Sweden are illustrated in Appendix, Figure 9.

The stem is by far the largest fraction of the tree, representing 48% (spruce), 55% (birch) and 60% (pine). Although other fractions of the tree, such as the bark, branches, stump, needles and leaves, may theoretically be used as feedstock in biorefineries, stemwood is at present the most promising substrate in ethanol-based biorefinery plants from a techno-economical perspective. Hence, only stemwood will be addressed in this report. Between 2009 and 2013, the annual volume increment of Norway spruce, Scots pine and birch in Swedish productive forest land summed up to 109.1 million m<sup>3</sup>. While it is common to express forest biomass supplies in volumes (m<sup>3</sup>), generalized conversion factors have been used in the following to facilitate comparisons between the supplies of agricultural and forest feedstocks (Joelsson, 2013):

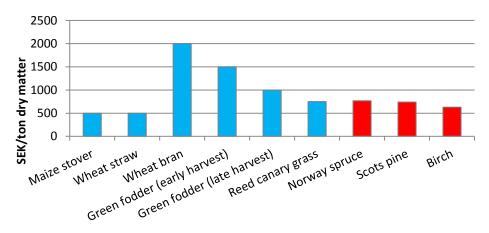
Norway spruce and Scots pine:	0.4 tons $dm/m^3$
Birch	0.5 tons $dm/m^3$

The annual supplies between 2009 and 2013 were in the order of 45 000 000 tons dm. Here, the supply of feedstocks were falling order Norway spruce > Scots pine > birch. Compared to lingo-cellulosic feedstocks of agricultural origin, forestry feedstocks are geographically more evenly distributed. The Southern region was the single most productive area, as defined by Official Statistics of Sweden (2014a). However, the largest volumes of forestry feedstocks (45%) were found in the North of Sweden if a geographical area division similar to that used in agricultural context was applied, i.e. when the Southern and Northern regions of North Sweden are merged.

It can be concluded that the annual supplies of forest feedstocks exceed those of agricultural origin by a factor of approximately x10. Further, it has been reported that the growing stock of Swedish forest biomass displayed positive net balances during 2000-2010 (Official Statistics of Sweden, 2014a), which implies that the available forest feedstock supplies were increasing during these years. There are no distinct seasonal variations in the supply of forest feedstock.

#### 2.2 PRICES AND COMPOSITIONS

Price approximations of major forestry (stemwood) feedstocks and lignocellulosic feedstocks of agricultural origin are presented in Figure 6. An overview of chemical compositions of relevance to biorefinery processes in these feedstocks is given in Figure 7 below. Detailed data and references are found in Table 6 and Table 8 in Appendix.



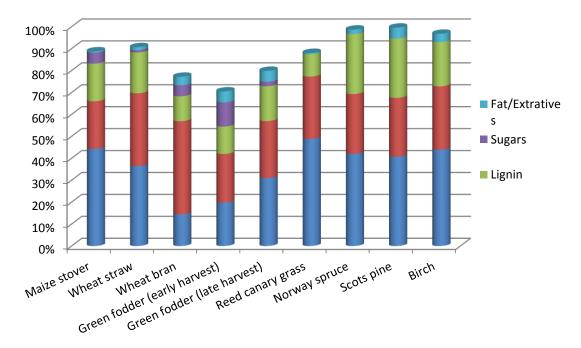


Figure 6. Approximated prices of agricultural feedstocks (blue) and forestry feedstocks (red).

Figure 7 General chemical compositions of lignocellulosic agricultural and forestry feedstocks.

#### 2.2.1 Prices and compositions of agricultural feedstocks

In general, prices are influenced by net supplies and demands. Thus, the price approximations of agricultural feedstocks illustrated in Figure 6 presuppose that regional supplies exceed demands of current consumers and that net volumes are made available. It may be assumed that prices reflect the market value of their use in current contexts, such as in animal feed or for energy purposes. In this study, maize stover and wheat straw were attributed the lowest prices per ton feedstock.

Depending on the market of interest and technical constraints of biorefinery processes, different feedstocks may come out as more or less interesting. However not indicated in Figure 6, all costs related to handling and transport of feedstocks will largely influence the margins in any biorefinery operation. Ekman et al. (2013) indicated that the energy required for 50 km transportation of straw by truck was equivalent to an average of 2.5% of the energy content of the biomass. This has particular implications for green fodder, as the water content of green fodder stored in bales and in bunker and tower silos varies naturally, and be as much as 30-80%. Therefore, the localization of a biorefinery and its' consequences on logistical operations is particularly critical if green fodder is considered as feedstock.

Approximate chemical composition values in Figure 7 originate from different information sources, and it should be emphasized that values do not illustrate the sometimes very large variations due to seasonal variation, differences in agricultural practices and analytical methodologies. More detailed figures on the chemical compositions, and their literature sources, are found in Figure 6, Appendix.

In general, the largest fractions of cellulose are found in maize stover and reed canary grass, while the largest fractions of hemicellulose are found in wheat straw and wheat bran. Green fodder contains the largest proportion of sugars, but this fraction diminishes during plant maturation and is consequently lower in late harvests than in early harvests. In Figure 7, the chemical constituents do not sum to 100% as some fractions are left out. For example, the contents of crude protein and ash may be substantial, as in the case of wheat bran. However, their contribution to sugar (C5+C6) formation in biorefinery processes is limited, or even negligible.

#### 2.2.2 Prices and compositions of forestry feedstocks

Forestry feedstocks are typically very rich in lignocellulose and relatively homogenous in composition compared to agricultural feedstocks. This, in combination with existing infrastructures and lack of land use competition for food (or animal feed), has made forestry feedstocks of particular interest to prospecting biorefineries.

In Figure 6, average annual pulpwood prices have been used to calculate average prices between 2009 and 2013 (Official Statistics of Sweden, 2014a). Here, prices are expressed in SEK/ton, following the generalized conversion factors as outlined previously. While it can be concluded that the prices of Norway spruce and Scots pine were comparable during 2009-2013, the price of birch stemwood would make it particularly interesting as feedstock in biorefinery operations. However, here it must be acknowledged that the comparatively higher density conversion factor (0.5 tDS/m<sup>3</sup>) attributed to birch (above) affects the price when expressed in metric tons. If birch would be assigned the same conversion factor as for Norway spruce and Scots pine (0.4 tDS/m<sup>3</sup>), the price per ton birch stemwood increases to 786 SEK (i.e. higher than the prices of Norway spruce and Scots pine).

Compared to the variation between different agricultural feedstocks, there are small variations in the chemical compositions of the forestry stemwood feedstocks (Figure 7). From a biorefinery perspective, a feedstocks' lignin content should preferably be kept low as it cannot be fermented to ethanol. The relatively low lignin content of birch stemwood is consequently an attractive feature. However, the hemicellulose content is highest in birch and the type of hemicellulose sugars is different compared to spruce and pine, which may pose restrictions on the biorefinery process, e.g. the pretreatment conditions and microorganisms used (discussed below). More detailed figures on the chemical compositions, and their literature sources, are found in Table 8, Appendix.

Although slight variations are found in the chemical composition of stemwood between tree species, it should be noted that other parts of the tree (e.g. stem, bark, branches, and stump) may exhibit more profound differences. Details on the chemical constituents of other parts of the tree have been compiled by Bergström & Matisons (2014).

# HIGHLIGHTS

### FEEDSTOCKS

- Green fodder and wheat straw are the most abundant lignocellulosic agricultural feedstocks studied here.
- Maize stover, wheat straw and reed canary grass display similar chemical compositions and complement each other with respect to seasonal availability, which facilitates flexibility in their use. Their geographical dispersion may however limit their alternating use in biorefineries.
- Forestry (stemwood) feedstocks display less variation in chemical composition and seasonal availability, and can be supplied in the magnitude of x10 compared to the lignocellulosic agricultural feedstocks studied.
- In total, the largest feedstock volumes are found in Northern Sweden (Norrland), but raw material flexibility in prospecting biorefineries is limited due to the domination of softwood.
- South of Sweden (Götaland) encompasses the second largest pool of raw materials. All feedstocks studied here, but reed canary grass, are abundant in South of Sweden, which facilitates feedstock flexibility in this region.

## 3 PRETREATMENT

Pretreatment is an important step in the biorefinery process. As illustrated in Figure 7 above, the incoming lignocellulosic biomass consists of cellulose, hemicellulose, lignin and extractives but also of other minor components like acetate and ash. In order to refine these feedstock components to value-adding products, the physical and chemical nature of the recalcitrant biomass needs to be altered. The overall aim of the pretreatment step in biochemical production routes is to make the biomass susceptible to enzymatic degradation. This is achieved by weakening of the protecting lignin and hemicellulose matrix or by changing the nature of the pores in the material. As reviewed by Sun & Cheng (2002), there is a wide range of different pretreatment methods, of which steam explosion and dilute-acid are among the most common. Other methods include the use of alkali, sulphur dioxide, carbon dioxide and ammonia.

Since lignocellulosic biomass is heterogenic, there are potentially large differences in recalcitrance and composition between and within different feedstocks. Adding to this, the optimal pretreatment conditions will depend on different factors such as the price of products (ethanol, biogas, hydrogen, district heat, biomass fuel etc.), the dynamic nature of the surrounding system (e.g. if connected to a district heating network with seasonal variations) and the choice of microorganisms used in the bioreactors (due to sensitivity to inhibitors for example). As outlined by Galbe & Zacchi (2012), the pretreatment step aims specifically to facilitate:

- High recovery of all carbohydrates
- High digestibility of cellulose in enzymatic hydrolysis
- Low generation of degradation products from lignin and hemicellulose
- High solids concentration
- Low net energy demand
- Low capital and operating costs

The design of front-end operations is another important factor potentially limiting the flexibility of feedstocks in biorefinery operations, as the preprocessing, storing and handling of feedstocks of forest and agricultural origin may differ substantially.

#### 3.1 FRONT-END OPERATIONS

The biorefinery process is, as discussed briefly in the introduction, always an integral part of a supply chain. Stuart & El-Halwagi (2012) stress that the profitability of new biorefinery processes depends not only on the production facility, but on the entire supply chain. Front-end operations, or storage and preprocessing of the feedstock, constitutes an important part of this chain. This is because the requirements for preprocessing of biomass differ substantially between the different types of feedstocks described previously. Forest biomass is normally chipped, whilst biomass of agricultural origin often comes in bales and requires different handling (Larsen et al. 2012). To achieve full flexibility between these types of feedstocks, two different parallel facilities for front-end operations would probably be required. Alternatively, the feedstock could be preprocessed into ready-to-use biomass at a separate location and distributed plants in the vicinity (Humbird et al. 2011).

#### 3.2 PRETREATMENT

A review of lignocellulosic biomass pretreatments for ethanol production was performed in the Sugar Platform-subproject report of the large Swedish Vinnova-funded Forest Chemistry research project. Reports are available at <u>http://www.processum.se/en/sp-processum/our-offer/forest-chemistry</u> (visited 2016-01-21). The descriptions of pretreatment methods in this report are largely based on that review. While there exist several methods for the pretreatment of lignocellulosic biomass, two principles aiming at hemicellulose (thermochemical pretreatments) and/or lignin (pulping pretreatments) are of particular interest here. This is because they are both commercially available, and of relevance to manufacturing flexibility, since a range of substances formed during the degradation of hemicellulose and lignin negatively affects the enzymatic hydrolysis of cellulose. Alternative options including e.g. acid hydrolysis, in which both the hemicellulose and the cellulose are hydrolysed, will not be discussed.

The contents of Table 1 summarizes the different types of pretreatments prior to enzymatic hydrolysis, commonly discussed in relation to lignocellulosic biomass refining.

 Table 1. Overview of methods addressed in this report for the pretreatment of lignocellulosic

 feedstocks prior to enzymatic hydrolysis of cellulose. The contents are based on Table 4.2.1 in the

 Sugar Platform sub-report of the Forest Chemistry research project.

Pretreatment methods included in the	Main effect, varieties and uses			
report				
Acid-based thermochemical methods	Hydrolysis of hemicelluloses to monosaccharides. Involves			
	catalysts such as H <sub>2</sub> SO <sub>4</sub> , SO <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub> , HCl.			
Thermochemical methods working	Solubilisation of hemicellulose without complete conversion to			
close to neutral conditions	monosaccharides. Includes steam explosion and			
	hydrothermolysis.			
Alkaline methods	Part of the hemicellulose is left intact. More severe conditions			
	have substantial effect on lignin. Include ammonia fibre			
	explosion (AFEX)			
Pulping processes	Methods that target lignin and to some extent hemicelluloses.			
	Includes the Kraft process, soda pulping, the sulphite process			
	and the organosolv process.			

Some alternative pretreatment methods, in which different solvents are used to e.g. disrupt the structure of lignocellulose and make the polysaccharides more accessible for enzymatic hydrolysis, need further research and are not included in this report. Here, three main questions are addressed:

- 1. What prerequisites do the feedstocks described impose on the pretreatment in order to reach the sugar platform?
- 2. What residual streams are produced in the pretreatment of these feedstocks?
- 3. How may the pretreatment system be designed in order to optimize the manufacturing flexibility?

#### 3.2.1 Short description of technologies

#### Thermochemical methods

The combined severity is a term used to describe the harshness of acid-based pretreatment (Galbe & Zacchi 2007). Parameters affecting the combined severity are:

- Reaction time in the pretreatment reactor. The combined severity increase with time.
- Reaction temperature. A higher temperature implies a more severe pretreatment.
- The pH, or the dosage of acids. A lower pH means a more severe pretreatment.

It is known that recalcitrant lignocellulosic biomass, such as softwoods, requires higher combined severity. For agricultural feedstocks, however, a lower pretreatment severity can be allowed than for forest based biomass. Due to the autohydrolysis and degradation of sugars in the biomass, the pretreatment liquid will turn acidic even if no acid is added to the process. In the case of agricultural feedstocks, it is therefore possible to only add water and get a milder pretreatment. This method, known as steam explosion without catalyst, is used in the Inbicon demonstration plant in Denmark (based on wheat straw), and in the Beta Renewable's plant in Crescentino, Italy (based on giant reed and straw). Alkaline methods constitute an alternative for less recalcitrant agricultural feedstocks, and dilute ammonia treatment is one example which Dupont Biofuel Solutions are currently working on commercializing.

#### Pulping

The chemical pulping methods are designed to target lignin in the biomass. These methods are well-developed since e.g. the Kraft-, soda- and sulphite pulping methods all have existed commercially for many decades. The pulping methods work well for recalcitrant woody biomass, softwood and hardwood, but Kraft and soda pulping are not economically viable for a biorefinery producing bulk products like ethanol. In general, the chemical recovery cycle for these processes is too expensive to be considered in a biorefinery producing ethanol, at least for a grassroot plant. Making use of already existing infrastructure and equipment could however make this type of processes interesting. It has been suggested that Na<sub>2</sub>CO<sub>3</sub> could replace NaOH in the pretreatment of hardwoods in biorefineries; a procedure which would erase the need for expensive chemical recovery cycle of NaOH. Whereas Na<sub>2</sub>CO<sub>3</sub> is not considered a feasible option in the treatment of softwood, it may prove interesting for e.g. hardwood or agricultural feedstock campaigns (Meng et al. 2014).

Sulphite pulping is a predecessor to the Kraft pulping method, but a few mills still exist in the Scandinavian countries. In Sweden, the Domsjö sulphite pulp mill in Örnsköldsvik, owned by Aditya Birla, produces cellulose for use in textiles. In parallel, ethanol is produced from the hemicellulose made available in this process. In Norway, a sulphite pulping pretreatment method for biorefinery processes with enzymatic hydrolysis has been developed and tested at demonstration scale in Sarpsborg (Rodsrud, 2011). The patented process is known as Borregaard Advanced Lignin (BALI).

Research aiming at finding the optimal pretreatment conditions for different feedstocks has generated data in relatively large intervals. Typical values described in literature are shown in Table 2.

Method	Catalyst	Feedstock	T [°C]	t [min]	Conc. [%]	Reference
<b>Thermo</b> - <b>chem</b> ical	H <sub>2</sub> SO <sub>4</sub> /SO <sub>2</sub>	Maize stover	160-190	1-5	0.5-3	Humbird et al. (2011); Galbe & Zacchi (2012)
	$H_2SO_4/SO_2$	Softwood	190-230	2-10	0.5	Söderström et al. (2003)
	H <sub>2</sub> SO <sub>4</sub> /SO <sub>2</sub>	Poplar (Hardwood)	190	1-5	2-3	Galbe & Zacchi (2012)
	None	Wheat straw	195	6-12	-	Østergaard Petersen et al. (2009)
Pulping	NaOH	Pine (Softwood)	180	180-300	15-23	Von Schenck et al. (2013)
	NaOH	Aspen (Hardwood)	170	90-300	15-22	Von Schenck et al. (2013)
	Na <sub>2</sub> CO <sub>3</sub>	Wheat straw	120	140	12	Geng et al. (2014)
	Na <sub>2</sub> CO <sub>3</sub>	Poplar (Hardwood)	160	60	20	Meng et al. (2014)
Alkaline	AFEX	Maize stover	140	15	1:1 (biomass:NH3)	Gao et al. (2014)

Table 2. Typical pretreatment conditions for agricultural and forest feedstocks.

#### 3.2.2 Flexibility

It can be deduced from the descriptions of pulping and thermochemical pretreatment methods in Table 2 that conditions may be varied in several different ways. The design of the pretreatment step will affect the capacity to process different feedstocks.

#### Thermochemical methods

The feedstock flexibility of thermochemical based processes is very much dependent on the design of the pretreatment reactor system. Research and experience of different pretreatment conditions and several different feedstocks from two openly available biochemical biorefinery demonstration plants allow for a concrete scrutiny.

A very flexible system is present in the National Renewable Energy Laboratory (NREL) biorefinery demo plant in Colorado, U.S. Here, the flexibility of feedstocks, volumes and products is increased by the design of a system with a number of reactors that can be connected in multiple ways. This solution leads to a large flexibility in reaction time (depending on the path through reactors, i.e. how many reactors are used in series) and production rate (different sizes of the reactors). Further, it potentially enables the running of parallel pretreatments of different feedstocks, thereby minimizing the heterogeneity of the pretreatment material.

At the SP Biorefinery Demo Plant in Örnsköldsvik, a number of different feedstocks of both forest and agricultural origin have been tested. The pretreatment section of this plant consists of one horizontal and one vertical reactor, connected with screw feeders which allows for differentiating pressure and temperature. The setup at this plant has been tested for temperatures up to well above 200°C, using both high acid concentration and reaction times well above the requirements in Table 2 for thermochemical methods.

Designing a flexible pretreatment system necessitates options to vary the parameters reaction time, temperature, pressure and pH. In both of the above mentioned demonstration plants the reaction time can be varied due to the design with several rectors connected in series. Connecting these reactors in parallel would further increase process and volume flexibility. Equipment materials and the utility system of the facility are critical to the flexibility in temperature, pressure and pH. Here, it can generally be assumed that the constraints are not technical, but rather economical, as in the scenario where a system is designed for the use of high acid concentrations.

#### Pulping

The nature of the pulping pretreatment displays some potential with respect to feedstock flexibility. In a demonstration plant test of the sulphite based BALI-process developed by Borregaard, the lignin of bagasse was almost completely dissolved in the liquid phase, while cellulose and hemicellulose was retained in the solid fraction (Martin et al. 2008). These results may prove viable to prospecting biorefineries in e.g. South of Sweden, given the seasonal variation in supply of agricultural feedstocks. Further, the long record of use of sulphite pulping processes in the pretreatment of woody materials makes it promising for biorefineries using forestry feedstocks. It should be noted that the BALI-process is patented but has not yet been commercialized and that the details of its design are not known to the authors. Hence, the potential of the BALI method in a biorefinery aiming for optimal flexibility is merely speculative.

Processes based on Kraft- and soda pulping pretreatment would themselves not be economically viable to greenfield biorefineries producing ethanol as the main bulk product. However, these processes may be interesting alternatives in specific cases, such as in connection to transformations of existing unprofitable pulp mills to provide wider product portfolios. The potential of pulping methods like the Kraft or soda pretreatments to fractionate cellulose, hemicellulose and lignin in lignocellulosic biomass, may imply a high degree of flexibility. Further, it is known that these alkaline methods generate relatively low levels of enzymatic and fermentation inhibitors.

# HIGHLIGHTS

### PREPROCESSING AND PRETREATMENT

- Preprocessing of feedstocks may limit manufacturing flexibility in subsequent processing steps. Centralized facilities may prove interesting from a supply chain perspective.
- Whereas a large number of alternative methods for pretreatment of lignocellulosic biomass exist, there are currently few commercially mature.
- A high degree of feedstock flexibility can be achieved with appropriate design of the thermochemical pretreatment step.
- Pulping pretreatment constitutes and interesting option to multiproduct biorefineries due to the ability to fractionate the incoming biomass. However, the recovery of chemicals used may be expensive.

## 4 HYDROLYSIS

Following pretreatment, the polysaccharides present in the lignocellulosic feedstock need to be hydrolysed prior to fermentation. There are three general methods for hydrolysis of lignocellulose polysaccharides to sugars; concentrated-acid hydrolysis, dilute-acid hydrolysis, and enzymatic hydrolysis.

#### 4.1 CONCENTRATED-ACID HYDROLYSIS

Hydrolysis with concentrated acid is an old technique made available in the end of the  $19^{th}$  century. A concentrated acid, such as  $H_2SO_4$ , is typically applied at moderate temperatures. The acid breaks the hydrogen bonding between the cellulose chains, whereby the cellulose becomes susceptible to hydrolysis. The addition of water facilitates a rapid hydrolysis of the polysaccharides to glucose (Sheehan & Himmel, 1999). The main advantages of hydrolysis using concentrated acid are that the process does not require high temperatures and that the glucose yields are high. The disadvantage is that the large amounts of acid required need to be recovered and reused to enable an economically viable process. Corrosion of the equipment constitutes another issue related to the use of concentrated acids (Galbe & Zacchi, 2002).

#### 4.2 DILUTE-ACID HYDROLYSIS

Dilute-acid hydrolysis is the oldest technique for converting lignocellulose to ethanol. Similar to concentrated-acid hydrolysis, H<sub>2</sub>SO<sub>4</sub> or other acids are added to the hydrolysis vessel, but in concentrations of approximately 0.5-3% and at higher temperatures. The advantages of the method are the fast reaction rate and the low acid consumption, whereas disadvantages include low sugar yield, high temperature requirements, hemicellulose sugar degradation, and generation of fermentation inhibitors. The degradation of the hemicellulose sugars can be reduced and the conversion yield of cellulose to glucose increased, by applying a two-step hydrolysis procedure. In the first step, the hemicellulose fraction is hydrolysed under relatively mild conditions (approx. 170-190°C) to generate sugar monomers, like arabinose, galactose, glucose, mannose, and xylose. In the second step, harsher conditions (approx. 200-230°C) are applied to hydrolyse the cellulose fraction into glucose. The two fractions may then be pooled together prior to fermentation (Galbe & Zacchi, 2002).

#### 4.3 ENZYMATIC HYDROLYSIS

Enzymatic hydrolysis is a method in which lignocellulose degrading enzymes are added to promote hydrolysis. The use of enzymes is a relatively new approach compared to facilitating hydrolysis by the use of concentrated or dilute acid. Enzymes involved in the hydrolysis of lignocellulose act in a synergistic way and include various cellulases, hemicellulases, polysaccharide monooxygenases, lignin degrading or modifying enzymes, etc. The reaction rate of enzymatic hydrolysis is highly dependent on the conditions of the pretreatment.

The advantages of enzymatic hydrolysis are high yields and moderate temperature requirements, while disadvantages include relatively slow enzyme reaction rates and high enzyme costs. Significant developments on technical performance and cost efficiency of enzymes have been made

during the last ten years, but further improvement are vital to the commercialization of ethanol produced from enzymatically hydrolysed lignocellulosic feedstock.

Today, most research efforts are focused on the enzymatic hydrolysis because of the high development potential. The dilute-acid and concentrated-acid hydrolysis are relatively mature techniques for which no major improvements are likely to happen.

The manufacturing flexibility of a biorefinery will largely depend on the constraints imposed by different processing steps. For example, it may be assumed that the diverse process equipment required in concentrate acid hydrolysis restricts the manufacturing flexibility. It should further be noted that some processing steps are more or less interdependent. The pretreatment method of acid catalysed steam explosion is one example in which subsequent switching between dilute-acid and enzymatic hydrolysis is enabled.

## 5 FERMENTATION

Lignocellulosic hydrolysates can be fermented to ethanol using different fermentation modes and microorganisms. Commercial ethanol production has historically been devoted to feedstocks rich in starch or sugar, i.e. first generation ethanol plants. Today, a few production facilities are currently commenced, or up and running, in which lignocellulosic feedstock is fermented to ethanol. Such second generation ethanol production plants are found in North and South America and Europe.

#### 5.1 BATCH-MODE FERMENTATION

In batch-mode fermentations, all medium nutrients are available from the starting point when the microorganism is inoculated. The fermentation is continued until the sugar is depleted. Advantages of batch-mode operations include the simplicity of the process, the low risk of contamination of unwanted microbes and the possibility to utilize the sugars efficiently. On the other hand, ethanol production via batch-mode fermentation is discontinuous because of the fermentation lag phase and the interruption which occurs when fresh medium is added to the fermentation vessel. Another disadvantage is that the batch process mode is considered relatively labour-intensive.

#### 5.2 FED-BATCH FERMENTATION

The fed-batch mode is very similar to the batch mode with the exception that fresh medium is fed into the fermentation vessel continuously. Thus, inhibitory compounds (e.g. furan aldehydes, phenolic compounds and aliphatic acids) that are present in the medium will be added little by little, whereby their negative effects ar reduced. Disadvantages include suboptimal utilization of the maximum working volume of the fermentation vessel and the additional time required because of interruptions during refilling.

#### 5.3 CONTINIOUS FERMENTATION

In continuous fermentation, fresh medium is constantly fed to the fermentation vessel and there is also a continious out-take of product. The rates of dilution, or feeding, and product withdrawal are equal and the productivity is dependent on the dilution rate. Continuous fermentation implies that the ethanol is produced continuously without interruptions, which enables high productivities and the use of low vessel volumes. Risks of process failure associated with continuous fermentation include biomass washout and microbial contamination due to the constant medium inflow. Another disadvantage is that the sugar conversion yield decreases at high dilution rates. The dilution rate can be reduced to increase the sugar utilization, but productivity will decline as a consequence. The use of microbial cell retention may be a way to improve the continuous fermentation process. Such a procedure can include the introduction of a step of recirculation and immobilization of microbial cells.

#### 5.4 MICROORGANISMS

Several different types of microorganisms can be considered as biocatalysts for the production of ethanol from lignocellulose. The most studied microorganisms for this purpose include the yeast *Saccharomyces cerevisiae* and the two bacteria *Zymomonas mobilis* and *Escherichia coli*. Table 3

gives an overview of advantages and disadvantages of these and other commonly studied microorganisms.

Microorganism	Туре	Advantages	Disadvantages
Native Saccharomyces cerevisiae	Yeast	GRAS <sup>(1)</sup> , robust, high ethanol tolerance, high yields on C6 sugars.	Cannot utlise C5 sugars <sup>(2)</sup> .
Genetically modified Saccharomyces cerevisiae	Yeast	Can utilize both C5 and C6.	Not GRAS <sup>(1)</sup> , less robust than native strains, comparatively low C5 conversion rate.
Native Zymomonas mobilis	Mesophilic bacteria	GRAS <sup>(1)</sup> , high ethanol tolerance, high yields on C6 sugars <sup>(2)</sup> .	Less robust than Saccharomycses cerevisae.
Genetically modified Escherichia coli	Mesophilic bacteria	Can utilize xylose and glucose, increased ethanol tolerance <sup>(2)</sup> .	Not GRAS, low robustness and ethanol tolerance <sup>(2)</sup> .
Thermoanaerobacter ethanolicus (Hild et al. 2003) Clostridium thermocellum	Thermophilic bacteria Strict anaerobic	Can utilize both C5 and C6; some express hydrolytic enzymes. Low contamination risk, strict anaerobes require	Low ethanol tolerance, low cell mass concentration resulting in low volumetric productivities, low yields in native strains.
(Lynd et al. 2002)		special equipment <sup>(3)</sup> .	

Table 3. The most studied microorganisms in ethanol production from lignocellulosic feedstocks.

<sup>(1)</sup>Generally regarded as safe (GRAS); a status allowing the microorganism to be used industrially with less safety measures.

(2)Lin & Tanaka (2006).

<sup>(3)</sup>Hild et al. (2003), Lynd et al. (2002), Sommer et al. (2004), Wu et al. (2006), Zhang & Lynd (2005).

Another group of promising microorganisms is thermophilic bacteria. The use of elevated temperatures (60-80°C), reduces the risk of contamination by other microorganisms during fermentation. This is particularly relevant to the option of using continuous fermentation mode. Operating at high temperatures also reduces the need for cooling, both following pretreatment and during fermentation. This feature facilitates continuous ethanol recovery through gas stripping or vacuum application (Hild et al. 2003). However, processing equipment adapted to the oxygen sensitivity of these microorganisms is required. This affects the spatial requirements of the biorefinery plant and possibly reduces the manufacturing flexibility of the plant.

The ability to ferment C5 sugars influences the selection of microorganisms of the process. While the fraction of pentose sugars is generally low in softwood hydrolysates, choosing hardwood or agricultural feedstocks increases the relevance of using microorganisms which possess the ability to ferment pentoses.

It is currently not common practice to alternate between different types of microorganism to increase the manufacturing flexibility of biorefinery operations. Although the same type of bioreactors would be suitable for ethanol production with *S. cerevisiae*, *E. coli* and *Z. mobilis*, alternating uses of microbes may potentially put constraints on the process due to differences in their productivity. Thus, bioreactors with increased volume capacity or additional bioreactors may be required to achieve the same productivity as in processes with another microorganism. In cases where microorganisms such as thermophiles or strict anaerobic species, are considered, other types of bioreactors or additional equipment might be needed to sustain such a process.

In conclusion, the choice of microorganism species and strain for ethanol production from lingocellulosic feedstock is highly dependent on the hydrolysate composition and the design of the fermentation process. The choice of microorganism may be flexible in many cases but could also require extensive remodelling of the production facility.

#### 5.5 PROCESS CONFIGURATIONS

There are three general process configurations that can be considered for the production of ethanol from lignocellulosic feedstocks; separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and consolidated bioprocessing (CBP).

#### 5.5.1 Separate hydrolysis and fermentation (SHF)

In the separate hydrolysis and fermentation (SHF) process, the polysaccharide hydrolysis occurs separately from the fermentation of their derivates. This means that the optimal temperatures for both the enzymatic hydrolysis and fermentation can be applied. Thus, the ability to manipulate the steps of hydrolysis and fermentation interdependently can be viewed as a characteristic enabling all four aspects of manufacturing flexibility (i.e. feedstock, volume, process, and product flexibility). One of the drawbacks of the SHF process is that the sugars generated can inhibit the hydrolytic enzymes (Mandels & Reese, 1963), and it is known that a range of other inhibitory compunds is formed during hydrolysis. An equipment design which allows for adjustments of the process characteristics may facilitate the reduction of these inhibitors, thereby increasing productivity and potentially manufacturing flexibility.

#### 5.5.2 Simultaneous saccharification and fermentation (SSF)

A process in which the hydrolysis of lignocellulose and sugar conversion to ethanol occurs at the same time is often denoted simultaneous saccharification and fermentation (SSF). In SSF, the sugars generated are immediately consumed by the fermenting microorganism, which implies a reduction of enzyme inhibition. The SSF approach consequently provides the possibility to operate at high substrate concentrations, which is a facilitating factor to the fermentation step and the subsequent distillation. The disadvantage of the SSF process is that the optimal temperatures for the lignocellulose degrading enzymes and the fermenting microorganism may differ. Hence, the selected temperature is a compromise, implying that neither hydrolysis nor fermentation will be performed under optimal conditions. In addition to inhibitory compounds formed during hydrolysis, it is known that the ethanol formed during fermentation also may inhibit the enzymes (Holtzapple et al. 1990). Furthermore, SSF makes it more difficult to separate yeast from the solid lignin-rich residue that is formed after hydrolysis. The recovery and reuse of microorganisms constitute important aspects to the economic viability of biorefinery operations.

#### 5.5.3 Consolidated bioprocessing (CBP)

Efforts have been made to combine enzyme production, hydrolysis and fermentation into a single process, called consolidated bioprocessing (CBP). Much of these efforts have addressed the design a microorganism able to perform these three steps simultaneously (Lynd et al. 2005a). There are two different strategies to manipulate CBP microorganisms, either through genetic modification of native cellulolytic microorganisms to generate high ethanol yields, or alternatively, through genetic modification of non-cellulolytic ethanol producing microorganism to express enzymes from other organisms (Lynd et al. 2005a).

Flexibility in process configurations could be possible, especially if changing between SSF and CBP. However, changing the process configuration between SHF and SSF, or CBP, may prove more challenging due to their differences in bioreactor designs. Further, the different configurations may require different sizes of equipment (e.g. bioreactors, distillation, collection tanks, etc.), additional equipment for unit operations such as separation of solids and liquids, and capacity of destructing genetically modified material (if CBP is applied) etc.

# HIGHLIGHTS

### ETHANOL FERMENTATION

- Large scale production of ethanol from lignocellulosic feedstocks is commercialized in a few facilities, but the potential of increasing the manufacturing flexibility is not fully exploited.
- Ethanol can be produced using batch-mode, fed-batch or continuous fermentation; each of which design has their technological, practical and economic advantages and disadvantages.
- Processes can be configured to allow for the hydrolysis and sugar fermentation to occur separately or simultaneously. Simultaneous hydrolysis and fermentation may benefit manufacturing flexibility, particularly if genetically modified microorganisms are used.
- Genetically modified microorganisms can utilize a wide range of substrates, which would increase feedstock flexibility, but their inferior robustness and ethanol tolerance requires further research.
- The effect of each process step requires thorough investigation prior to implementation of configurations to increase the manufacturing flexibility of the process.

### 6 BIOFUELS OTHER THAN ETHANOL

The last decades' efforts made in the research and development of alternative biofuels including butanol, hydrogen and biogas, now challenge the dominant position of ethanol as the successor of petroleum based fuels. It is however becoming increasingly clear that no single biofuel is likely to replace diesel or gasoline entirely, but that the future demands will encompass a range of different fuels. Uncertainties related to such future scenarios highlight the importance of high flexibility in biorefinery operations. Depending on site-specific conditions, existing ethanol plants may alter their process configurations to variable degrees in order to increase their product flexibility.

#### 6.1 BUTANOL

Butanol is an interesting biofuel alternative to ethanol, as it is more energy dense, less corrosive and displays a lower "heat of vaporization". In addition, butanol blends are less susceptible to separation in the presence of water compared to blends of ethanol and gasoline. Butanol can be produced from petroleum (e.g. hydroformylation of propene) or from sugars via fermentation. Alternatively, butanol may be produced via chemical conversion of ethanol i.e. via the ethanol  $\rightarrow$  acetealdehyde  $\rightarrow$  acetaldol  $\rightarrow$  crotonaldehyde  $\rightarrow$  n-butyraldehyde  $\rightarrow$  butanol pathway (Weissermel & Arpe, 2003).

Fermentation of sugars to generate butanol is traditionally performed using the principle denoted "acetone, butanol, and ethanol fermentation" (ABE fermentation). The bacterium *Clostridium acetobutylicum* is commonly used for ABE fermentation and it mainly produces acetone, butanol and ethanol in a ratio of 3:6:1, respectively. The metabolism of *C. acetobutylicum* includes two typical phases, acidogenesis and solventogenesis. During acidogenesis butyric, propionic, lactic and acetic acid are produced. As the pH of the culture eventually drops, *C. acetobutylicum* undergoes a metabolic shift and enters the solventogenesis. Here, butanol, acetone, iso-propanol and ethanol are produced. A number of issues need to be resolved before the production of butanol for biofuel applications can become commercial viable. For example, the *Clostridium* species are natural producers of butanol, but their need of anaerobic growth conditions restraints on the process design, and consequently manufacturing flexibility. Further, *Clostridium* spp. have proven difficult to culture in comparison to e.g. *E. coli* and *S. cerivisea*. At present, very few tools are available to genetically engineer *Clostridium* species for improved titres and productivity.

Another obstacle is that the butanol produced is toxic to bacteria. The cell growth and fermentation process can be significantly inhibited at butanol concentrations of 10-20 g/L. Extractive fermentation, e.g. two phase liquid-liquid extraction during fermentation, has been tested in order to improve butanol production and reduce product inhibition during ABE fermentation. Other attempts include cell recycling and cell immobilization to increase cell density and increase the productivity. Despite several improvements of the ABE fermentation process, the butanol yield from glucose is low, typically less than 25%. Thus, butanol yields are generally below 4.5 g/L/h and titres rarely exceeds 20 g/L (Afschar et al. 1985; Marlatt & Datta 1986). A novel approach to increase the butanol yield is to co-culture two organisms. In principle, such an approach involves one bacterium producing butyric acid (e.g. *C. tyrobutyricum*) and one other bacterium which converts the formed butyric acid to butanol (e.g. *C. acetobutylicum*). This concept can be carried out in a single or two separate fermentation vessels (Bahl et al. 1982; Bergström & Foutch 1985). Yet another alternative is to first produce butyric acid and subsequently convert it to butanol by chemical methods.

Other non-native butanol producers, such as *E. coli* and *S. cerevisiae*, have been considered for production of butanol. Today, *E. coli* is widely used in industrial production of recombinant proteins and is simple to modify genetically. Analogously, genetic modification can easily be performed in *S. cerevisiae*, and yeast strains generally display high solvent tolerance and display long records of use in ethanol production.

An important difference between the production of ethanol and butanol is found in the downstream processing. While ethanol recovery is normally performed through distillation, it is not suitable for butanol as the boiling point of butanol is higher than that of water; making such an approach very energy demanding. Alternative butanol recovery methods, including adsorption, pervaporation, liquid extraction, and gas stripping are considered the most promising techniques for low-energy-demanding butanol recovery (Chuang et al. 2014).

While some biorefinery process equipment can be regarded generic and allow for alternating production of ethanol and butanol (e.g. raw material handling, pretreatment, enzymatic hydrolysis, waste management), different types of bioreactors or supplementary equipment for fermentation might be required. Furthermore, as argued above, the equipment required for down stream processsing or recovery of the butanol is substantially different from that of ethanol. Biorefineries designed to produce both ethanol and butanol will consequently imply significantly higher investment costs, than biorefineries producing ethanol or butanol alone.

#### 6.2 HYDROGEN

Hydrogen constitutes a promising option in future biofuel production and hydrogen fuelling stations are currently under construction (<u>www.vatgas.se</u>, visited 2016-02-24). The use of microorganisms in the production of hydrogen is comparatively immature, i.e. at a technology readiness level (TRL) of 2-5, but the field is advancing rapidly. It has been argued that the major challenges to the full realization of hydrogen as biofuel are rather related to technical aspects of storage and transportation (Guo et al. 2010).

In general, the metabolism and physiology of the microorganisms of relevance to hydrogen production is relatively similar to those used in butanol production. Hence, such similarities may potentially be exploited to increase the manufacturing flexibility. For example, the oxygen sensitivity is similar between the two types of microorganisms, meaning that certain equipment (e.g. bioreactors) can be shared. The hydrogen production process may possibly be integrated with that of ethanol, since some hydrogen producing bacteria utilize C5 (e.g. the thermophile *Caldicellulosiruptor saccharolyticus*) in favour of C6 (preferred by e.g. *S. cerevisae*). Such synergistic features may exert positive effects on both feedstock and product flexibility.

A disadvantage of *C. saccharolyticus* is that is grows only at low cell densities. Thus, the exploittation of *C. saccharolyticus* requires bioreactor designs that enable high biomass contents. One such design involves the use of up-flow anaerobic blanket (USAB), in which biofilm formation is facilitated (Pawar et al. 2015). Because the product generated is gas mixture of a H<sub>2</sub> and CO<sub>2</sub>, in proportions of 60:40, an upgrading step is required. It has been shown that upgrading technologies similar to those applied in biogas production can be used (Willquist et al. 2012). Alternative uses of hydrogen include its' use as a reducing agent in the production of chemicals and its' conversion to heat and power using a combined heat and power fuel cell. Such cells display high energy efficiencies of up to 90%, depending on the application.

#### 6.3 BIOGAS

Processes characterized by anaerobic digestion have traditionally been used to produce methane for biogas as fuel, and aim at reducing the carbon oxygen demand (COD) in the effluents. Methane production processes have proven robust, efficient in reducing the COD and are considered very flexible in terms of feedstock heterogeneity. However, these processes are normally run with long residence times, resulting in low volumetric productivities and demands of large digestion tanks.

In order to increase the manufacturing flexibility of biorefineries, different principles of biogas integrations exist. By introducing an anaerobic digestion reactor as the natural endpoint of the process, substrates not utilized by the sugar fermenting microorganisms will be converted to biogas. Thus, a biogas production unit may allow for high productivities and small reactor volumes using e.g. the USAB design, or other continuously operating reactors. A high productivity and stability of the biogas production can be expected following these processes, as acetate and small amounts of sugars residues will be the main substrates (Willquist et al. 2012).

Since residues of ethanol, acetate and sugars are all easily digested, the integration of methane processes with ethanol production exhibit large potential with respect to most aspects of manufacturing flexibility. It should be noted, however, that the conditions applied prior to methane production may negatively influence the conditions of the biogas tank. For example, the use of sulphuric acid in the pretreatment of feedstocks may favour sulphate reducing microorganisms and disfavour methanogenic microorganisms, and consequently reduce methane production. Appropriate control systems addressing variables such as the SO<sub>4</sub>/COD and NO<sub>3</sub>/COD ratios are required in the processing management. The role of other methanogenesis inhibiting compounds, such as ammonia, lignin and phenols are described by e.g. Op den Camp et al. (1988); Parkin et al. (1990); Pender et al. (2004); Lefebvre O. & Moletta R. (2006); Chen et al. (2008), and Hemandeza & Edyneand (2008).

The concept of connecting biogas units to effluent streams of neighbouring industries is gaining increasing attention. Biogas production is a particularly appealing variant of industrial symbiosis, due to the robustness of the process. The concept is applied at the Domsjö Fabriker in Örnsköldsvik where effluents from Domsjö Fabriker's, Akzo Nobel's and Sekab's primary production lines are digested. Here, the three industries share the investment cost of the biogas plant. While it may prove economically advantageous to share investment costs and increase the substrate volumes, the effects of variability in physical and chemical nature of different substrates on biogas productivity may be limiting.

The biogas produced may either be used internally in the biorefinery as an energy carrier, or as a vehicle fuel following an upgrading step. A number of options for biogas upgrading exists, out of which the water scrubber technique is the most predominant. Investment costs are however significant, and the impact of upgrading technologies on energy balances and process economy is currently under investigation (in an f3 project titled "Techno-economic analysis of biomethane production with novel upgrading technology").

# HIGHLIGHTS

### **BIOFUELS OTHER THAN ETHANOL**

- Butanol is a viable alternative to ethanol. The conversion of both C5 and C6 sugars to butanol facilitates feedstock flexibility and the use of substrates with high hemicellulose contents, like wheat bran.
- The equipment required for production, separation and upgrading of butanol differs from that of ethanol, which may put economical and spatial constraints on a biorefinery. Minimizing process inhibitory factors and maximizing microbial cell concentrations under strict anaerobic conditions are key challenges in butanol production.
- Similar to butanol, microbial hydrogen production implies high feedstock flexibility, but processing conditions different from those in ethanol production. The hydrogen formed must be used in short time, which may limit its role in a fluctuating market.
- Analogies in the requirements of processing conditions between butanol and hydrogen enable an option of flexibility in between the production of these biofuels.
- Integrating a biogas production unit with that of ethanol increases the manufacturing flexibility, more of less irrespective of the process design. Biogas production implies high feedstock flexibility and adds environmental benefits to the biorefinery process. Further, it can be used as a recipient of neighboring industrial waste streams.

## 7 BIOCHEMICALS AND OTHER PRODUCTS

Microorganisms fermenting sugars from lignocellulosic feedstocks do not only generate biofuels. A number of other metabolites are also produced, some of which can be concentrated and marketed as co-products, or in times of high market demand, even as the main products. The production rates depend on e.g. physical conditions and the types of microorganism used, wherefore several aspects of technology and microbiology must be assessed jointly.

#### 7.1 LACTIC ACID

Lactic acid is a versatile chemical mainly produced through fermentation of sugars from agricultural crops. Today, lactic acid is used in the food-, medicine-, material-, and cosmetics industry. The world market for lactic acid is in the range of a few hundred thousand tons per year. A dramatic increase in the lactic acid demand is expected in the future due to an increased interest in bioplastics made from poly lactic acid (PLA). Production of lactic acid from lignocellulosic feedstock by fermentation is a promising process that could be realized at industrial scale within a few years.

Lactic acid bacteria are the most commonly used organisms for production of lactic acid. They are considered very robust and are used in various industrial applications, not the least in the food processing industry. Similar to yeast, these microorganisms are facultative anaerobes that thrive in aerobic conditions but may switch to a fermentation mode under anaerobic conditions. Some lactic acid bacteria produce very high yield of lactic acid from glucose (theoretical yield: 1 g of lactic acid/g consumed glucose). The downstream processing of lactic acid production is on the other hand quite complex and includes process operations such as precipitation, extraction, and electrodialysis. Thus, the major cost in lactic acid production is related to downstream processing and not the feedstock, as in the case of the production of many bulk chemicals (e.g. ethanol).

A reasonable size of a lactic acid production plant can be estimated to that of a normal-sized or small ethanol plant (approx. 50 000 tons/year). The possibility to switch between production of ethanol and lactic acid may prove a viable concept. It is most likely that the same processing equipment, excluding the downstream processing step, could be used for both processes. Costs of additional equipment needed in downstream processing need to be weighed against the potential benefits of manufacturing flexibility.

#### 7.2 OTHER ORGANIC ACIDS

A wide range of organic acids can be produced by fermentation of sugars derived from lignocellulose. Examples, other than lactic acid, that potentially can be produced in a flexible biorefinery are: succinic acid, itaconic acid, acetic acid, 3-hydroxypropionic acid, ascorbic acid, adipic acid, acrylic acid, and malic acid (Wyman, 2003; Carole et al. 2004; Kamm & Kamm, 2004). The production processes of these organic acids may differ slightly, but will in general be similar to that of lactic acid. Hence, the main challenges to increase manufacturing flexibility with respect to these products are likely to be related to the complexity of the downstream processing.

#### 7.3 POLYHYDROXYALKANOATES (PHA)

Biopolymers such as polyhydroxyalkanoates (PHA) exhibit a concrete potential to replace traditional plastics based on petroleum for a variety of mainstream applications (Keshavarz & Roy, 2010; Laycock et al. 2013). Examples of these applications include biodegradable packaging materials and high-value products in the biomedical industry (Philip et al. 2007). A number of naturally occurring microorganisms possess the ability to convert activated sludge biomass from industrial and municipal water management into PHA (Keshavarz & Roy, 2010). Other substrates which are easily converted by microorganisms to PHA include acetate; a by-product commonly formed during pretreatment of lignocellulosic feedstock prior to ethanol fermentation. Since the rate of acetate formation in lignocellulosic biomass may be manipulated by the addition of acids, the conditions of the pretreatment step may theoretically be designed to maximize acetate formation, and subsequent PHA production. Because acetate is also a by-product formed during hydrogen production of *Clostridia*, another option to increase the yield of acetate, and consequently PHA, is to direct the sugars formed during hydrolysis towards the fermentation of hydrogen, rather than ethanol. Thus, given that the different demands on processing equipment of hydrogen and ethanol are met in a biorefinery, acetate and PHA formation may constitute important aspects of manufacturing flexibility to meet fluctuations in market demands. It should be emphasized here, that the theoretical grounds of this hypothesis needs further validation in laboratory experiments.

The variety of microorganisms capable of converting a range of substrates to PHA has generated an increasing scientific interest (Nikodinovic-Runic et al. 2013). At present, a challenge to wider applications and commercialization of the technique lies in the extraction and transformation process, since PHA is generated intracellularly. The potential of utilizing the entire microorganism, including its' PHA contents, has not been fully explored.

#### 7.4 SINGLE CELL PROTEIN (SCP)

All biorefinery processes described in this report are based on the activity of microorganisms exhibiting metabolic activities which can be utilized for the valorisation of lignocellulosic feedstock. While the focus of biorefineries primarily lies on the production of biofuels and other products, there is now growing interest in utilizing the microorganisms as such. The term single cell protein (SCP) is used in relation to the nutritive value of protein-rich microorganisms, such as yeast, filamentous fungi, bacteria and algae. During the 20<sup>th</sup> century, significant attention was directed towards SCP during periods of wars or other crises when food scarcity was an issue. During the last few years the interest for SCP has increased again, mainly as an alternative protein source in animal feed (Alriksson et al. 2014). Much of this interest derives from concern raised regarding the environmental sustainability of traditional protein sources, including fish meal and soybean meal. A full, or even partial, replacement of these feedstuffs in the animal feed industry would require gigantic volumes of alternative protein sources, making SCP a biorefinery product with a significant future potential.

The SCP can be produced from lignocellulosic sugars and simple nutrients by aerobic cultivation. The downstream processing is relatively simple compared to that of biochemicals. It consists in general of a cell separation step (filtration or centrifugation), washing, and drying step. The size of a production plant for SCP would likely be in the same range of that of an ethanol plant. Since the process is aerobic, slightly modified versions of the bioreactors used for ethanol production (i.e.

stirred tank reactor) could be used for production some types of SCP. However, other types of SCP require completely different process equipment, such as air lift reactors and bubble column reactors. The possibility to alternate between the production of ethanol and SCP could be feasible if bioreactors suitable for both applications are chosen. The equipment for downstream processing and product storage and packaging is also quite different and needs to be taken into consideration.

# HIGHLIGHTS

### **BIOCHEMICALS AND OTHER PRODUCTS**

- Lactic acid and other organic acids display future market potential. Whereas the yield of lactic acid from sugars generally is high, the downstream processing constitutes a major barrier in costeffectiveness and manufacturing flexibility.
- Polyhydroxyalkanoates (PHA) exhibit potential to replace petroleum plastics, and can be produced using a number of microorganisms and substrates, such as acetate. Manipulating the pretreatment of lignocellulosic feedstock is a possible means to increase PHA productivity.
- Single cell protein (SCP) is receiving renewed market interest and can be cultivated using lignocellulosic sugars, simple nutrients and processing equipment similar to that of ethanol production.

## 8 CONCLUDING REMARKS

Biorefineries which solely rely on the production of single high-volume low-value products, such as ethanol, are highly dependent on the efficiency of their processes and optimal utilization of their equipment. Because of feedstock and product market prices fluctuations, there is typically little room for a complete remodelling of the production process. Such facts stress the usefulness of flexible systems allowing for simultaneous adjustments.

This report sheds light on the role of manufacturing flexibility in a biorefinery producing ethanol. The complexity of biorefinery operations and the interdependency of the processing steps involved, do not allow for a comprehensive and coherent picture. However, a number of options illustrated in research and in practice have been emphasized.

Sweden holds excellent prerequisites for biorefinery enterprises. Both forestry and agricultural feedstocks are abundant, although their geographical and seasonal dispersion may limit a full flexibility in their interchangeability. Their chemical constituents will largely determine the design of a facility, and their intra- and inter-variation are likely to influence processing conditions.

The choice of feedstock pretreatment methods will have significant impact on subsequent processing steps and product yields. Not only do pretreatment methods differ in their effect on the feedstock, but chemical residues and inhibitors formed may infer substantial consequences later in the process.

Products such as biobutanol, biogas, hydrogen, various biochemicals, and single cell protein could potentially be produced in biorefineries aiming at high manufacturing flexibility. The equipment required in many processing steps can be considered as generic, and be used in the production of several different products with only minor modifications. However, processes used for separation and purification of different products can vary vastly, and in many cases represent the largest cost in production. The potential benefits of flexibility need to be weighed against the cost for additional process equipment and the after-effects of process remodelling.

Prospects of increasing the manufacturing flexibility of any biorefinery operation must be based on comprehensive studies of the effects on the production as a whole, and the interdependency of the different processing steps, complemented with techno-economic assessments of different options. To identify the most promising options to increase the manufacturing flexibility of biorefineries, and potential bottlenecks thereof, further studies may apply a scenario-based case study from a techno-economic perspective.

Table 4 summarizes the technological maturity and general advantages and disadvantages of some biofuels, biochemicals and other products of relevance to biorefineries, and the prerequisites for the integration of their production in an ethanol plant.

Table 4. A summary of the technological maturity and general advantages and disadvantages of some
biofuels, biochemicals and other products of relevance to biorefineries, and the prerequisites for the
integration of their production in an ethanol plant.

Product	TRL	General advantage	General disadvantage	Prerequisites for integration with an ethanol plant
Butanol	8	High market potential as fuel additive and precursor for JET fuels.	Low yields and - Requires special equipment for productivities, fermentation and upgrading.	
Hydrogen	MEDI - Requ Fogen 2-5 reducing agent for e.g. lignofuels and biodiesel + Prefet		MEDIUM - Requires special equipment for fermentation and upgrading <sup>(1)</sup> . - Difficult to store. + Prefers the C5 sugars. + High substrate flexibility.	
Biogas	9	Several applications as vehicle fuel and chemical.	Low productivity.	<ul> <li>HIGH</li> <li>Requires special equipment for gas upgrading.</li> <li>+ Uses all by-products from an ethanol process (C5, acetate and ethanol).</li> <li>+ Low investment cost of the reactor vessel.</li> <li>+ Enables effluent water treatment.</li> </ul>
Lactic acid	7	High yields. High market potential.	MEDIUM Complex - Requires additional equipme downstream downstream processing	
РНА	7-8	High market potential of biodegradable plastics.	Difficult to extract the polymer from the cell.	<ul> <li>HIGH</li> <li>Sensitive to high phosphorus contents.</li> <li>+ Enables effluent water treatment.</li> <li>+ Uses weak acids from the ethanol process.</li> <li>+ Low investment cost for the vessel.</li> <li>+ Polymer extraction can be made off-site.</li> </ul>
Single cell protein	6	High price and volume market potential. Simple downstream processing.	tial. Complex + High utilization of complex substrate	

 $^{(1)}$  The produced hydrogen can be used directly in fuel cells to produce electricity, and the same upgrading facility as for ethanol can be used for CO<sub>2</sub> and CH<sub>4</sub> removal.

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### 10 APPENDIX

Table 5. Gross annual supplies (tonnes, dm in 2013) and geographical distributions of lignocellulosic agricultural feedstocks in Sweden. Percentages indicate the relative contribution of each region to the national supply of each feedstock. See Figure 8 (Appendix) for definitions of areas.

	Maize stover <sup>1</sup>	Wheat straw <sup>1</sup>	Wheat bran <sup>1,2</sup>	Green fodder (early harvest) <sup>1</sup>	Green fodder (late harvest) <sup>1</sup>	Reed canary grass <sup>3</sup>	Total
South <sup>4</sup>	7 000 (100%)	858 000 78%	40 000 (66%)	1 368 000 (57%)	1 008 000 (72%)	0 (0%)	3 281 000
Mid⁵	0 (0%)	242 000 (22%)	20 000 (33%)	600 000 (25%)	252 000 (18%)	200 (5%)	1 114 200
North <sup>6</sup>	0 (0%)	0 0%	0 (0%)	408 000 (17%)	140 000 (10%)	3 800 (95%)	551 800
Total	7 000	1 100 000	60 000	2 376 000	1 400 000	4 000	4 947 000

<sup>1</sup>Values recalculated from Official Statistics of Sweden (2014b).

<sup>2</sup>Refers to volumes used in animal feed, not in food. Values are approximated.

<sup>3</sup>Reed canary grass gross supply was estimated using cultivated areas in Sweden 2014

(www.bioenergiportalen.se) and expected hectare yields (Börjesson, 2007).

<sup>4</sup>The south region roughly translates to Götaland and includes sub-regions 1, 2, 3 and 5 in Figure 8 below.

<sup>5</sup>The mid region roughly translates to Sveland and includes sub-regions 4 and 6 in Figure 8 below.

<sup>6</sup> The mid region roughly translates to Norrland and includes sub-regions 7 and 8 in Figure 8 below.

Table 6. Approximate prices (SEK/ton dm) and chemical compositions (in dm) of lignocellulosic
agricultural feedstocks in Sweden.

ugi icuitui ui iccu	Maize stover	Wheat straw	Wheat bran	Green fodder (early harvest)	Green fodder (late harvest)	Reed canary grass
Approximate price <sup>1</sup>	500	500	2 000	1500	1000	750
Approximate composition						
Assumed dm	88%	88%	88%	83%	83%	88%
Cellulose <sup>2</sup>	44%	36%	14%	20%	31%	49%
Hemicellulose <sup>2</sup>	22%	33%	43%	22%	26%	28%
Lignin <sup>2</sup>	17%	19%	12%	13%	16%	10%
Sugars <sup>2</sup>	5%	1%	5%	11%	2%	N/A
Protein <sup>2</sup>	4%	4%	17%	12%	8%	6%
Ash <sup>2</sup>	7%	5%	6%	7%	7%	6%

<sup>1</sup>Values are approximated, based on common trade in Sweden.

<sup>2</sup>Values drawn, or recalculated from Official Statistics of Sweden (2014b), Buranov et al. (2008), Manavalan et al. (2015), Pahkala et al. (2007), Lindgren et al. (1980).

Table 7. Mean annual volume increment (tons dm/year) on productive forest land and geographical distribution in Sweden<sup>1</sup>; protected productive forest land excluded. Percentages indicate the relative contribution of each region to the national supply of each feedstock. See Figure 9 (Appendix) for definitions of areas.

	Norway spruce	Scots pine	Birch	Total
South	7 900 000	3 100 000	1 800 000	12 800 000
(Götaland)	(38%)	(18%)	(24%)	
Mid	5 700 000	4 800 000	1 600 000	12 100 000
(Svealand)	(28%)	(28%)	(21%)	
S. North	4 800 000	4 700 000	2 300 000	11 700 000
(S. Norrland)	(23%)	(28%)	(30%)	
N. North	2 300 000	4 200 000	1 900 000	8 500 000
(N. Norrland)	(11%)	(25%)	(25%)	
Total	20 600 000	16 900 000	7 600 000	45 100 000

<sup>1</sup>Values used, or recalculated, from Official Statistics of Sweden (2014a).

# Table 8. Average pulpwood prices (SEK/ton dm) in 2009-2013 and chemical compositions (in dm) of stemwood of Norway spruce, Scots pine and birch.

	Norway spruce	Scots pine	Birch
Average pulpwood price <sup>1</sup>	769	740	629
Approximate composition			
Cellulose <sup>2</sup>	42.0%	40.7%	43.9%
Hemicellulose <sup>2</sup>	27.3%	26.9%	28.9%
Lignin <sup>2</sup>	27.4%	27.0%	20.2%
Extractives <sup>2</sup>	2.0%	5.0%	3.8%

<sup>1</sup> Official Statistics of Sweden (2014a).

2 Bergström & Matisons (2014)

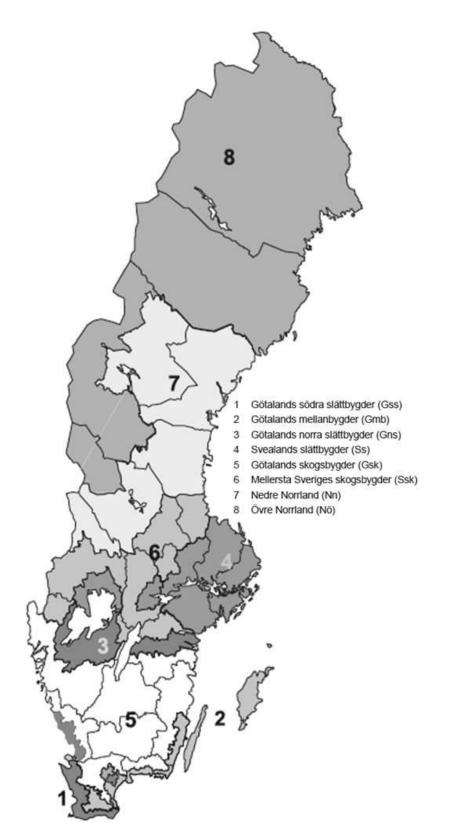


Figure 8 Geographical division of agricultural production areas of Sweden. Modified from Official Statistics of Sweden (2014b).



Figure 9 Geographical division of forest production areas of Sweden. Modified from Official Statistics of Sweden (2014a





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