COMPARISON OF DIFFERENT ROUTES FROM LIGNOCELLULOSE TO ETHANOL

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ABSTRACT: The production of bio-ethanol from lignocellulosic biomass via two different routes is compared. The pulping and fermentation route as state-of-the-art-process is discussed briefly, as well as presently discussed possibilities to improve this process. On the other hand, a production process with gasification, gas cleaning and synthesis gas conversion is described. The comparison of these production routes based on carbon conversion, energy conversion (efficiency) and cost price shows the potential of the synthesis gas route to become competitive. It shows higher carbon conversion from biomass to ethanol, slightly higher energy efficiency (compared to the improved fermentation process) and much lower cost price for the ethanol produced.
Keywords: bio-ethanol, efficiency, costs

1 MOTIVATION

Besides the use of ethanol as basic chemical the use as transportation fuel is easy. It can be blended into gasoline for Otto engines without any changes up to 5 %, as ETBE up to 15 %, using flexible fuel technology up to 85 %. In combination with low or zero taxes on bio-ethanol this leads to a strong increase in ethanol production by fermentation of cereals such as rye in Europe as well as corn in the USA. Therefore, the interest in second generation bio-ethanol from lignocellulosic biomass (LCB) for transportation fuel purposes is rapidly growing. Lignocellulosic biomass reveals no conflict in utilization to nutrition purposes. There are two different routes to produce ethanol from LCB: Decomposition of lignocellulose to sugars followed by classical fermentation and gasification of lignocellulose to synthesis gas followed by ethanol synthesis reaction.

2 ETHANOL PRODUCTION VIA FERMENTATION

2.1 State of the art [1]

Besides water, lignocellulosic biomass mainly consists of three components:
- cellulose (40 – 60 %, dry basis),
- hemicellulose (20 – 40 %, dry basis) and
- lignin (10 – 35 %, dry basis).

For classical fermentation, only C_6-sugars can be used. Cellulose completely consists of oligomers of C_6-sugars, hemicellulose is a mixture from oligomers of C_5- and C_6-sugars, while lignin contains no sugars at all. Hemicellulose and lignin form a strong framework around the cellulose, and for fermentation purposes this framework has to be disintegrated. The aim of the disinte-gration process must be to separate the lignin and the C_5-sugars from the hemicellulose from the rest of the biomass and convert this remaining part into an aqueous solution of monomeric C_6-sugars.

The first step in the biomass disintegration process is crushing. The wood is chipped to pieces of about 10 to 30 mm and then milled to particle sizes between 0.2 to 2 mm. Afterwards, a first hydrolysis with weak sulfuric acid takes place. In this hydrolysis, the C_5-sugars from the hemicellulose are dissolved. Liquid and solid fractions from this hydrolysis are separated. From the liquid fraction parts of the sulfuric acid are regenerated, the C_5-sugars are

fed to an anaerobic digestor to produce biogas (methane and carbon dioxide).

The solid fraction from the first hydrolysis is then treated with diluted sulfuric acid at higher temperature to dissolve the C_6-sugars from the cellulose and hemi-cellulose. The remaining solid fraction mainly consists of lignin, which after drying is fed to a combustion chamber together with the biogas. High pressure steam is gene-rated and expanded in a turbine to produce electricity for own requirements and as valuable by-product.

The liquid fraction from the second acid hydrolysis step is neutralized and further processed with yeast in the fermenter. Pure alcohol is then produced from the fermentation broth mostly with thermal separation process. Figure 1 shows a sketch of the complete process.
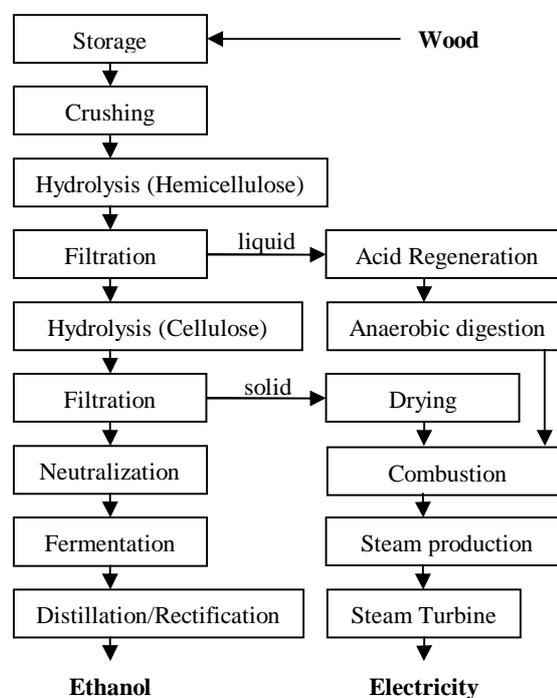

Figure 1: Sketch of fermentation process (state of the art)

2.2 Potential for improvements

Several alternative processes for the biomass disinte-gration like steam explosion, ammonia fiber explosion or carbon dioxide explosion are under development. These

processes may reduce cost and increase conversion rate of cellulose to monomeric C_6-sugars. The most promi-sing process under development to increase ethanol yield from biomass is the breeding of special bacteria culture (Clostridia, Thermoanaerobacter ethanolicus) that is able to convert C_5-sugars from hemicellulose to ethanol [2], because this is the only approach to increase biomass fraction which can be converted to ethanol within the fermentation.

3 ETHANOL PRODUCTION VIA SYNTHESIS GAS

3.1 Process outline [4]

The alternative route to produce ethanol from biomass is the thermo-chemical conversion. The process consists of four major steps:
- biomass gasification,
- synthesis gas conditioning,
- gas compression and
- ethanol synthesis.

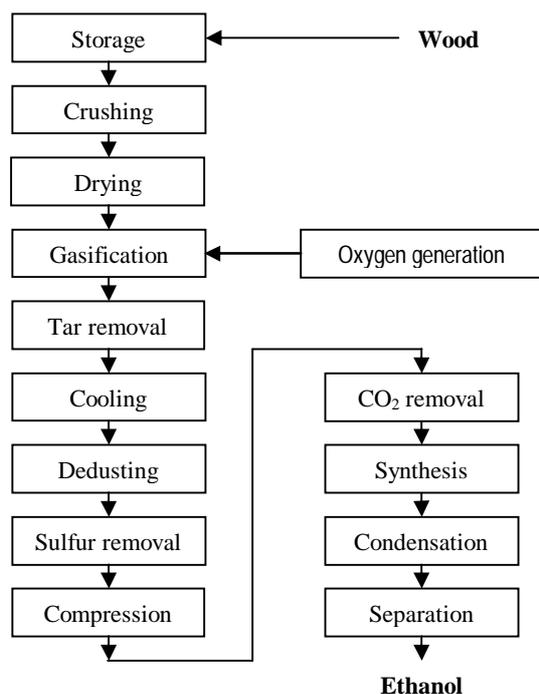The complete outline of the process is shown in figure 2.

Figure 2: Sketch of synthesis gas process

3.2 Biomass gasification

Also the production route via gasification starts with crushing of the biomass. Hereby the biomass is only chipped to pieces of around 50 mm (depending on gasifier used). The wood chips are then dried to a remaining moisture content of around 12 %. Then it is fed to the gasifier, which converts solid biomass into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, water, methane and depending on the selected gasifier several unwanted byproducts and nitrogen.

As will be explained later it is desirable to produce a synthesis gas with nearly equal fractions of hydrogen and carbon monoxide. Therefore a steam gasification process like the FICFB-system (fast internally circulating fluidized

bed) developed at TU Vienna and successfully demonstrated at Güssing (Austria) or the Taylor-system from the USA is not the gasification method of choice, because here the hydrogen content is much higher than the carbon monoxide content (see Table 1 for gas compositions).

Air blown gasification systems like the circulating fluidized bed test gasifier at Fraunhofer UMSICHT produce a synthesis gas with nearly equal fractions of hydrogen and carbon monoxide, but the nitrogen content of about 48 %, which is not easily to be separated from the synthesis gas, constitute a great inert mass diluting the gas and hence reducing reaction rate and conversion.

Table I: Gas composition of different gasifiers on dry basis (1: TU Vienna, 2: Taylor, 3: UMSICHT, 4: Chrisgas, 5: Carbo-V, 6: CUTEC)

	1	2	3	4	5	6
CO	23	18	18	19	39	27
H2	42	46	16	19	40	32
CO2	23	19	14	44	20	35
CH4	12	11	4	13	-	3
N2	-	-	48	-	-	-

A pressurized oxygen/steam gasification system as developed in the CHRISGAS project will give a nearly nitrogen free synthesis gas with a hydrogen and carbon monoxide content of 19 % each and the synthesis gas is already pressurized. A great disadvantage is the high carbon dioxide content, which on one hand hinders the synthesis an on the other hand reduces carbon conversion to ethanol.

Best choice for the synthesis of ethanol from biomass based synthesis gas is a pure oxygen gasification like the Carbo-V-system developed by Choren. Here we find the optimal hydrogen to carbon monoxide ratio of about 1 and a carbon dioxide content which is only one half of the carbon monoxide content. A potential alternative is the atmospheric steam/oxygen CFB process demonstrated by CUTEC in small scale.

3.3 Synthesis gas conditioning

The synthesis gas which leaves the gasifier is contaminated with several unwanted components, which must be removed prior to ethanol synthesis reactor. The contamination level of these components depends on the gasifier system chosen, but in common they are always too high to feed the synthesis gas directly to the synthesis reactor. The most common contaminants are
- tars,
- dust,
- sulfurous compounds (organic and inorganic) and
- nitrogen containing compounds (ammonia and hydrogen cyanide).

For each of these component groups separation processes must be applied. Tars and ammonia can be decomposed in a catalytic steam reforming at temperatures around 900 °C at surfaces containing Ni(0). Tars are reformed to additional hydrogen and carbon monoxide while ammonia is decomposed to hydrogen and nitrogen. As there is only little amount of nitrogen in natural wood, this will give only low amount of nitrogen in the gas.

Afterwards the gas should be cooled down to an intermediate temperature of 500-600 °C and then the dust can be removed in commercial metallic or ceramic filters.

The removal of H_2S can be done with a ZnO-Adsorber at temperatures around 350 °C. Other sulfurous compounds – if contained in the raw synthesis gas, depending on feedstock and gasifier – must be converted to H_2S before. Because of the high hydrogen content in the raw synthesis gas this is easily done nickel-molybdenum or a cobalt-molybdenum catalyst.

3.4 Gas compression

The ethanol synthesis is done under elevated pressure of around 100 bar. Therefore a multistage-turbo compressor is needed to reach the desired pressure. As carbon dioxide is hindering the ethanol synthesis by dilution and negative effects on kinetic and reaction equilibrium, it must be removed to a level of about 1 %. Best available method is washing with methyldiethanol-amine (MDEA) at an intermediate pressure of around 20 bar.

3.5 Ethanol synthesis

The synthesis of ethanol from hydrogen and carbon monoxide can be made in principle by two different reactions

$$3\ CO + 3\ H_2 \Leftrightarrow CH_3\text{-}CH_2\text{-}OH + CO_2 \quad \Delta H_R = -297\ kJ/mol$$
$$2\ CO + 4\ H_2 \Leftrightarrow CH_3\text{-}CH_2\text{-}OH + H_2O \quad \Delta H_R = -256\ kJ/mol$$

The first reaction requires a H_2/CO-ratio of 1, the second reaction requires a ratio of 2. Commercial methanol catalysts based on Cu/Co/ZnO can be modified to also catalyze the second reaction with a medium selectivity towards ethanol (<60 % C_2-components). A higher selectivity of ≈75 % ethanol can be achieved with supported rhodium catalysts and a synthesis gas with equal hydrogen and carbon monoxide concentrations at temperatures around 275 °C. Obviously reaction 1 (as brutto reaction) is enhanced. This reaction can take place in different reactors. It is possible to use fix bed, circulating fluidized bed or slurry reactor. Due to the high heat release during reaction, the fix bed is less suitable for this purpose. As the abrasion is much lower in slurry reactor than in CFB, the slurry reactor would be best choice due to the high price of the active element in the catalyst, which is concentrated on the outer surface of the catalyst particle. An alternative approach could be to perform the reaction under homogenous catalytic conditions, where rhodium is solved in the carrier liquid as complex.

4 COMPARISON

4.1 Technical comparison

A comparison of both routes to produce ethanol from lignocellulosic biomass can be based on conversion rates. Figure 3 shows different conversion rates of carbon from biomass to ethanol, while figure 4 shows the conversion rates of energy content from biomass to ethanol.

For the described process of two stage acid hydrolysis followed by fermentation as the state-of-the-art process a carbon conversion of 27 % can be measured. Theoretically, if the C_5-sugars from the hemi-cellulose can be fermented to ethanol and the efficiency of all stages can be improved, a maximum carbon conversion from biomass to ethanol of

35 % can be reached. A production route of ethanol using pure oxygen gasification and chemical synthesis with rhodium catalyst in heterogenous conditions may reach a conversion rate of 42 %. However, the additional energy demand for the synthesis route is not accounted for.
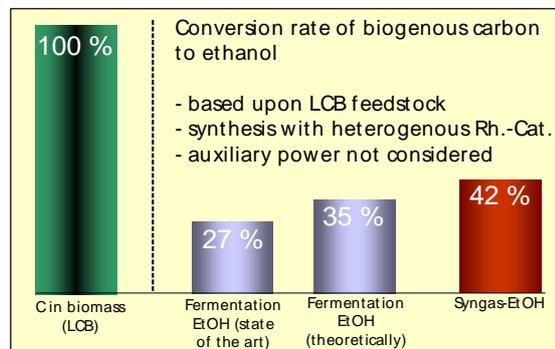

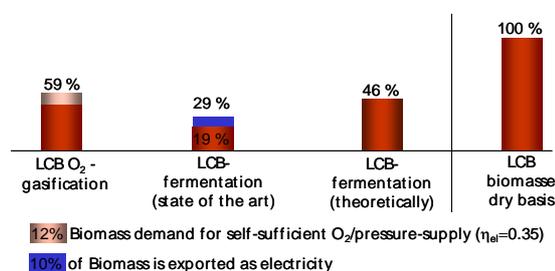**Figure 3:** Carbon conversion rates [3, 4]

Figure 4: Energy conversion rates

Figure 4 shows the energy conversion rate for both processes. For an ethanol production plant with a state-of-the-art fermentation process 19 % of the energy content of the feed biomass is transferred to the ethanol. In addition, the process is self sufficient (waste streams from biomass disintegration are used to produce steam for drying and distillation) and exports additional 10 % of the original biomass energy content as electricity. Al together, nearly 30 % of the energy content of the biomass are transferred into usable energy carrier.

For a fermentation process with increased yield in the disintegration stages and with the additional fermentation of C_5-sugars, a maximum conversion of 46 % of the biomass input energy into chemically stored energy in the ethanol is possible. The process is still self sufficient (waste streams are used for steam production) but there is no excess electricity left.

For a gasification/synthesis process it seems to be possible to produce ethanol which contains 59 % of the energy fed to the gasifier with the wood. But this figure only becomes true, if the energy demand for oxygen production and compression is exported from the grid. For a self sufficient gasification/synthesis process approx. 12 % of the biomass have to be used to produce the necessary energy for oxygen production and compression, so that at the end about 47 % of the biomass energy content is transferred to the liquid product.

4.2 Economical comparison

For an equal production of 100 000 t/a Ethanol, investment cost as well as operating costs have be evaluated for both routes. For fermentation the standard process with two-stage acid hydrolysis and only C_6-sugar

conversion is calculated. For synthesis gas route a cold gas efficiency of 80 %, a loss of 5 % due to carbon dioxide separation and an ethanol selectivity of 75 % are assumed. As can be seen from table II, the investment cost for a fermentation plant is much bigger than for a thermo-chemical conversion plant (roughly a factor of 1.5). But although in the fermentation plant a valuable by-product – electricity – is being produced, the ratio of cost price of ethanol from both routes is even worse for the fermentation route (roughly a factor of 2). The underlying assumptions are biomass water content of 35 %, 8 000 operating hours a year.

Table II: Economic parameters of both routes (basic case) [4]

	Fermentation	Synthesis gas
Investment cost	263.5 Mio €	180 Mio €
Wood input	144.2 t/h	44.1 t/h
Biomass price	50 €/t (db)	50 €/t (db)
Electricity credit	0.03 €/kWh	-
Ethanol cost price	**0.85 €/l**	**0.44 €/l**

The high cost price of fermentation ethanol mainly results from 2 factors: the high biomass demand (more than three times the biomass demand of the synthesis gas route) and the relatively low credits for electricity. Figure 5 shows the variation of the ethanol cost price of the fermentation route as a function of electricity credits. Only above electricity credits of 17.5 ct/kWh the ethanol cost price for fermentation ethanol becomes lower than the cost price for synthesis gas ethanol at a wood price of 50 €/t_db.
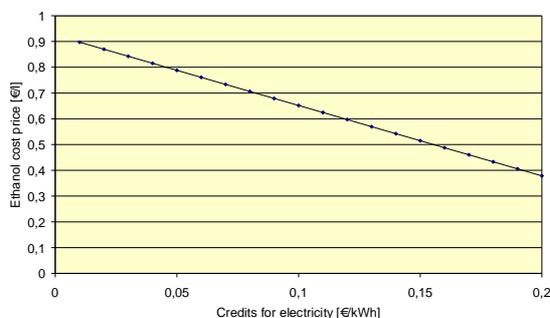

Figure 5: Ethanol cost price as function of electricity credits

The largest individual item within operating costs is the biomass price. Figure 6 shows the variation of ethanol cost price for the basic case for both routes in comparison.
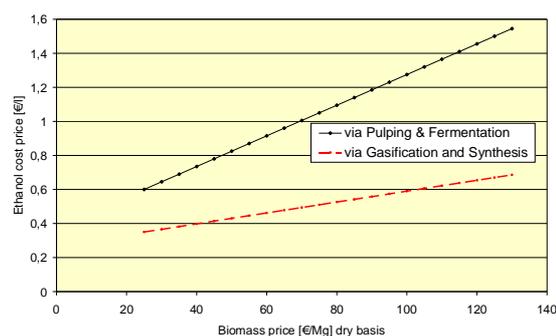

Figure 6: Ethanol cost price as function of biomass price

As can be seen clearly from the graphs, the dependency of the cost price from biomass price is larger for the fermentation route, the slope of the graph is higher. This is directly connected with the much bigger biomass demand for fermentation.

5 FUTURE WORK

Most publications dealing with the synthesis gas process are focussed on catalyst development. The published experiments were all conducted in small batch reactors. To further develop the process a continuous test facility in laboratory scale is being built. Different catalysts in different types of reactor (fixed bed, bubbling fluidized bed, slurry) will be tested. Operating conditions are around 275 °C and 100 bar. Mixtures of hydrogen, carbon monoxide, carbon dioxide and argon as diluent will be compressed together with an adjustable recycle stream. The product gas will be rapidly cooled down by multi-stage heat exchangers or quenched with liquid product followed by heat exchanger. The liquid product will be analyzed after test runs while the remaining gas stream will be analyzed online with IR. (see figure 7)

6 SUMMARY

The state of the art of bio-ethanol production through fermentation process and possible future improvements have been presented briefly. A promising alternative approach to ethanol production from biomass is the gasification/synthesis process, where the biomass is used completely while in the fermentation process only the sugars can be converted. The comparison of both routes based on carbon conversion and energy conversion shows that the synthesis gas route has the potential to be more effective than fermentation route, even if all presently discussed improvements for fermentation process come true. The economical comparison shows the clear potential of the synthesis gas route for the production of ethanol at reasonable costs.
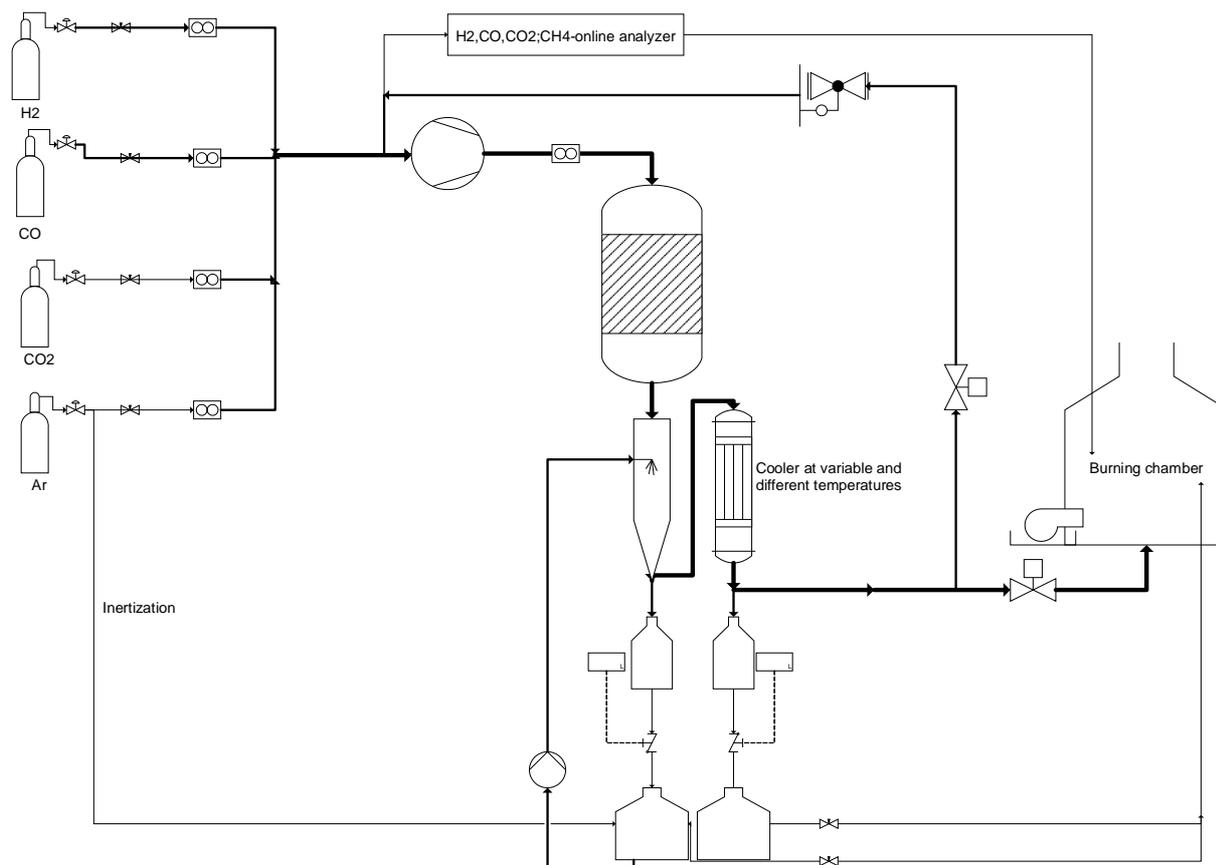
Figure 7: Sketch of synthesis gas process

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