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## **DAS BIOLIQ-VERFAHREN**

KONZEPT, TECHNOLOGIE

UND STAND DER ENTWICKLUNG

## **THE BIOLIQ PROCESS**

CONCEPT, TECHNOLOGY

AND STATE OF DEVELOPMENT



# THE BIOLIQ PROCESS CONCEPT, TECHNOLOGY AND STATE OF DEVELOPMENT

Synthetic fuels from residual biomass may contribute considerably to the global motor fuels demand. Gasoline and diesel of high quality can be produced by that way. For large scale use of biomass logistical and technological obstacles are to be considered, resulting in bioliq process currently developed at the Karlsruher Institute for Technology (KIT). A de-central pre-treatment of biomass for energy densification by fast pyrolysis allows for the economic supply of centralized industrial facilities in large scale, in which synthesis gas is produced and further converted to the desired synthetic fuels.



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## BACKGROUND

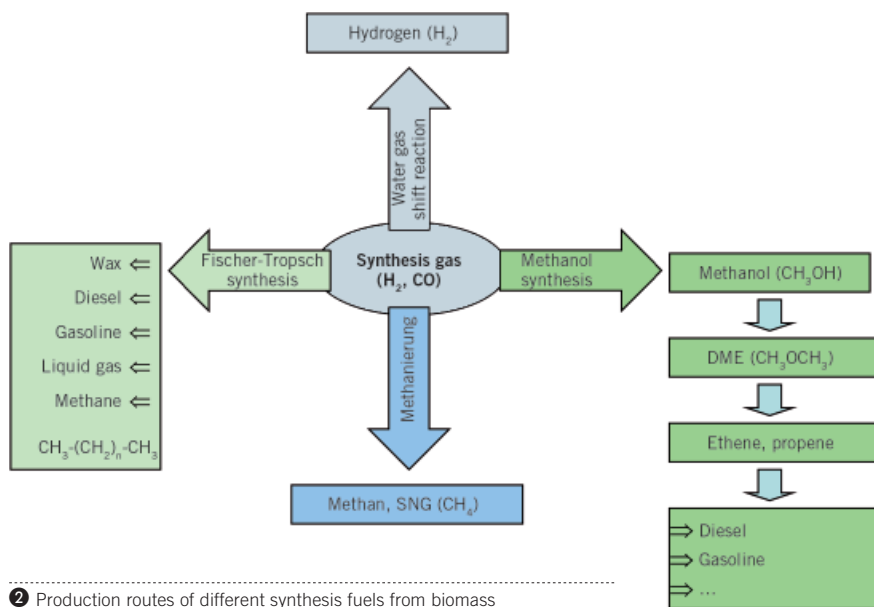
Fossil energy sources, in particular crude oil, are the basis of today's supply of fuels. Even if the forecasts about their date of depletion differ greatly, there is no doubt about their long-term shortage. The widely varying and increasing energy demand of emerging states such as India and China accelerates this effect. In addition to that, apart from the finite nature of fossil resources, problems with securing energy supplies, costs of exploitation and transport and the demand for environmentally compatible handling of resources play a major role. As shown by the recent developments of the world market prices for crude oil, even small disruptions already suffice for causing massive variations in price on a global scale with serious consequences for the world economy.

The consistent use of renewable energy sources is a way of reducing the dependence on fossil raw materials (crude oil, natural gas and coal) in particular in the industrialized countries. Moreover, the use of renewable energy sources can make a considerable contribution to reducing CO<sub>2</sub> emissions and thus diminishing the anthropogenic greenhouse effect. Among the renewable energies, biomass is the only renewable carbon source and should therefore be used in the long run as raw material for producing carbon-containing products and energy sources. Even if the proportion of biomass in the primary energy consumption has exceeded the 10 % mark in Germany in 2009, presently it is used predominantly for the generation of heat and power (combined 80 %). Biofuels, in particular biodiesel, make up 20 % of the energetic use of biomass. The contribution of biomass to mobility is being discussed controversially in the public and in professional circles. However, without any doubt, liquid fuels with their so far unattained high energy densities will continue to make a significant contribution to passenger and cargo transport for a long time to come. Up to now, the focus has been on bioethanol and biodiesel from sugar-containing crops and oil seeds as first generation biofuels, along with critical questions about their effects on the food and feed market and worldwide applicable and sustainable plant growing standards.

Second generation biofuels rely on residues and side products from agriculture and forestry, which are available in large quanti-

HYDROCARBONS	MTG	FT (CO-CAT.)	FT (FE-CAT.)
LIGHT GAS	1.4	5	8
ETHANE, ETHENE	5.5	0	4
PROPANE, PROPENE	0.2	3	13
ISOBUTANE	8.6	1	1
N-BUTANE	3.3		
BUTENES	1.1	2	9
GASOLINE FRACTION (C <sub>5+</sub> )	79.9	19	36
GASOIL, MEDIUM DISTILLATE	–	22	16
HEAVY OIL, WAXES	–	46	5
OXYGENATES	No data available	1	5

① Hydrocarbon compositions of the MTG process and of products from Fischer-Tropsch synthesis obtained from cobalt- or iron-catalysts



processed on a large industrial scale in Mossel Bay, South Africa, and in Bintulu, Malaysia, at an annual capacity of approximately 2 (South Africa) and 1 (Malaysia) million t, respectively, to give synthetic fuels. In addition to fuels, the production and further processing of methanol also allow a large number of important key chemicals to be prepared. Currently, a whole series of methanol plants based on natural gas and coal are built in particular in the Middle East and in China, which already today is the main consumer and producer of this substance. If the world's annual production in 2008 was 45 million t, the production capacity in 2010 is estimated at 85 million t.

### THE BIOLIQ PROCESS

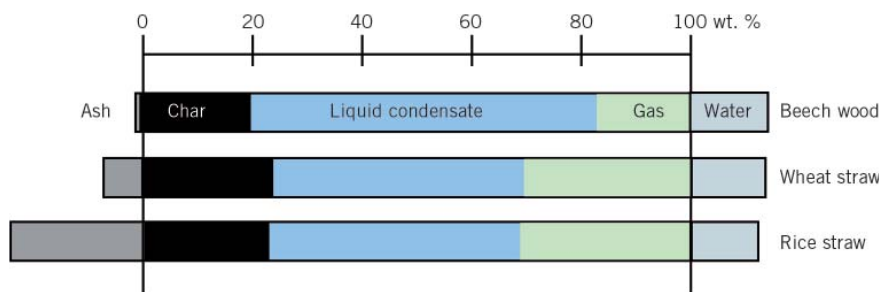
The use of biogenic starting materials is a particular challenge for the production of synthesis gas products, for which an adequate technology still has to be developed. The collective term biomass comprises a wide range of different materials, most of which have low volumetric energy density and are distributed over a wide space. On the other hand, in order to enable economical operation, the complex technology of producing synthetic fuels requires large-scale production plants. The Karlsruhe Bioliq process allows decentralized pre-treatment of biomass in regionally distributed plants. The high-energy intermediate biosyncrude can be transported economically even over large distances and subjected to further processing in the required large-scale plants. The process comprises several process steps, which are currently set up at the Karlsruhe Institute for Technology (KIT) in the form of a pilot plant:

The pre-treatment of biomass is performed by a so-called fast pyrolysis. The finely comminuted feedstock is heated in the absence of air together with hot sand

ties. These synthetic fuels include hydrogen, methane, (SNG – Substitute Natural Gas), ethanol from lignocellulose and the wide range of BTL fuels (Biomass to Liquid) generated from synthesis gas. The latter comprise methanol, ethanol, dimethyl ether and BTL diesel and gasoline. The route whereby such fuels are generated from fossil raw materials, predominantly from coal and natural gas, has been basically known for a long time and already introduced as Gas to Liquid (GTL) or Coal to Liquid (CTL) processes proceeding via synthesis gas as intermediate. Coal or natural gas is first reacted with steam and oxygen to give a crude synthesis gas, a mixture of hydrogen and carbon monoxide. The crude synthesis gas is freed from particles, CO<sub>2</sub>, HCl and trace elements, which would interfere in the subsequent synthesis, in which the syngas is reacted catalytically at high pressures and temperatures to the desired product. XTL fuels

can be very similar to conventional fuels or even better in terms of their combustion and emission behavior. They can be used directly using the presently available distribution infrastructure, require no new drive technology and allow a similar radius of action as petroleum-based fuels.

Different catalytic processes lead from the synthesis gas either directly to hydrocarbons. In the Fischer-Tropsch process hydrocarbons of different chain length are produced, which have to be separated, depending on the desired product range. Another route proceeds via methanol to give dimethyl ether or olefins (Methanol to Olefins – MTO), and finally to gasoline (Methanol to Gasoline – MTG) or diesel fuels (Methanol to Synfuel – MTS), ① and ②. This is how Sasol produces approximately 6 million t/a in the worldwide largest Fischer-Tropsch plants, which corresponds to about one third of the fuel consumption in South Africa. Natural gas is



③ Product yields of fast pyrolysis using different feedstocks

as heat transfer agent in a twin-screw reactor to 500 °C within seconds. A large portion of the vapors can be condensed to give brownish pyrolysis oil that has a strong smell of smoke aromas. The rest is made up of a flammable gas, which can be used for reheating the circulated sand. Their proportions in the product differ, depending on the biomass used, ③. In addition to approximately 20 % of coke, 50 to 60 % of pyrolysis oil and 20 to 30 % of gas on a water- and ash-free basis are formed, which contain about 10 % of the heating value. Coke and pyrolysis oil are admixed to the biosyncrude, which contains about 85 % of the energy originally contained in the biomass, but has only less than a tenth of its original volume and an energy density that is comparable to that of lignite. This intermediate is stable on storage and transport and constitutes a fuel that is highly suitable for the next process step: In entrained flow gasification, the biosyncrude is reacted with oxygen at more than 1200 °C to give a tar-free synthesis gas low in methane, as required for the subsequent chemical syntheses. As these processes take place under high pressures of between 30 and 80 bar, the Bioliq process also performs gasification under high pressure in order to avoid expensive compression of the synthesis gas. The Bioliq entrained flow gasifier is designed for an operating pressure of 80 bar at a thermal fuel capacity of 5 MW. To account for the high ash contents of the biomasses to be used, the pilot gasifier is equipped with a cooling screen with a refractory material. By maintaining the gasifier at a temperature optimized to the slag melt properties of the biomass, a firmly adhering slag coat is applied to the refractory cladding, protecting the material from abrasion and the reactor from corrosion. The draining slag melt is discharged, after passing through a water quench, via a slag sluice as a solid material. Apart from being highly compatible with fuels of high ash content, the cooling screen also results in a high reactor life and allows quick start-up and discharge, thus ensuring safe operation. The crude synthesis gas is purified and conditioned. For this, the KIT pilot plant uses an alternative hot gas purification method, which, compared with the conventional method used on a large industrial scale, has better energy efficiency



④ Process building of the pyrolysis pilot plant at the KIT

and lower investment costs, in particular with smaller plant sizes. This is based on the fact that the order of magnitude of, for example, a mineral oil refinery having a production capacity of 10 million t/a cannot be achieved using biomass as raw material, but is lower by a factor of about 10 and thus would be a priori less economical. To compensate this scale effect, an efficient technology would be, among other things, is required.

The gas purification unit designed for 80 bar removes a partial flow of 700 Nm<sup>3</sup>/h (2 MW<sub>th</sub>) and precipitates particles by means of ceramic filter candles, removes acid gas components and alkalis by means of inorganic adsorbents and catalytically converts NH<sub>3</sub>, HCN and organic components in a final catalyst stage at a continuous temperature level of initially 500 °C, which can be varied later on, in order to optimize the heat balance of the process. In the synthesis stage, the pre-purified synthesis gas is freed of CO<sub>2</sub> in a conventional solvent wash and then converted directly to DME in a single-step synthesis. In preliminary work on the process, it has been shown that no adjustment of the hydrogen/carbon monoxide ratio (for example one with biomass as feedstock, while for methanol synthesis, it would have to be

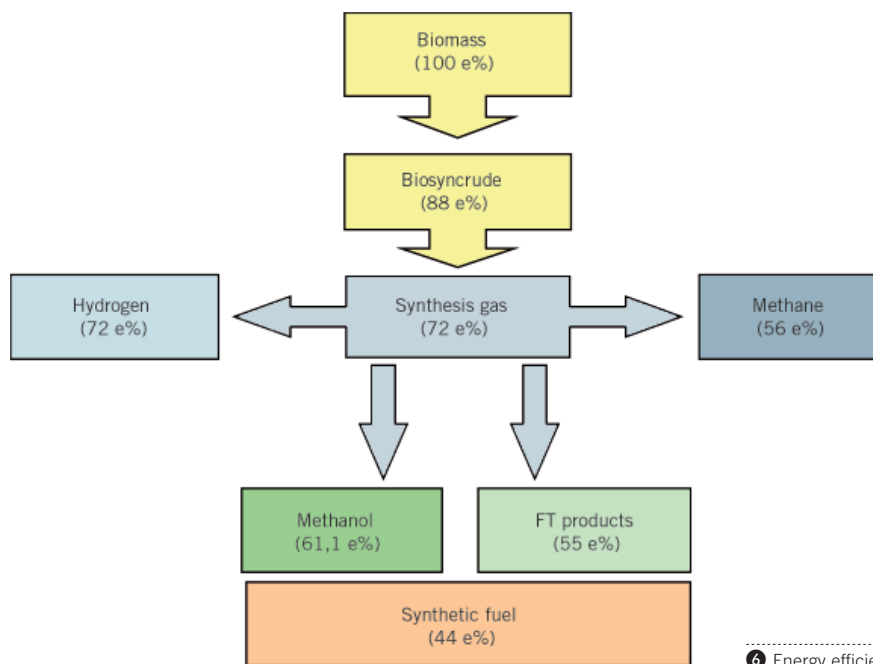
set to 2) via a separate water gas shift reaction ( $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$ ) is required. The next step is a zeolite-catalyzed dehydration of the DME with oligomerization and isomerization of the hydrocarbons used. Whereas the fuel synthesis proceeds with practically quantitative conversion, only about half of the synthesis gas is converted in the DME stage, the other half being fed back to the DME synthesis.

## NEW PLANTS

In accordance with the process stages, the KIT pilot plant is being set up in several phases. Starting in 2005, first the pilot plant for fast pyrolysis was set up and put into operation in 2008, ④. In the same year, the gasification stage was started, which is still in the setup stage. Both plants were set up and operated in cooperation with Lurgi, Frankfurt. 2009 saw the kick-off of the planning of the gas purification (MUT Advanced Heating, Jena) and synthesis stages (Chemieanlagen Chemnitz CAC, Chemnitz). Plant construction takes place in parallel to the gasification stage, so that the simultaneous completion of all plants in construction is expected for the end of 2011. The project for building the pilot plant is

	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5
PROCESS	Fast pyrolysis	Entrained flow gasification	Gas purification	DME synthesis	Gasoline synthesis
PRESSURE [BAR]	–	80	80	55	50
TEMPERATURE [°C]	500	> 1200	500	250	300
THROUGHPUT	500 kg/h of biomass (2 MW <sub>th</sub> )	1000 kg of biosyncrude (5 MW <sub>th</sub> )	700 Nm <sup>3</sup> (2 MW <sub>th</sub> )	50 kg/h	30 kg/h
PRODUCT	Biosyncrude	Crude synthesis gas	Pure synthesis gas	DME	Gasoline

5 Characteristics of the Bioliq pilot plant



6 Energy efficiencies of different synthetic products from biomass

funded by BMELV and the agency of renewable resources FNR, Gülzow.

A few data on the KIT pilot plant are summarized in 5. Approximately 40 % of the energy originally contained in the biomass are expected to show up again in the fuel 6. Depending on the process, additional products such as liquid gas or chemicals will be formed. An important aspect is that heat and power are formed as byproducts, which are used to cover a large portion of the energy demand of the process. This results in a high CO<sub>2</sub> reduction potential of BTL fuels. However, 6 also shows that the generation of pure hydrocarbons from biomass gives the lowest energy efficiencies (relative to the energy content of the products, compared with the starting material). Hydrogen preserves the highest energy content,

whereas further processing of the synthesis gas by exothermic reactions leads to a lower energy content. Moreover, biomass with its averaged empirical formula of C<sub>5</sub>H<sub>9</sub>O<sub>4</sub> has a high oxygen content, compared with fossil raw materials. When pure hydrocarbons are prepared, the oxygen is cleaved off in the form of water and carbon dioxide. This leads to a hydrogen deficiency within the process and a lowering of the carbon efficiency, which, however, is undesirable in terms of using the carbon contained in the biomass. A more advantageous method for preserving energy and carbon efficiencies is to prepare oxygen-containing products that allow a large portion of the oxygen present in biomass to be preserved in the product. In that respect, biomass is suitable in the short term for providing synthetic oxygen-

ates (anti-knock agents), which find a useful application in blends with mineral fuels. Oxygen-containing pure fuels are also a longer-term option without restrictions or drawbacks whatsoever in driving applications and with respect to their combustion and emission behavior. On the other hand, their lower energy density compared with pure hydrocarbons leads to a shorter range at the same tank volume. However, pure synthetic hydrocarbons are also useful as high-quality fuels if grades can be produced that meet the requirements of the engine combustion concepts. This is the focus of current research and development activities at the KIT in chemical catalysis, whose successful development concepts will then also be tested and put into practice in the Bioliq pilot plant.

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