EVALUATION OF LIGNOCELLULOSIC BIOMASS UPGRADING ROUTES TO FUELS AND CHEMICALS

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The study evaluates wood and non-wood lignocellulosic conversion into biofuels and renewable intermediate chemical products, on the basis of material efficiency, heat content in final products (lower heating value) and properties of fuel components, as related to their use, existing cars and storage. This type of conversion efficiency analysis can be viewed as a first step in biorefinery route optimization. The upgrading routes considered here include gasification, pyrolysis with subsequent gasification, ethanol, anaerobic acetic acid and ABE-fermentation, digestion and chemical conversion of sugars into fuel. The material efficiency is calculated on the basis of potential yields. In addition, the subsequent conversion of these intermediate products to fuel components through chemical reactions has been considered. Intermediate chemicals, such as ethylene, propylene, ethyl acetate and acetic acid, have also been analyzed. Chemical upgrading of sugars, acetic acid fermentation and gasification converted most of the raw material heat content in the products. The components with good properties containing some oxygen, such as butanol, methyltetrahydrofuran (MTHF) and ethers, appeared as promising from the viewpoint of both fuel properties and biomass conversion.

Keywords: biorefinery, biofuels, biofuel properties, biomass conversion evaluation, lignocellulosic biomass upgrading

INTRODUCTION

The sustainable use of forest biomass for fuels and chemicals, instead of fossil fuels and petrochemicals, can significantly reduce carbon dioxide emissions. According to a recent estimate of Parikka,[1] the worldwide total sustainable biomass energy potential is of 104 EJ/a, representing about 30% of today's total global energy consumption. Since biomass cannot cover the whole global energy demand, to play a significant role in preventing climate change, it needs to be efficiently used. Therefore, it is important to find routes that retain the maximum amount of material and energy content of feedstocks in the products.

However, good material and heat content are not sufficient if the products do not have suitable properties. For fuels, the important properties include octane or cetane number, vapor pressure, emission produced upon combustion, cold properties, toxicity, energy density, corrosiveness, etc. Often, the properties are also related to the value of the products. Considering such factors can be also seen as a step in optimizing biomass utilization in a biorefinery. These results can be used to find potential routes that can be further analyzed more rigorously by including production costs.

Gasification based routes

Lignocellulosic biomass utilization involves converting the biomass into intermediates and subsequently converting such intermediates into chemical or fuel components. The most common intermediates are synthesis gas (mixture mainly of CO and H_2), pyrolysis oil, sugars, lignin, cooking liquor and biogas. If the intermediate, for example synthesis gas, can be purified to a level suitable for subsequent processes, the same procedures can be applied for intermediates, as in oil refining or petrochemical industry. The synthesis gas can be produced by the gasification of dried biomass at high temperatures (around 800 °C), using oxygen or steam. Alternatively, gasification can be performed directly on wet biomass under supercritical water conditions (under which water will react with the biomass). Supercritical gasification of paper sludge and black liquor was described by Rönnlund *et al.*[2] The synthesis gas can be used in numerous applications for both fuel and chemical production. For example, methanol can be produced by methanol synthesis from synthesis gas containing a very low level of sulfur below 1 vol ppm, but a high fraction of residual CO_2, by a catalytic reaction. Examples of low-pressure processes are, for example, the ICI process, using[3,4] a copper oxide catalyst at 50-100 bar, and the Lurgi process, demonstrated in Germany in the 1970s.

Alternatively, the synthesis gas can be converted into hydrocarbons by the well-known Fischer-Tropsch process, used in Germany in the Second World War to produce synthetic gasoline. FT synthesis is a nonselective process producing a wide range of hydrocarbons with 1 to 100 carbons. Iron and cobalt catalysts are mostly used. High selectivity can only be achieved for methane and high molecular mass wax. The FT process is operated[5] both at high temperatures (330-350 °C), for the production of gasoline and light olefins, and at low temperatures (220-250 °C), for the production of waxes and diesel. FT synthesis was traditionally done in circulated fluidized bed reactors but, nowadays, slurry reactors or tubular fixed bed reactors are mostly used. The high molecular wax can be hydrocracked and isomerized in an oil refinery into high quality diesel fuel, lube oils and naphta, which can be cracked into olefins.

Dimethylether (DME) is another fuel component that can be obtained from syngas, with properties similar to liquefied petroleum gas. It can be used as diesel, but it requires an infrastructure suitable for liquefied gas. Synthesis gas can be converted directly through methanol into DME, with a dual function catalyst, which involves the methanol synthesis reaction, shift reaction and the DME synthesis reaction. When the DME reaction is performed simultaneously with the methanol synthesis one, the equilibrium in the methanol reaction is shifted towards the product. Therefore, by this route, a much higher conversion is achieved and lower pressure can be used than by methanol synthesis.[6]

Methanol can be also converted into olefins in the MTO process with ZSM-5 catalyst,[7] or into gasoline with methanol, in the gasoline (MTG) process. However, gasoline has a high olefin content, exceeding the specification for gasoline. The olefins produced can be either hydrated into alcohols with water, or recovered as such.[8]

Clean synthesis gas (CO and H_2) and steam can be catalytically converted by shift reactions to hydrogen and carbon dioxide. The process is usually performed stepwise, over a high temperature range, between 310 and 500 °C, using iron–chromium oxide catalysts, and over low temperatures (approximately 180-270 °C), using copper–zinc catalysts.[9]

Alternatively, the synthesis gas can be converted into methane containing a gas called SNG (Synthetic Natural Gas). Carbon monoxide and dioxide are converted with, for example, nickel catalyst into methane and water.[10] The process is used in hydrogen production plants and for ammonia production, to remove the carbon monoxide from hydrogen gas. The reaction is strongly exothermic.

There are no commercial plants yet to perform mixed alcohol synthesis. The low selectivity and conversion prevented the commercialization of mixed alcohol synthesis. The obtained yields are recorded by the US Renewable Energy Department.[11] Also, isosynthesis, which produces branched hydrocarbons, such as isobutane and isobutene, has not been commercialized yet.[12] Temperatures of approximately 400 °C and pressures from 150 to 1000 bar are needed.

On the other hand, oxosynthesis, also called hydroformulation, has been commercialized in chemical industry for producing, for example, butyraldehyde or propenaldehyde. It involves the reaction of CO and H_2 with olefinic hydrocarbons, to form an isomeric mixture of normal and isoaldehydes. Oxosynthesis is a rapid reaction catalyzed by soluble cobalt or rhodium complexes.[13] In this paper, mixed alcohol synthesis, isosynthesis, MTG process and hydroformulation were not considered. Hydroformulation was not considered, as the process producing biofuel alcohols would need many processing steps, if all components are produced from lignocellulosic biomass.

In addition, acetic acid is produced commercially from methanol and carbon monoxide through carbonylation. Catalyzed processes are used, for example Monsanto or Cativa, with rhodium or iridium metal complexes.[14]

Pyrolysis

Another main technology is the pyrolysis of biomass into bio-oil, which means heating of biomass in the absence of oxygen, leading to its decomposition into different products. Fast pyrolysis is a high-temperature process in which biomass is rapidly heated (in seconds), then converted into gases, bio-oil and charcoal. The bio-oil from pyrolysis is corrosive, contains water and has to be upgraded prior to its usage as a traffic fuel. The pyrolysis upgrading routes presented by Gabrieli *et al.*,[15] including decarboxylation and hydrodeoxygenation or cracking, are all based on the reduction of the oxygen content in the bio-oil.

Fermentation route

Cellulose and hemicellulose, which are polymers of different sugar monomers, can be separated from lignin and extractives, and hydrolyzed into their monomer units by acid, alkaline or enzymatic hydrolysis. The monomer units or the monosaccharides can be processed into chemicals or fuels either by biochemical routes, using microorganisms, or by thermo-chemical routes. In conventional ethanol fermentation, traditional yeast or bacteria can only ferment hexoses (C6 sugars). A variety of bacteria are able to metabolize and ferment both hexose and pentose sugars, but all produce a mixture of fermentation products.[16]

Anaerobic acetic acid fermentation has the advantage that no carbon is lost as carbon dioxide. The disadvantage is that the already low concentration of acetic acid is toxic for the *Clostridium* bacteria. The acetic acid can be esterified with ethanol, using acid catalyst to ethyl acetate. The low boiling azeotrope of the ethyl acetate with water and ethanol can be used to drive the reaction equilibrium towards the product. Ethyl acetate is less corrosive than acetic acid. Esters can be hydrogenated into alcohols using suitable catalysts, usually at a fairly high temperature (250 °C) and high pressure (200-300 bars).[17] By this route, the yield of ethanol is significantly higher than that obtained by ethanol fermentation. The needed hydrogen can be produced by gasification into synthesis gas and converting CO into hydrogen and CO_2, by the water gas shift reaction.

Butanol can be produced by dehydrogenation from ethanol into acetaldehyde, followed by aldol condensation into crotonaldehyde, with subsequent hydrogennation into n-butanol. Partial hydrogenation of crotonaldehyde yields butyraldehyde. Ethylene can be obtained[18] by the dehydration reaction with solid acid catalyst above 200 °C with alumina, silica, manganese and ferric oxides, special zeolites with a high yield of 99%. Correspondingly, propylene can be obtained from isobutanol. For the commonly used petrochemicals, these routes are interesting, due to the less severe reaction conditions, compared to the traditional steam crackers used in the petrochemical industry. Under acidic conditions, combined with the removal of the formed water butyraldehyde and ethanol, diethoxybutane with attractive diesel fuel properties can be obtained.

The ABE (acetone, butanol, ethanol) fermentation of sugars with *Clostridium acetobutylicum* bacteria produces n-butanol, acetone, ethanol, hydrogen and carbon dioxide. The hydrogen produced can be used, for example, to hydrogenate acetone into isopropanol and to produce methanol from hydrogen and carbon dioxide through methanol synthesis. Butanol, isopropanol and ethanol can be converted into ethers (dibutylether, di-isopropylether and diethylether) with attractive fuel properties as a diesel fuel.

Obviously, sugars can be also used as raw materials for microbes in the production of raw material for biopolymers, such as lactic acid, succinic acid, etc.

Other routes

The production of alkanes, similar to that of FT-diesel from sugar, has been described by Huber *et al.*,[19] who reported selective formation of alkanes (C7 to C15) with dehydration/hydrogenation over bifunctional catalysts at around 250 °C and 52-60 bars, in a four-phase system. The hydrogenated phase is separated from the water phase when the reaction proceeds. Alternatively, sugars or sorbitole obtained through hydrogenation of sugars can be treated by hydrogenolysis, to obtain ethylene glycol, used as an anti-freezing fluid, and glycerol, as described by Dasari.[20]

Sugars can be also converted to valuable gasoline fuel components, by dehydration through 5-hydroxymethylfurfural (HMF) and hydrogenolysis by various paths, as presented by Román-Leshkov *et al.*[21] The gasoline components have high octane numbers, low solubility in water and a higher energy content than ethanol, which enables them to be mixed in a higher fraction than ethanol. By the Biofine process, levulic acid and a valuable chemical intermediate can be produced,[22] to be further used for the production of methyl tetrahydrofuran gasoline fuel, succinic acid – raw material for biopolymers, etc.

Biomass can be also converted into biogas by anaerobic digestion using mesophilic (30-35 °C) or thermophilic (50-55 °C) bacteria. The process is relatively slow, 50% of the dry matter being decomposed[18] within 10 days. However, not all biomass can be converted, for example, lignin does not decompose. The produced biogas contains carbon dioxide, methane and small amounts of sulfur compounds, nitrogen and ammonia. Methane can be further converted, with steam reforming, into synthesis gas.

Objective

The routes presented here are evaluated for both material efficiency, product heat content and product properties. Gasification, calculated by Gibbs energy minimization, gives maximum potential yields. The subsequent reactions, fermentation and digestion, are considered on the basis of chemical reactions assuming stoichiometrical yields. The maximum potential amounts of synthesis gas and of its derivatives were calculated upon gasification of the whole biomass for eight different wood and non-wood lignocellulosic feedstocks. A second case was calculated for biomass conversion to pyrolysis oil, with subsequent gasification and conversion into fuel components. In addition, the maximum potential amount of synthesis gas and conversion products that could be obtained from the lignin and extractives of pine and birch was calculated. The maximum potential amount of products should be seen as a first step in evaluating upgrading paths. Then, feasible routes can be studied in more detail, by taking into account the selectivities with particular catalysts for given chemical reactions. A comparison of the maximum potential amount with the experimental yield of synthesis gas has been made by Melin *et al.*[23] As, in some upgrading paths, hydrogen is needed, the question is whether hydrogen could be produced by gasification of both lignin and biomass extractives. Further on, the amounts of different components that could be obtained through hydrolysis and fermentation, digestion or chemical conversion of the sugars from cellulose and hemicellulose were calculated. For the products obtained through hydrogenation, the necessary amount of hydrogen was computed.

METHODS

The following raw materials were considered: Pine, Spruce, Black Alder, Aspen, Silver Birch, Eucalyptus, Larch, bagasse and wheat straw. The composition was analyzed for stem wood. The composition of bark and needles differs significantly from that of stem wood.

The raw materials used in the calculation are presented in Table 1. The ultimate analysis and composition obtained after hydrolysis was used as a basis in the calculations. The lower heating value was either calculated or obtained directly from the references shown. For the sake of comparison, pyrolysis oil was also included as a feedstock. The composition of pyrolysis oil was in accordance with IEA.[24] According to IEA, for pyrolysis, the typical yield of liquid hydrocarbons is of 75%, on an anhydrous basis. For lignin, the composition of the remaining liquor was calculated by subtracting the cellulose and hemicellulose amounts from the original feedstock. The lignin heating values were assumed for both lignin and extractives.

For products and intermediates, the material efficiencies were calculated, *i.e.* mass of product (fuel components or chemicals), compared to the mass of the raw material on dry basis. In addition, the amount of heat in the products (fuel components) based on lower heating values were compared with the lower heating value of the raw material. The mass of carbon and hydrogen in the product was also calculated and compared with that of the raw material. This is important, since the rest of carbon is generally lost as carbon dioxide during processing.

For biofuel components, the important fuel properties, such as vapor pressure, flash point, octane or cetane number, water solubility and corrosiveness, were obtained from literature. Different fuel components were evaluated as to their use in conventional diesel and gasoline cars and as to their storage. The material and energy efficiency of a small number of petrochemicals that could be obtained in biofuel production as intermediates or bioproducts were also considered in this study. The application of these chemicals was also discussed.

Gasification

Due to the endothermic nature of the gasification process, one should take into account the enthalpy balance when calculating the yield of product from syngas, since the required heat is produced by the partial combustion of the raw material. The composition of the synthesis gas was calculated by Gibbs energy minimization, with a simulation software. The Gibbs energy minimization determines the reaction equilibrium and the maximum theoretical conversion under given conditions.

Methane, acting as an inert gas in many refining processes, was further reformed by autothermal reforming into CO and H_2. Both gasification and reforming were simulated by minimization of Gibbs energy. Solid carbon, CO, H_2O, O_2, CO_2, S, SO_2, N_2, CH_4 and C_2H_4 were selected as reacting components. Ash was modeled as CaO and it was assumed that it does not react, even though in reality it may react with carbon dioxide. In most feedstocks, the amount is so small that it can be neglected. The product gas contained only CO, H_2O, N_2, CH_4 and SO_2 in significant concentrations. For wood and non-wood biomass, it was assumed that the biomass feedstocks contained 50 wt% water and 50% biomass. The biomass feedstock was dried to 15 wt% water with hot gases after gasification, so that the hot exhaust gas temperature was of at least 200 °C. The evaporated water was fed to the gasification stage with the biomass. Pyrolysis oil was assumed to contain 25 wt% water and the lignin part was assumed to be in a solution containing 60 wt% lignin and 40 wt% water.

Gasification was performed at 800 °C, at 5 bar. Sufficient oxygen was added to raise the temperature of the feed to 800 °C. After the gasification stage, the gas mixture was reformed to convert residual methane into synthesis gas by heating to 950 °C. Reforming was modeled with Gibbs energy minimization and enough oxygen was added to raise the temperature from 800 to 950 °C.

Gasification with oxygen at 5 bar was preferred in this study because Kurkela *et al.*[25] concluded that the gas produced from such a process is suitable for all known fuel and chemical production processes. In addition, the reformation of synthesis gas produced with indirect gasification by steam is more challenging. They reported that only limited benefit can be obtained by increasing the gasification pressure beyond about 5 bar in methanol synthesis.

FT synthesis was calculated by assuming that the chain growth follows the Anderson-Schulz-Flory distribution with a chain growth probability $\alpha = 0.87$,[26] giving mainly diesel range products. The product distribution as a function of α is provided in literature.[27]

Subsequent upgrading reactions

The potential material efficiencies were calculated for reactions (1) to (7). The ratio between CO and H_2 was first adjusted for the synthesis gas, by the gas shift reaction. Reaction 1 was also considered to be employed in hydrogen production.

Shift reaction $$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (1)$$

Methanol synthesis $$CO + 2H_2 \rightarrow CH_3OH \quad (2)$$

Methanol carbonylation into ethanol $CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$ (3)

Methanol carbonylation to acetic acid $CH_3OH + CO \rightarrow CH_3COOH$ (4)

DME synthesis $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO2$ (5)

The synthesis reaction represents the total reaction, when methanol synthesis (2) and the gas shift reaction (1) occur simultaneously.

MTO to olefins from DME $\frac{n}{2}CH_3OCH_3 \rightarrow C_nH_{2n} + \frac{n}{2}H_2O$ (6)

where n is 2, 3 and 4.

Hydration of olefins into alcohols $C_nH_{2n} + H_2O \rightarrow C_nH_{2n+1}OH$ (7)

Methanisation $CO + 3H_2 \rightarrow CH_4 + H_2O$ (8)

FT synthesis $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (9)

The weight fractions of the fraction with different chain lengths can be estimated with Eq. 10. The weight fraction of different hydrocarbons with n carbons in Ft synthesis is:

$$W_n = n(1-\alpha)^2(\alpha-1)^{n-1} \qquad (10)$$

where W_n is the weight fraction of hydrocarbons with n carbons.

Fermentation and oxygen removal from sugars by hydrogen

Since the aim of this study is to establish the total amount of the components that can be produced by various routes, the hydrolysis of both cellulose and hemicellulose was considered. It was also calculated how much biogas could be produced from the sugars obtained through total hydrolysis. It was assumed that lignin is not degradable by methane-producing bacteria. Ethanol fermentation of the hexose sugars was calculated according to Eq. 11.

The conversion of ethanol into butanol was calculated according to Eq. 12. The total reaction involves the combination of dehydrogenation of ethanol into acetaldehyde, aldol condensation into crotonealdehyde and subsequent hydrogenation into butanol. The further dehydration of the alcohol into ether (dibutylether and diethylether) was calculated according to Eq. 13. The dehydration of the alcohol into alkene ethylene and propylene was calculated according to Eq. 14.

Eq. 15 involves the reaction of two molecules of ethanol with one molecule of butyraldehyde. Butyraldehyde is produced from ethanol by dehydration into acetaldehyde, aldol condensation to crotonaldehyde and hydrogenation into butyraldehyde, which also gives one mole of hydrogen as by-product. Acetic acid is produced by anaerobic fermentation of glucose, according to Eq. 16, and pentose – according to Eq. 17. The acetic acid is esterified with ethanol to ethyl acetate (Eq. 18) and the ethyl acetate is hydrogenated into ethanol (Eq. 19).

ABE fermentation involves many reaction products, their dependence on the others being indirect. The assumed ABE fermentation yields were of 0.42 g ABE/g sugar[28] for C6 sugars and of 0.28 g/g sugar[29] for xylose. The fermentation gas was assumed to consist[32] of 40 mol% H_2 and 60 mol% CO_2, in the final stage of fermentation.

The hydrogenation of acetone into isopropanol was calculated according to Eq. 20. Methanol can be also obtained from carbon dioxide, according to Eq. 21.

Sugar can be also upgraded by hydrogenation, for example, by the reaction presented by Huber *et al.*[19]

Pentose sugars can be reacted into, for example, methyl tetrahydrofuran (MTHF) shown in Eq. 22 by dehydration of sugar into furan and subsequent hydrogenation *via* methylfuran. Hexose sugars can be reacted, for example, into C12 alkane type of products, according to Eq. 23. Hydrogenation involves dehydrogenation of hexose into HMF hydromethylfurfural, hydrogenation and aldol condensation of two C6 molecules into one larger molecule producing C12 hydrocarbon.

Digestion

The digestion of the organic substance is represented by Eq. 24. Finally, the produced methane could be steam-reformed into a synthesis gas, according to Eq. 25. The reaction is endothermic, *i.e.* the energy content of the produced syngas is larger than that of the methane gas, if the reaction heat is supplied from an external heat source.

Hexose ethanol fermentation	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	(11)
Butanol from ethanol	$2C_2H_5OH \rightarrow C_4H_9OH + H_2O$	(12)
Dehydration	$2C_nH_{n+1} -> C_n - O - C_n + H_2O$	(13)
Dehydration	$C_nH_{2n+1}OH \rightarrow C_nH_{2n} + H_2O$	(14)
Diethoxybutane reaction	$4C_2H_5OH \rightarrow CH_3CH_2CH_2CH(OC_2H_5)_2 + 3H_2O + H_2$	(15)
Hexose acetic acid fermentation	$C_6H_{12}O_6 \rightarrow 3CH_3COOH$	(16)
Pentose acetic acid fermentation	$2C_5H_{10}O_5 -> 5CH_3COOH$	(17)
Esterification	$CH_3COOH + C_2H_5OH \rightarrow CH_3COOCH_2CH_3 + H_2O$	(18)
Hydrogenation	$CH_3COOCH_2CH_3 + 2H2 \rightarrow 2C_2H_5OH$	(19)
Acetone hydrogenation	$CH_3COCH_3 + H_2 \rightarrow CH_3CHOHCH_3$	(20)
Methanol synthesis from CO_2	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	(21)
Pentose hydrogenation	$C_5H_{10}O_5 + 4H_2 \rightarrow C_5H_{10}O + 4H_2O$	(22)
Hexose hydrogenation	$2C_6H_{12}O_6 + 13H_2 \rightarrow C_{12}H_{26} + 12H_2O$	(23)
Digestion	$C_XH_yO_Z + \left(x - \frac{y}{4} - \frac{z}{2}\right)H_2O \rightarrow \left(\frac{x}{2} - \frac{y}{8} + \frac{z}{4}\right)CO_2 + \left(\frac{x}{2} + \frac{y}{8} - \frac{z}{4}\right)CH_4$	(24)
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2O$	(25)

RESULTS AND DISCUSSION

Gasification

The potential yields obtained, according to the methods described, for the selected raw material and for the derivatives are shown in Table 2. For the gasification reaction, it can be observed that the highest amount of energy remains in the synthesis gas, compared to the upgraded products.

The calculated potential heat content (LHV) in the synthesis gas ranges from 84 to 73% for different raw materials. For materials with a high ash content, such as wheat straw and sugar cane bagasse, the heat content remaining in the synthesis gas is the lowest. For fast pyrolysis with subsequent gasification of the pyrolysis oil, the remaining heat content of the synthesis gas is of approximately 50% of the original biomass.

For gasification of lignin+extractives, 23.5% of the heat content of pine can be transferred into the heat content of the synthesis gas. Also, for birch lignin, 13.3% of the original heat content of birch can be recovered by gasifying the lignin+extractives part.

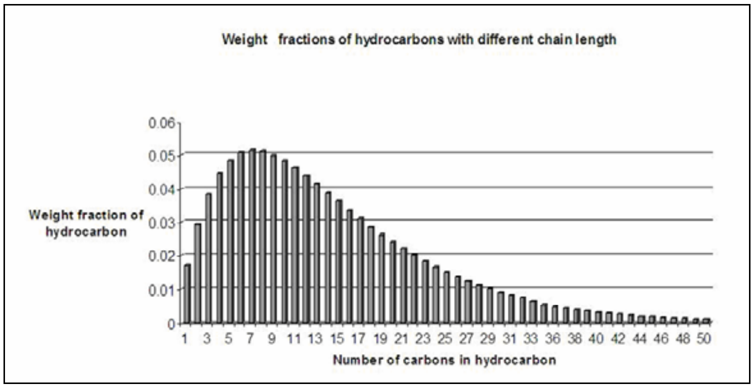

Figure 1: Distribution of hydrocarbon chain length for FT synthesis with α = 0.87

In the case of the derivatives, the remaining heat content of the product is lower than that remaining for synthesis gas. The upgrading methods studied show that the lowest amount of heat remains in the Fischer-Tropsch product, followed by methanisation. The largest amount of heat remains in the synthesis gas when this is converted into hydrogen. Second in heat conversion efficiency is methanol synthesis. Compared to the original raw material, the carbon conversion efficiency in the products ranges from above 70 to 0%.

The remaining hydrogen ranges from 0 to 200%, because the obtained carbon monoxide can be converted – according to Eq. 1 – into carbon dioxide and hydrogen with the aid of steam at a high temperature. Therefore, the hydrogen content of the product can exceed that of the raw material.

For FT synthesis, the average chain length was 14 carbons, the distribution of the molecular chain length obtained being shown in Figure 1.

Fermentation

Tables 3 to 14 list the potential yields, the material efficiencies and the carbon ratios (%) remaining in the original raw material for products obtained through fermentation, as well as through further upgrading. Ethanol, acetic acid and ABE (acetone ethanol butanol) fermentation are considered. Also, the results of the subsequent upgrading reactions are presented.

Table 4 shows that the yield of ethanol from hexose fermentation is lower than that of the raw material containing more pentose sugars, such as birch, compared to, for example, pine.

The material yield of butanol, *e.g.* for pine, is of 256 kg to 319 kg, as shown in Table 5 *vs*. Table 6. This value is significantly lower when butanol is produced from ethanol. However, in the conversion of butanol from ethanol, only approximately 2% of the liquid energy content is lost, based on LHV%.

When butanol is further converted to dibutylether, the material yield is reduced from about 256 to 225 kg, as shown for pine in Tables 5 and 6. However, the lower heating value of the fuel increases (0.2%), which indicates that the reaction should be slightly endothermic.

Anaerobic acetic acid fermentation gives a high yield because, in the reaction, no carbon is lost as carbon dioxide. Furthermore, when hydrogen is added to the acetic acid product, the material yield is decreased by approximately 200 kg from acetic acid to ethanol, while the energy content of the liquid increases from around 42 to 72% for pine, as shown in Tables 7 to 9. Also, a high amount of hydrogen (45.4 kg) is needed for pine, slightly more than it can be obtained through the gasification of pine lignin and extractives, as shown in Table 2.

The amount of energy, LHV%, in the product increases when converting ethanol into ethylene, as a result of the endothermic dehydration reaction, as shown in Table 11. It also means that external heat is needed to drive the dehydration reaction. Table 12 shows the conversion of ethanol to diethoxybutane, with hydrogen as a by-product. The amounts of energy present in the products were only slightly reduced.

The total material yield of ABE fermentation (Table 13) is lower than that for the conventional ethanol fermentation (Table 3). However, the energy content of the products is significantly higher. The *Clostridium* bacteria can also utilize pentose sugars.

When acetone is hydrogenated into isopropanol and the remaining hydrogen gas is used to hydrogenate the carbon dioxide into methanol, a slight reduction is observed in the total energy content of the products – as shown in Table 14. However, the total yield of liquid products and their usefulness increase.

Starting with the acetic acid, a high yield of butanol can be theoretically obtained. In practice, the material yield might be significantly lower, due to multiple reactions, if the selectivities in the reactions are low.

Chemical upgrading of sugars

The results of upgrading sugars through hydrogenation are shown in Table 15.

Table 1
Ultimate analysis and chemical composition of a calculated amount of raw material

Species	C, %	H, %	O, %	N, %	S, %	Ash, %	Higher heating value, MJ/kg	Lower heating value, MJ/kg	Ref.	Xylan	Cellulose	Extractives	Glucan	Mannan	Galactane	Xylane	Ref.
Pine	52.34	6.09	41.19	0.08	0.01	0.74	20.6	19.31	30	0.1	0.41	0.04	0.41	0.124	0.019	0.076	31
Spruce	52.43	5.86	40.63	0.01	0.03	1.04	20.3	19.05	25	0.11	0.41	0.02	0.41	0.136	0.028	0.056	25
Black alder	49.09	5.22	43.78	0.44	0.55	0.92	20.0	18.9	25			0.06	0.405	0.015	0.008	0.161	25
Aspen	46.21	5.77	46.40	0.15	0.55	0.92	19.9	18.7	25			0.06	0.432	0.022	0.005	0.151	25
Silver birch	47.43	5.22	46.05	0.07	0.55	0.68	19.7	18.62	25	0.33	0.4	0.03	0.407	0.017	0.007	0.2	25
Eucalyptus	57.20	5.25	36.38	0.00	0.00	1.17	20.3	19.2	25				0.523	0.011	0.01	0.16	32
Larch	48.80	6.10	44.90	0.10	0.01	0.10	19.5	18.2	25				0.46	0.11	0.02	0.063	33
Bagasse	44.8	5.35	39.55	0.38	0.01	11.2	17.33	16.2	34		0.334	0.060	0.410	0	0	0.252	35
Wheat straw	43.2	5.00	39.40	0.61	0.11	8.9	17.51	16.4	36	0.210	0.400	0.072	0.411	0.003	0.006	0.210	37
Pyrolysis oil	56	6.5	37.5	0.1					24	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table 2
Potential material yield, material efficiencies for synthesis gas and its derivatives (first part)

Material heat efficiency of syngas-derived products	Type of raw material											
	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass		Biomass derivatives		
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Sugar cane bagasse	Wheat straw	Pyrolysis oil	Pine lignin+ extractives	Birch lignin +extractives
Syngas												
H_2, kg/ton dry biomass	79.1	75.9	72.1	73.7	70.7	67.3	69.1	59.2	62.8	52.2	21.0	13.4
CO, kg/ton dry biomass	664.3	657.6	610.7	568.9	564.7	669.2	559.7	467.1	483.1	474.3	302.2	159.8
LHV, MJ/kg dry biomass	16.2	15.8	14.8	14.6	14.2	14.8	14.0	11.8	12.4	11.1	5.6	3.2
LHV, %	83.9	82.8	78.5	78.1	76.3	77.4	76.7	73.1	75.6	50.3	23.5	13.3
C material efficiency, %	54.4	53.8	53.4	52.8	51.1	50.2	49.2	44.7	48.0	36.3	21.9	13.1
H material efficiency, %	129.8	129.6	138.1	127.8	135.5	128.2	113.3	110.7	125.7	80.3	35.1	71.8
Hydrogen production												
Hydrogen, kg/ton dry biomass	126.9	123.3	116.1	114.7	111.4	115.5	109.4	92.8	97.6	86.3	42.8	24.9
LHV, MJ/kg dry biomass	15.2	14.8	13.9	13.8	13.4	13.9	13.1	11.1	11.7	10.4	5.1	3.0
LHV, %	78.9	76.6	72.2	71.3	69.2	71.8	68.0	57.7	60.7	53.7	26.6	15.5
C material efficiency, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H material efficiency, %	208.3	210.4	222.3	198.8	213.3	220.0	179.4	173.5	195.2	132.8	71.4	133.4
Methanol synthesis												
Methanol, kg/ton dry biomass	672.2	653.1	614.9	607.7	590.0	611.8	579.6	491.9	517.2	457.3	226.5	132.0
LHV, MJ/kg dry biomass	14.2	13.8	13.0	12.8	12.4	12.9	12.2	10.4	10.9	9.6	4.8	2.8
LHV, %	73.4	72.3	68.6	68.5	66.8	67.3	67.2	64.1	66.4	45.3	20.1	11.5
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	138.9	140.2	148.2	132.5	142.2	146.6	119.6	115.7	130.2	88.5	47.6	88.9
Methanol carbonisation												
Ethanol, kg/ton dry biomass	483.3	469.5	442.0	436.9	424.1	439.8	416.7	353.6	371.8	328.7	162.8	94.9
LHV, MJ/kg dry biomass	13.4	13.0	12.3	12.1	11.8	12.2	11.6	9.8	10.3	9.1	4.5	2.6
LHV, %	69.4	68.3	64.8	64.8	63.1	63.6	63.5	60.6	62.7	42.9	19.0	10.9
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	86.8	87.6	92.6	82.8	88.9	91.7	74.7	72.3	81.4	55.3	29.7	55.6
Methanol carbonisation												
Acetic acid, kg/ton dry biomass	944.9	901.8	864.2	854.1	829.2	860.0	814.7	691.4	727.0	642.7	318.4	185.6
C material efficiency, %	72.21	68.80	70.42	73.94	69.94	60.14	66.78	61.73	67.32	45.91	21.48	14.17
H material efficiency, %	104.17	103.32	111.16	99.39	106.66	109.98	89.68	86.76	97.62	66.39	35.69	66.70

Table 3
Material yield, material efficiencies for synthesis gas and its derivatives (second part)

DME (dimethylether) synthesis	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Sugar cane bagasse	Wheat straw	Pyrolysis oil	Pine lignin+ extractives	Birch lignin+ extractives
DME, kg/ton dry biomass	483.2	469.5	442.0	436.8	424.1	439.8	416.7	353.6	371.8	328.7	162.8	94.9
LHV, MJ/kg dry biomass	13.9	13.5	12.7	12.6	12.2	12.7	12.0	10.2	10.7	9.5	4.7	2.7
LHV, %	72.2	71.1	67.4	67.4	65.7	66.2	66.1	63.0	65.2	44.6	19.7	11.3
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	104.2	105.2	111.2	99.4	106.7	110.0	89.7	86.8	97.6	66.4	35.7	66.7
MTO process from methanol												
Ethylene, kg/ton dry biomass	147.1	142.9	134.6	133.0	129.1	133.9	126.9	107.7	113.2	100.1	49.6	28.9
Propylene, kg/ton dry biomass	147.1	142.9	134.6	133.0	129.1	133.9	126.9	107.7	113.2	100.1	49.6	28.9
LHV, MJ/kg dry biomass	13.7	13.3	12.5	12.4	12.0	12.4	11.8	10.0	10.5	9.3	4.6	2.7
LHV, %	70.8	69.8	66.2	66.1	64.5	64.9	64.8	61.8	64.0	43.8	19.4	11.1
C material efficiency, %	48.1	45.9	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	69.4	68.9	74.1	66.3	71.1	73.3	59.8	57.8	65.1	44.3	23.8	44.5
n-Propanol and ethanol through hydration of olefins												
Etanol, kg/ton dry biomass	241.6	234.7	221.0	218.4	212.1	219.9	208.3	176.8	185.9	164.4	81.4	47.5
Propanol, kg/ton dry biomass	210.1	204.1	192.2	189.9	184.4	191.2	181.2	153.7	161.7	142.9	70.8	41.3
LHV, MJ/kg	13.0	12.7	11.9	11.8	11.4	11.9	11.2	9.5	10.0	8.9	4.4	2.6
LHV, %	67.5	65.6	61.7	61.0	59.2	61.4	58.2	49.4	51.9	45.9	22.7	13.3
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	98.4	99.3	105.0	93.9	100.7	103.9	84.7	81.9	92.2	62.7	33.7	63.0
Methanisation of syngas												
Methane, kg/ton dry biomass	252.4	245.2	230.9	228.2	221.5	229.7	217.7	184.7	194.2	171.7	85.1	49.6
LHV, MJ/kg dry biomass	12.6	12.3	11.5	11.4	11.1	11.5	10.9	9.2	9.7	8.6	4.3	2.5
LHV, %	65.3	64.4	61.1	61.0	59.5	59.9	59.8	57.1	59.1	39.1	17.9	10.2
C material efficiency, %	36.1	35.0	35.2	37.0	35.0	30.1	33.4	30.9	33.7	23.0	10.7	7.1
H material efficiency, %	104.2	101.2	95.3	94.2	91.4	94.8	89.8	76.2	80.1	70.9	35.1	20.5
Once-through Ft synthesis												
Hydrocarbons, kg/ton dry biomass	268.3	257.7	244.6	250.2	239.9	228.4	234.5	200.9	213.3	177.0	71.2	45.5
Water, kg/ton of biomass	341.1	327.6	311.0	318.2	305.1	290.4	298.2	255.5	271.2	225.1	90.6	57.9
LHV, MJ/kg dry biomass	11.8	11.3	10.8	11.0	10.6	10.1	10.3	8.8	9.4	7.8	3.1	2.0
LHV, %	61.2	58.7	55.8	57.0	54.7	52.1	53.5	45.8	48.6	40.4	16.2	10.4
C material efficiency, %	43.4	41.7	42.2	45.9	42.9	33.8	40.7	38.0	41.8	26.8	10.2	7.4
H material efficiency, %	128.7	128.5	137.2	126.9	134.6	127.6	112.7	110.6	125.4	80.6	37.2	80.1

Table 4
Potential yield from hexose sugars obtained through ethanol fermentation

Ethanol fermentation (only C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Ethanol, kg/ton dry biomass	318.6	303.2	243.1	260.2	236.0	309.0	335.0	233.0	238.6
CO_2, kg/ton dry biomass	304.3	289.6	232.2	248.6	225.5	295.2	320.0	222.6	227.9
LHV, MJ/kg dry biomass	8.8	8.4	6.7	7.2	6.5	8.6	9.3	6.5	6.6
LHV, %	45.7	44.1	35.7	38.6	35.1	44.7	51.1	39.9	40.2
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	85.9	82.1	86.4	85.6

Table 5
Potential yield of butanol obtained from ethanol through hexose fermentation

Ethanol fermentation (only C6 sugars)→butanol	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	256.3	243.9	195.6	209.3	189.9	248.6	269.5	187.4	191.9
H_20, kg/ton dry biomass	62.3	59.3	47.5	50.9	46.2	60.4	65.5	45.6	46.7
LHV, MJ/kg dry biomass	8.5	8.1	6.5	6.9	6.3	8.2	8.9	6.2	6.4
LHV, %	43.9	42.4	34.3	37.1	33.8	42.9	49.1	38.3	38.7
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	88.5	82.1	86.5	86.8

Table 6
Potential yield of dibutylether obtained by hexose ethanol fermentation and subsequent dehydrogenation of butanol into dibutyether

Ethanol→butanol→dibutylether	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Dibutyl ether, kg/ton dry biomass	225.1	214.3	171.8	183.9	166.8	218.4	236.7	164.6	168.6
Water, kg/ton dry biomass	8.5	8.1	6.5	7.0	6.3	8.3	8.9	6.2	6.4
LHV, MJ/kg dry biomass	8.5	8.1	6.5	7.0	6.3	8.3	8.9	6.2	6.4
LHV, %	44.1	42.5	34.4	37.2	33.9	43.0	49.2	38.5	38.8
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	88.5	82.1	86.5	86.8

Table 7
Potential yield of acetic acid through anaerobic acetic acid fermentation of hexose and pentose sugars

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Acetic acid, kg/ton dry biomass	676.3	646.2	658.3	680.4	741.0	786.0	726.6	741.9	490.4
LHV, MJ/kg dry biomass	8.0	7.7	7.8	8.1	8.8	9.3	8.6	8.8	5.8
LHV, % raw material	41.6	39.7	40.5	41.8	45.6	48.3	44.7	45.6	30.1
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 8
Potential yield of ethyl acetate obtained through acetic acid fermentation, hydrogenation of half of it into ethanol and its esterification with acetic acid

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Acetic acid, kg/ton dry biomass	676.3	646.2	658.3	680.4	741.0	786.0	726.6	741.9	490.4
LHV, MJ/kg dry biomass	8.0	7.7	7.8	8.1	8.8	9.3	8.6	8.8	5.8
LHV, % raw material	41.6	39.7	40.5	41.8	45.6	48.3	44.7	45.6	30.1
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 9
Potential yield of ethanol obtained through anaerobic acetic acid fermentation and subsequent hydrogenation;
amount of hydrogen necessary to convert acetic acid into ethanol

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
H_2 needed, kg/ton dry biomass	45.4	43.4	44.2	45.7	49.8	52.8	48.8	49.8	32.9
Ethanol produced, kg/ton dry biomass	518.8	495.8	505.0	522.0	568.5	603.0	557.5	569.2	376.2
LHV, MJ/kg dry biomass	14.4	13.7	14.0	14.5	15.8	16.7	15.5	15.8	10.4
LHV, % raw material	74.5	72.1	74.1	77.4	84.6	87.2	84.9	97.5	63.4
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 10
Potential yield of butanol obtained through acetic acid fermentation, hydrogenation and conversion of ethanol into butanol

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton biomass	417.4	398.8	406.3	419.9	457.3	485.1	448.4	457.9	302.6
LHV, MJ/kg dry biomass	13.8	13.2	13.5	13.9	15.1	16.1	14.8	15.2	10.0
LHV, % raw material	71.6	69.3	71.2	74.3	81.3	83.8	81.6	93.7	61.0
C material efficiency, %		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 11
Potential yield of ethylene obtained through acetic acid fermentation, hydrogenation and dehydration of ethanol into ethylene

Anaerobic acetic acid fermentation →ethanol→ethylene	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Ethylene, kg/ton dry biomass	315.9	301.9	307.5	317.8	346.2	367.2	339.5	346.6	229.1
LHV, MJ/kg dry biomass	13.8	13.2	13.5	13.9	15.1	16.1	14.8	15.2	10.0
LHV, % raw material	77.2	74.7	76.7	80.2	87.7	90.3	88.0	101.0	65.7
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 12
Potential yield of diethoxybutane obtained through acetic acid fermentation, hydrogenation and conversion of ethanol and butyraldehyde produced from ethanol into diethoxybutane

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Diethoxybutane, kg/ton dry biomass	411.7	393.4	400.8	414.2	451.1	478.5	442.4	451.7	298.5
LHV, MJ/kg dry biomass	14.0	13.4	13.6	14.1	15.3	16.3	15.0	15.4	10.1
LHV, % raw material	72.5	70.2	72.1	75.3	82.4	84.8	82.7	94.9	61.7
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 13
Yield of ABE fermentation based on reported yields for different raw materials

ABE fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	166.9	159.3	153.8	160.1	168.2	186.0	178.3	168.0	122.0
Acetone, kg/ton dry biomass	83.4	79.6	76.9	80.0	84.1	93.0	89.2	84.0	61.0
Etanol, kg/ton dry biomass	27.8	26.5	25.6	26.7	28.0	31.0	29.7	28.0	20.3
Total ABE, kg/ton dry biomass	278.1	265.5	256.3	266.8	280.4	310.0	297.2	280.0	203.3
Hydrogen, kg/ton dry biomass	12.9	12.3	13.6	14.0	16.2	16.3	14.1	16.3	8.7
CO_2, kg/ton dry biomass	352.1	334.7	371.8	381.9	442.2	445.7	385.6	444.3	237.3
LHV, MJ/kg dry biomass	10.2	9.8	9.6	10.0	10.7	11.6	11.0	10.7	7.4
LHV, % raw material	53.0	51.2	51.0	53.5	57.4	60.7	60.3	66.1	44.9
C material efficiency, %	81.6	82.5	80.6	80.1	76.9	76.8	79.9	76.8	87.6

Table 14
Potential yield of products from ABE mixture (Table 13), when acetone and carbon dioxide are hydrogenated into isopropanol and methanol

ABE fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	166.9	159.3	153.8	160.1	168.2	186.0	178.3	168.0	122.0
Isopropanol, kg/ton dry biomass	86.3	82.4	79.6	82.8	87.0	96.2	92.3	86.9	63.1
Etanol, kg/ton dry biomass	27.8	26.5	25.6	26.7	28.0	31.0	29.7	28.0	20.3
Metanol, kg/ton dry biomass	53.0	50.3	58.0	59.4	70.4	69.4	58.5	70.8	34.9
H_2, kg/ton dry biomass	10.0	9.5	11.0	11.2	13.3	13.1	11.0	13.4	6.6
CO_2, kg/ton dry biomass	279.3	265.6	292.0	300.3	345.5	350.3	305.3	347.1	189.4
LHV, MJ/kg dry biomass	10.0	9.6	9.4	9.8	10.5	11.4	10.7	10.5	7.2
LHV, % raw material	51.9	49.5	48.8	50.7	54.2	59.0	55.6	54.1	37.5
C material efficiency, %	85.4	86.2	84.8	84.3	82.0	81.7	84.1	81.9	90.1

Table 15
Potential yield of products from ABE mixture (Table 12), when butanol is dehydrated into dibutylether, ethanol into dethylether and acetone into isopropanol (through hydrogenation), followed by dehydration into propylene

ABE fermentation+ butanol→dibutylether; ethanol→diethylether, isopropanol→propylene	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Dibutylether, kg/ton dry biomass	146.6	139.9	135.1	140.6	147.8	163.4	156.7	147.6	107.1
Propylene, kg/ton dry biomass	60.4	57.7	55.7	58.0	60.9	67.4	64.6	60.9	44.2
Diethylether, kg/ton dry biomass	22.4	21.4	20.6	21.5	22.6	24.9	23.9	22.5	16.4
H2, kg/ton dry biomass	10.0	9.5	11.0	11.2	13.3	13.1	11.0	13.4	6.6
CO2, kg/ton dry biomass	279.3	265.6	292.0	300.3	345.5	350.3	305.3	347.1	189.4
LHV, MJ/kg dry biomass	10.3	9.8	9.7	10.0	10.7	11.7	11.0	10.7	7.4
LHV, % raw material	53.2	51.4	51.2	53.7	57.7	60.9	60.6	66.3	45.1
C material efficiency, %	81.6	82.5	80.6	80.1	76.9	76.8	79.9	76.8	87.6

Around 160 kg of ethers could be produced from 1 t of biomass through ABE fermentation, followed by dehydration into dibutylethers and diethylether. Due to the easy peroxide formation of the di-isopropylether, the dehydration of isopropanol into propylene is considered instead. A relatively small amount of propylene (around 50 kg) can be obtained from isopropanol dehydration. The C5 sugars are not deoxygenated fully to alkane-type product, but left at the MTHF stage, due to the undesirable high vapor pressure of pentane.

Also, when the sugars are hydrogenated to MTHF and C12 alkane, as shown in Table 15, a high amount of hydrogen is needed. The needed amount of hydrogen is however lower than that required for hydrogenating acetic acid into ethanol. In the case of pine, the hydrogen obtained through the gasification of lignin and extractives would be sufficient. The advantage is that part of the oxygen present in the biomass sugars can be removed by dehydration, when converting pentose sugars into furan and hexose sugars into HMF in the first step.

Digestion

The results calculated for sugar conversion into biogas (carbon dioxide and methane) are shown in Table 16. In Table 17, the upgrading of biogas into synthesis gas by steam reforming is considered. One possibility would be to combust non-degradable by digestion lignin and use the combustion heat to drive the steam reforming reaction of the synthesis gas. The reverse shift reaction conversion of hydrogen and carbon dioxide into water and carbon monoxide (the opposite of the shift gas reaction shown in Eq. 1) is not considered here. Due to the endothermic nature of the reverse shift gas reaction, the heat content of the product could be further increased. However, a very high temperature is needed to make the reaction thermodynamically feasible.

Table 17 shows that less than 200 kg of methane can be obtained from the digestion of pentose and hexose sugars. The energy content in the methane gas, however, is similar to that obtained with ethanol or ABE fermentation. For biogas, the separation from solution is easy, however.

By steam reforming, which is an endothermic process, the energy content in the gas could be increased to 59-77% of the raw material, as shown in Table 18. Synthesis can be viewed as a further process, according to a reaction shown in the subsequent upgrading reaction section.

Fuel properties and application of chemicals

The most important fuel properties of the different fuels here discussed are summarized in Table 19. A comparison is made between the properties of conventional fossil fuels and conventional biofuels, such as FAME (fatty acid methyl ester). The problem of both methanol and ethanol is their high water solubility and their corrosive nature. In addition, the vapor pressure of these components is high. Therefore, only low amounts of ethanol (up to 10 vol%) can be mixed, at a cold temperature. In addition, the energy content of these fuels is low, compared to gasoline, which leads to higher fuel consumption and wrong fuel–air ratio, if excessive amount of biofuel is mixed with gasoline in conventional cars. The octane numbers shown in Table 19 are however high. Other alcohols, such as butanol and propanol, are much more suitable to be used in a higher fraction in gasoline, due to their lower corrosiveness, vapor pressure and higher energy content. Ethers, such as ETBE, have been conventionally added to gasoline, to enhance clean burning. The dibutylether, diethylether and diethoxybutane have similar characteristics. These substances can be possibly blended in the existing diesel engines, to improve the cetane number of fossil diesel. However, the ethers tend to form peroxides, exposure to which may be dangerous. It should be studied whether these compounds can be safely used by adding antioxidant to the fuel mixture, for preventing peroxide formation. MTHF could be blended in larger volumes, up to 30%, in gasoline.[38]

FAME can be blended into fossil diesel fuels only in relatively low amounts (around 5%), if the mixture is used in conventional diesel engines. Possible problems refer to increased emissions and unfavorable cold properties. Below the cloud point, a part of the components present in the mixture get solidified, causing plugging of the fuel filters. The diesel range alkanes obtained through FT synthesis are similar to the components present in fossil diesel. They have very high cetane numbers, which makes them burn clean. Therefore, they can be blended into conventional diesel in very high fractions, or the diesel fuel can even be used without adding any fossil diesel. However, it is important to know that the product obtained from FT synthesis does not have sufficiently good properties. The heavy part needs to be hydrocracked to hydrocarbons with right chain length. In addition, alkanes solidify even at room temperature.

Therefore, they may be partially isomerized, to lower the cloudpoint of the mixture. Isomerization can be performed in an oil refinery, involving, nevertheless, losses, because a side reaction of isomerization assumes cracking of the diesel range hydrocarbon into smaller hydrocarbons.

DME and methane have favorable combustion properties. DME has a reasonably high cetane number and methane has a high octane number. The disadvantage refers to the storage and safety of these components. DME can be stored similarly to liquefied natural gas, requiring new infrastructure, fuel stations, etc. Methane, which cannot be liquefied at room temperature, needs to be stored under high pressure in tanks. The ether diethoxybutane and dibutylether have favorable cetane numbers. In addition, dibutylether has[39] very favorable cold properties (melting point -97.9 °C). The chemicals obtained as by-products and intermediates in biofuel production, including ethylene and propylene, appear as important raw materials for polyethylene and polypropylene. These chemicals are conventionally produced from oil or natural gas. Produced from biomass, they would have a much better carbon footprint and replace the use of oil. Ethyl acetate is commonly used as a solvent. Acetic acid is used not only in the food industry, but also as a chemical reagent.

Table 16
Potential yield of hydrocarbons and hydrogen demand
when pentose sugars are converted into MTHF and hexose into C12 alkane

Hydrogenation of C5 sugars→MTHF and C6 sugars→ C12 alkanes	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
H_2 needed, kg/ton biomass	38.6	38.0	38.3	40.3	39.7	53.3	46.2	43.4	40.2
C12 alkane produced, kg/ton biomass	313.2	298.6	242.6	259.6	236.2	308.7	330.0	233.5	238.7
MTHF, kg/ton biomass	30.6	30.6	105.0	98.4	160.4	104.3	41.1	164.3	13.7
Total, kg/ton biomass	343.8	329.3	347.6	358.0	396.5	413.1	371.1	397.8	252.4
LHV, MJ/kg dry biomass	14.8	14.2	14.1	14.6	15.5	17.0	15.9	15.6	11.0
LHV, % raw material	76.6	74.3	74.4	78.1	83.5	88.4	87.2	96.1	66.7
C material efficiency, %	100	100	100	100	100	100	100	100	100

Table 17
Potential yield of biogas methane and carbon dioxide
when hexose and pentose sugars are digested into biogas

Digestion	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Methane, kg/ton biomass	180.7	172.6	175.9	181.8	198.0	210.0	194.1	198.2	131.0
CO_2, kg/ton biomass	684.7	651.7	522.5	559.3	507.3	664.2	720.1	500.8	512.8
LHV, MJ/kg dry biomass	9.0	8.6	8.8	9.1	9.9	10.5	9.7	9.9	6.5
LHV, % raw material	46.8	44.7	45.5	47.1	51.3	54.4	50.3	51.3	33.9
C material efficiency, %	64.3	66.1	70.9	67.0	70.8	68.3	59.7	69.5	67.6

Table 18

Potential yield of synthesis gas when the biogas obtained through digestion is converted into synthesis gas by steam reforming

Steam reforming of biogas	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black Alder	Aspen	Silver Birch	Eucalyptus	Larch	Bagasse	Wheat straw
CO, kg/ton biomass	315.4	301.4	307.0	317.3	345.6	366.6	338.9	346.0	228.7
H_2, kg/ton biomass	68.1	65.1	66.3	68.5	74.6	79.2	73.2	74.7	49.4
LHV, MJ/kg dry biomass	11.4	10.9	11.1	11.4	12.5	13.2	12.2	12.5	8.2
LHV, % raw material	58.9	57.0	58.5	61.2	66.9	68.9	67.1	77.1	50.1
C material efficiency, %	64.3	66.1	70.9	67.0	70.8	68.3	59.7	69.5	67.6

Table 19

Most important properties of different fuels

(*e.g.* vapor pressure, cetane or octane number, flashpoint, boiling point)

	Gasoline	Diesel	FAME	Methanol	Ethanol	DME dimethyl-ether	Parafic diesel, *e.g.* FT diesel	E85e	Dibutyl ether	Diethyl ether	Diethoxy-butane	n-butanol	Iso-propanol	MTHF[40]	Methane[41]
Formula	C4-C12	C12-C20	C19H34O2	CH_4O	C_2H_6O	C_2H_6O	Roughly C_{12}-C_{20}	$\sim C_{2.7}H_7O_{0.85}$	$C_8H_{18}O$	$C_4H_{10}O$	$C_8H_{18}O$	C_4H_9OH	C_3H_7OH	$C_5H_{10}O$	CH_4
Mol., wt g/MOL	100-105	~200	~294	32.04	46.07	46	170-280	~55	130	74	146.23	82	82.2	86.13	16.01
C/H/O, wt%	85-88/ 12-15	85-88/ 12-15	78/12/10	38/13/50	52/13/ 35			58/13/29	74/14/12	65/14/22					
Density, kg/m3	~750	~840	880	796	794	660	750-800	780	767	720				813	0.72
Boiling point, °C	30-190	170-340	300-340	64	78	24	180-360	30-190	141	35		118	82.3	80	-161
Octane number RON	95-98			122-133 (RON)	121-130 (RON)	-		100				94	~100	80	130
Cetane		>45	>50		8	55-60	80-110[42]		91-100	140	96.6	12	17		
Vapour pressure, kPa RVP, actual (blend kPa)	45-90c	<1		32 (210+)	16 (124)		<1	40-80				0.7 (at 20 °C)	4.4 (at 20 °C)	39	Super-critical
Flash point, °C	<0	>56	>100	7	13	-42	>56		25	-45	45	37	11.8	-11	-188
Heat value, MJ/kg	43	43	36	20	26	27.6-28.8	44-43	29.2	42.8		~34	33.11	30.15	32	50

CONCLUSIONS

According to the calculations, the highest amount of the original heat content in the products is retained in sugar hydrogenation and acetic acid fermentation. In the gasification of the whole feedstock biomass, also, a high amount of original heat content – up to 80% – could be converted into synthesis gas. When producing alcohols, such as isopropanol, more energy of the raw material could be retained in the products than when upgrading synthesis gas into alkanes. Therefore, it might be more feasible to convert synthesis gas into higher alcohols, such as propanol, butanol and their ethers. The alkanes produced by gasification cannot be used without isomerization as diesel or gasoline components. This further reduces the yield of the products. The pyrolysis of biomass and the gasification of only the most easily transported bio-oil convert a lower amount, around 50%, of the original biomass heat content into synthesis gas. On the other hand, in the pyrolysis stage, heat or by-products, such as charcoal, might be recovered.

In the case of acetic acid fermentation and chemical conversion of sugars, if all the needed hydrogen for upgrading cannot be produced by gasification of the lignin and extractives part of the biomass, the product heat content is misleading. According to the calculations made for pine, the necessary hydrogen could be produced through hydrogenation, when the sugars are upgraded through hydrogenation. For the hydrogenation of acetic acid into ethanol, slightly more hydrogen is needed than what can be obtained through the gasification of the lignin and extractives part of the biomass. For spruce, only approximately 50-60% of the needed hydrogen can be produced through the gasification of the biomass lignin and extractives. Therefore, fuel components that have favorable fuel properties, but do not need full oxygen removal, should be considered, such as, for example, dimehylfuran or methylfuran.[21] Alternatively, hydrogenolysis of sugars with hydrogen into ethylene glycol[20] and etherification of components, such as ethylene glycol with alcohols, might provide upgrading routes to high quality fuels needing less hydrogen than full hydrodeoxygenation.

In alcohol fermentation, the lowest amount of raw material heat content was converted into products. However, when alcohol fermentations were combined with gasification of lignin and extractives, only a slightly lower amount of energy was converted to products, as compared to the gasification of the entire biomass. It is also important to note that obtaining sugars as an intermediate product in the process enables the production of other types of valuable products, such as biopolymers and chemicals. The disadvantage of micro-biological processes compared to thermochemical routes is the slow reaction. Therefore, larger reactor volumes are needed.

The digestion of biomass into biogas converts approximately an equal amount of raw material heat content into product, as compared to that converted by fermentation. In addition, the separation of the gas from the raw material is easy, compared to the separation of fermentation products from relatively dilute water solutions. Notably, the energy content of the biogas could be increased significantly by steam reforming, producing syngas in a simpler way than by gasification of solid biomass or pyrolysis oil. It could be a feasible alternative for the utilization of low-value, wet biomass.

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