Synthesis Gas from Biomass – Problems and Solutions en route to Technical Realization

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Abstract

A thermochemical two-step process called bioliq® for the conversion of biomass in tailored synthetic fuels and organic chemicals via the production of syngas as a versatile intermediate is being developed. The research and development work has been focused on synthesis gas generation from liquefied biomass in a pressurized entrained flow gasifier. The sequential process steps have been successfully investigated in the laboratory and on the pilot plant scale. Fast pyrolysis for liquefaction of the ligno-cellulosic biomass has been conducted with the Lurgi twin-screw mixing reactor successfully. Pumpable, homogenous slurries of the pyrolysis liquids with high loadings of pyrolysis char powder have been prepared with colloid mixers for subsequent gasification. Efficient and smooth slurry gasification to a tar-free, low methane synthesis gas has been obtained with a number of different slurries in four testing campaigns in the 3–5 MW_{th} entrained flow pilot gasifier of Future Energy, Freiberg, at 26 bar. A complete process line with around 2 MW_{th} capacity from fast pyrolysis to synthesis with an 80 bar gasifier is under design, the pyrolysis plant already under construction in co-operation with Lurgi AG.

Introduction

Lignocellulose in the form of straw, hay or residual wood is the most inexpensive and abundant biomass by far. Presently, biomass is covering about 3% of the primary energy need in Germany. Consistent use of all biogenous residual and waste materials will increase this proportion to about 12% [1]. As biomass is the only renewable carbon source, it may replace part of the fossil resources and energy carriers in the long term. Transition of organic chemical industry to biomass as a raw material represents a long-term and great challenge in chemical research and development. Apart from the already practiced utilization of natural substances, there is hardly any economic incentive to intensify the chemical use of biomass for mass production. Early development of the corresponding technologies, however, is a precaution that may reduce today's dependence on petroleum and improve our competitiveness. Use of biomass for the production of tailored synthetic fuels and organic chemicals should therefore be given priority to its use on the electricity or heat market.

Synthetic chemicals and fuels from biomass might replace part of fossil energy carriers in the short term already and, hence, contribute to reducing CO_2 emissions. Further increasing crude oil prices, aspects of supply security as well as existing emission limits give new political and economic impulses in the search for solutions. For example, the European Union wishes to increase the current share of biofuels to 5.75% in 2010.

In principle, the method of producing synthetic chemicals and fuels from fossil materials, mainly coal and natural gas, has been known for a long time. For biogenous solid fuels, however, an adequate technology still remains to be developed. Coal or natural gas are first converted into a synthetic raw gas by a reaction with water vapor and oxygen. After cleaning and conditioning, the product desired is obtained by a catalytic conversion at increased pressures and temperatures. The main chemical processes established for the production of synthetic chemicals and fuels are the Fischer-Tropsch synthesis (FTS) and methanol synthesis (Fig. 1) [2, 3]. The FT raw product consists of a large spectrum of hydrocarbons that are separated and processed depending on the target product desired. Methanol is the intermediate product of the MtG process (methanol to gasoline). However, it can also be used directly as a fuel. It is applied for the synthesis of the anti-knock additive MTBE (methyl-tert. butylether), the production of RME (rape methyl ester, biodiesel) by esterification of rape oil, and as a direct fuel and hydrogen carrier in DMFC fuel cells. Fully synthetic fuels or 2nd generation biofuels have a higher purity and environmental compatibility than petroleum-based fuels and may be tailored to specific requirements of e. g. automotive manufacturers and stricter emission standards.

Problem

Compared to the use of fossil fuels, synthesis gas production from biomass is more complex and sophisticated. For use on a large technical scale, the following problems have to be solved:

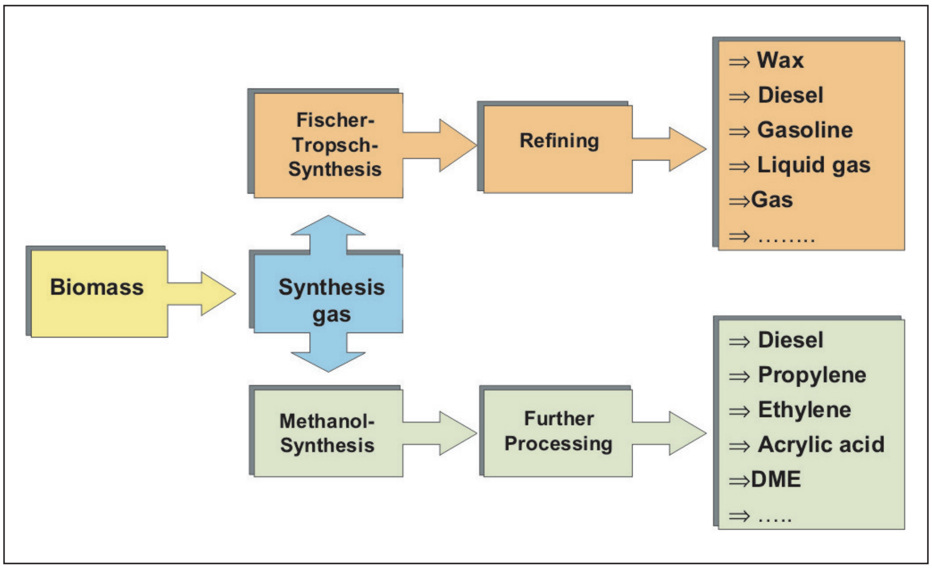

Fig. 1 Utilization paths of synthesis gas

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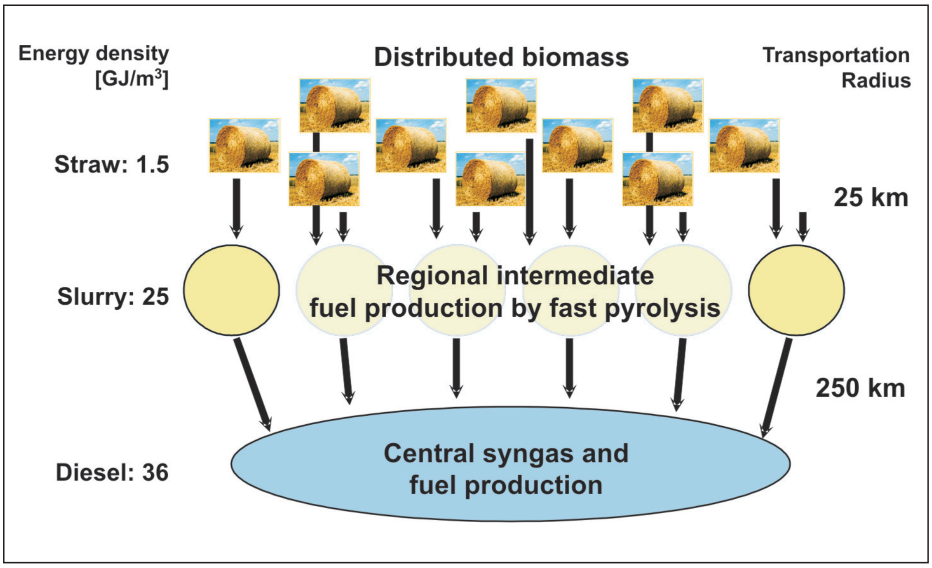

Fig. 2 The decentralized/central slurry gasification concept

- Biomass arises in a regionally distributed manner, i. e. it has to be collected over large areas and transported over accordingly long distances
- The less valuable, ash-rich biomass in particular has a low volumetric energy density (e. g. straw bales about 2 GJ/m^3). Also here, the problem of economically acceptable transport distances has to be solved
- A large variety of usable biomasses exists. It must be ensured that the processes applied are suited for a maximum number of feed stocks
- Biomass is taken from the biosphere; for long-term use, an ecologically compatible extraction of the raw material must be ensured
- Biomasses are heterogeneous solid fuels of partly variable chemical composition; solid fuels in principle require a higher technical expenditure. Use of existing technologies for the processing of fossil materials, for instance, helps to shorten development times and reduce the risks
- The high ash contents of fast growing biomasses (straw, hay, etc.) in particular cause problems in thermochemical processes due to corrosion, sticking, and plugging of the technical components
- Fuel syntheses require a tar-free, methane-depleted synthesis gas at high pressures (FTS up to 30 bar, methanol and DME up to 80 bar) and a crucial elimination of trace substances to avoid poisoning of the catalyst
- Gasification of biomass of an average chemical composition of $C_6H_9O_4$ results in a C/H ratio of about 1 that is insufficient for direct production of hydrocarbons. An additional step, the water-gas shift reaction, is necessary, in which part of the CO is converted into hydrogen and CO_2 by the addition of water
- The use of biomass also has social aspects, as new logistics and income and labor structures have to be established in the agricultural, grassland, and forestry sectors for them to be able to supply and process energy materials.

The bioliq® Process

The Karlsruhe bioslurry gasification process has been designed for the conversion of ligno-cellulosic biomass into organic chemicals and tailored synfuels with electricity and power as inevitable by-products [4, 5]. The development has been focused on the front-end steps for syngas generation. The tail-end steps for syngas cleaning, synthesis and product conditioning are well known from many technical applications in the chemical industry and the huge CTL and GTL plants of Sasol and Shell. The bioliq® concept meets the logistical and technical requirements resulting from the widely distributed occurrence of biomass and the needs for an economic production of chemicals and fuels in industrial scale (Fig. 2). Syngas production is the key issue of the process: a slagging entrained flow gasifier operating at high pressure above downstream synthesis pressure and temperatures above the ash melting point has been selected because of the following advantages: (1) tar-free, low methane syngas, (2) high carbon conversion >99%, (3) high potential throughput up to the GW_{th} range, (4) short start-up and sudden shut-down, (5) high feed flexibility. For pre-treatment of biomass, its liquefaction by fast pyrolysis can serve different aims: (1) to generate valuable chemicals, (2) to prepare a liquid fuel for more convenient and efficient combustion for heat, power or electricity, (3) to prepare a pumpable fuel for convenient and efficient gasification to produce syngas. Usual objective of flash pyrolysis is a high yield of a stable, clean and ash-free bio-oil for direct use in boilers, diesel engines or turbines. High quality oil for these applications requires much effort during production and eventual downstream upgrading procedures. For gasification however, high purity is not needed. Any suspension of pulverised pyrolysis char and liquids with LHV >10 MJ/kg which can be pumped and pneumatically atomised with pure oxygen is suited for the gasifier.

Step 1: Bio slurry production

In a first step of the bioliq® process, pyrolysis oil and pyrolysis char are generated from the biomass by de-centralized flash pyrolysis (Fig. 2). The transported bed LR-type (Lurgi-Ruhrgas) mixing reactor applied for this purpose has been used as a “sand cracker” in the industrial flash pyrolysis of various refinery products for about 40 years already [7]. In the present process, the finely chopped biomass particles are heated up rapidly to about 500 °C by hot sand in the twin screw mixing reactor (Fig. 4). After a short residence time of a few seconds, the hot pyrolysis vapors leave the reactor together with the fine char powder [6]. The main portion of gas is cooled to form liquid pyrolysis products: a single step condensed bio-oil phase is less stable than a separated tar and aqueous phase. The remaining pyrolysis gas produced may be used in the process for heating up the heat carrier. The pyrolysis char and condensates are mixed in a colloidal mixer to a transport-stable, pumpable slurry, the volumetric energy density of which is higher by more than a factor of 10 compared to the original biomass. These slurries are stable mixtures of organic tar and aqueous condensate with more than 30 wt.% of char. Main objective of the fast pyrolysis is the production of sufficient organic and aqueous liquid for complete char suspension [8, 9]. In addition to the ca.

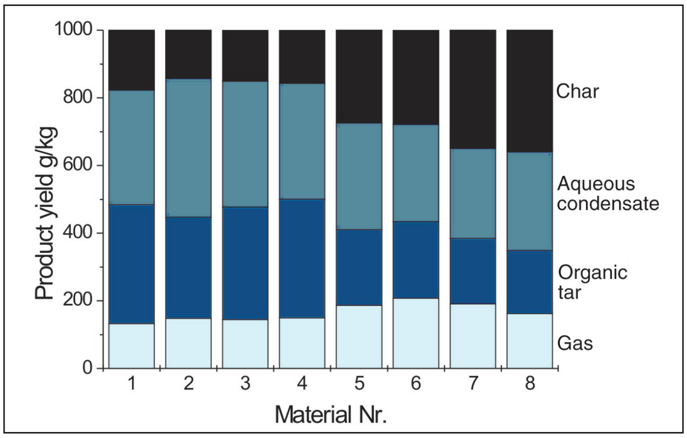

Fig. 3 Yields of the flash pyrolysis of different kinds of wood meal and straw

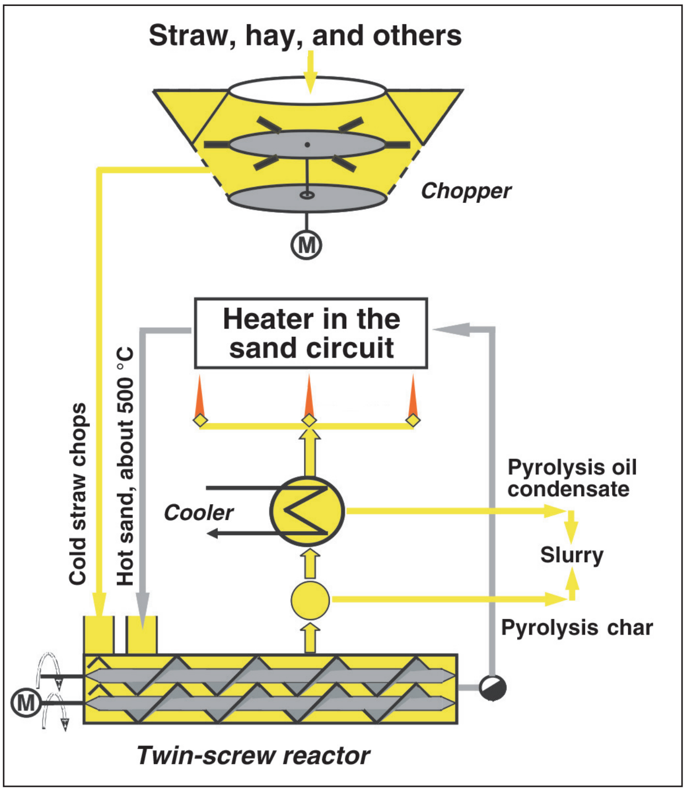

Fig. 4 Flowchart of flash pyrolysis with a twin-screw mixing reactor

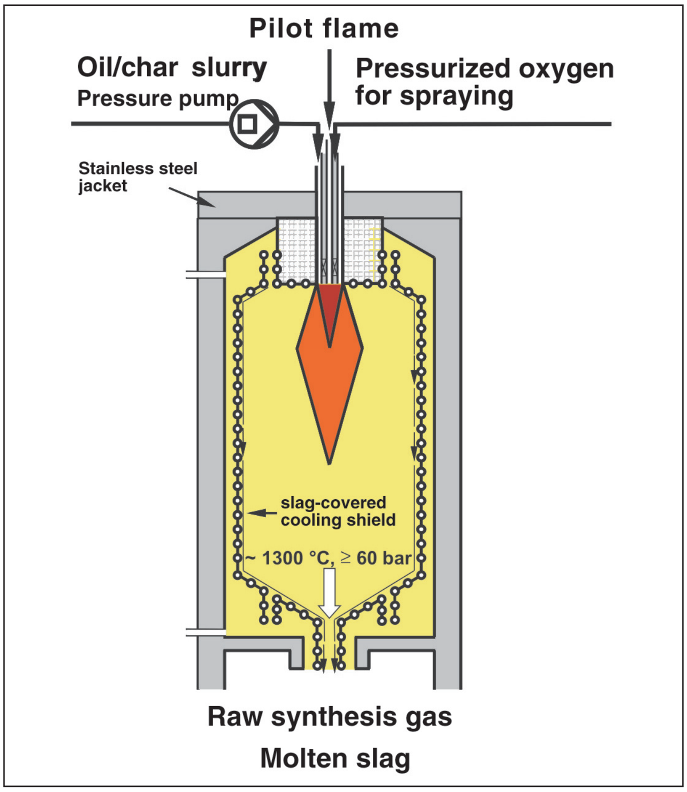

Fig. 5 Flowchart of the GSP high-pressure entrained-flow gasifier

50–65% energy in the liquid condensates now also the ca. 25–40% fraction in the char is contained in the slurry ready for gasification. Some results of fast pyrolysis obtained for various feedstocks are plotted in Figure 3. The materials 1–4 are different types of wood, materials 5–8 are different types of straw. The yields differ significantly for different materials, but also for materials of the same group of biomass.

Step 2: Bio slurry gasification

The slurry prepared from the pyroylsis products is then transported to a central plant for syngas production and conversion and sprayed into a large-scale high-pressure entrained-flow gasifier together with oxygen and converted substoichiometrically ($\lambda \approx 1/3$) at temperatures above 1200°C to a tar-free and methane-depleted raw synthesis gas [10–12]. Gasification takes place at a pressure exceeding that of the downstream synthesis, such that no complex interim compression is needed. The entrained-flow gasifier of the GSP type (Gaskombinat “Schwarze Pumpe”) is suited in particular for the gasification of ash-rich biomasses. It was developed originally for the gasification of the salt lignite existing in Central Germany [13]. The gasifier is equipped with a cooling screen, onto which the molten ash is deposited in the form of a liquid slag leaving the reactor (Fig. 5). Suitability of this type of gasifier has been demonstrated by four test campaigns with various bio-slurries and operation parameters using the only 3–5 MW pilot gasifier of Future Energy, Freiberg. The test runs have been conducted with slurries from different pyroylsis products from hard and softwood as well as from wheat and rice straw. The slurry properties ranged between LHV from 10–24 MJ/kg, densities of 1100–1300 kg/m^3 and viscosities (20 °C) of 1–10 Pas. In all experiments, a practically tar-free, methane-depleted (<0.1 vol.%) synthesis gas was produced. It typically consisted of 43–50 vol.% carbon monoxide, 20–30 vol.% hydrogen, and 15–18 vol.% CO$_2$.

The synthesis gas is cleaned, conditioned, and transferred to chemical synthesis at process pressure already. By the above mentioned routes (Fig. 1) synthetic chemicals and fuels can then be produced. This process allows to generate about 1 t synthetic fuel from about 7 t air-dried straw or wood. Nearly 50% of the energy initially contained in the biomasses remains in the liquid product. As by-products, heat and electricity are generated, by means of which the energy consumption of the process can be covered completely.

After technical feasibility of the process had been confirmed by demonstrating the suitability of all process steps, it is now concentrated on the further development of the process. For this purpose, a pilot plant along the complete process chain with a biomass throughput of 500 kg/h is being built at the Forschungszentrum Karlsruhe with support by the Agency of Renewable Resources (Fachagentur Nachwachsende Rohstoffe, FNR). This pilot plant will serve to demonstrate and further develop the process, prepare upscaling to a commercially relevant scale, demonstrate the feasibility of the pro-

Fig. 6 Process building for biomass conditioning, fast pyroylsis and slurry preparation

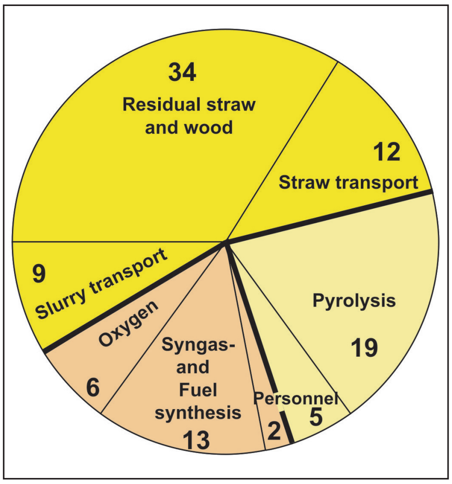

Fig. 7 **Percentage shares in the costs of production of BTL synthesis fuel by the Karlsruhe bioliq® process**

cesses used, and help to make a reliable cost estimation. The first construction phase, comprising biomass cutting, flash pyrolysis, and continuous slurry mixing, was started in 2005. Figure 6 shows the process building under construction. The clearly visible tower-like construction accommodates the pyrolysis plant that will be operated from 2007 together with the Lurgi AG, Frankfurt.

Cost Study and Potential

The Karlsruhe bioliq® process is tailored to the distributed biomass arisings in agriculture. Fast pyrolysis and slurry production with energy densification of the feedstock may take place in a larger number of decentralized plants, whereas gasification and subsequent gas conditioning and synthesis will be carried out centrally in economically efficient large-scale plants for fuel or chemical synthesis. The slurry will be transported to these plants favourably by railway. When assuming about 40 flash pyrolysis plants with a capacity of 200,000 t/a each that produce slurries for a central syngas and fuel production plant with a capacity of 1 million t fuel and a price of the feedstock of 70 Euro/t air-dry material, production costs of less than 1 Euro per kg fuel result. The survey of the costs (Fig. 7) shows that about half is due to the supply of biomass in Germany.

Today, the production costs of synthetic chemicals and fuels from biogenous feedstocks correspond to or exceed those of fossil fuels. The high specific mass throughput, feeding of the solids and residues and their discharge from the process zones as well as complex cleaning of the synthesis gas, however, lead to higher process costs. The gas generation and synthesis plants should have the size of refinement facilities, but will probably remain at the lower size limit. As a result of cost degression these facilities will be more expensive. A wider spectrum of feedstocks will improve the flexibility, utilization, and economic efficiency of the plants. In this respect, the feedstocks are by no means limited to pure biomass. In principle, any mixtures of biomass, fossil fuels or organic wastes and any mixtures with calorific values in excess of 10 MJ/kg are suited. By integrating the gasifier in a plant complex of chemical industry, diversification and value of the usable products may be increased.

Process development is presently focusing on so far hardly used, low-value biomass, such as excessive straw, low-quality hay or residual wood. Use of whole wood is considered a non-profitable solution in the long term. Although this less problematic feedstock may facilitate an earlier technical implementation, increasing consumption as construction material, for cellulose production, and for decentralized and domestic power and heat production is expected. Use of whole plants seems to be more reasonable for cereals or specially grown energy plants. According to accompanying systems analysis [1, 14] about 5 million t of synthesis fuel could be expected to be produced from a total of about 30 million t dry matter of residual wood and excessive straw already today. This corresponds to about 10% of the current consumption of gasoline and diesel fuels in Germany [15].

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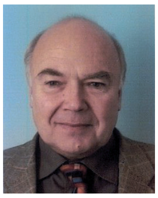

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