The Karlsruhe Process bioliq®

Synthetic Fuels from the Biomass

BY NICOLAUS DAHMEN | ECKHARD DINJUS | EDMUND HENRICH

*Biofuels could replace a part of the currently-used fossil energy carriers in the near term. To make this possible, raw materials produced over wide- spread areas would have to be made accessible to industrial users of fuels and chemical raw materials on a large scale. The two-stage gasification concept **bioliq** offers a solution to this problem.*

bioliq
Biomass to Liquid Karlsruhe

Fossil energy carriers form the basis of today's energy supplies. Even though predictions of the time remaining until they are completely exhausted differ widely, there can be no doubt that they will in the long run be used up. As current developments of the prices for petroleum and natural gas on the world market demonstrate, even minor perturbations on a global scale can occasionally produce serious price rises with corresponding negative effects on the world's economy. A consistent utilization of renewable energy sources would alleviate these uncertainties and would at the same time contribute to a reduction of CO_2 emissions into the atmosphere.

While hydroelectric power, geothermal heat, solar energy and wind power are suitable primarily for the production of electric power and space heating, the biomass, uniquely among renewable carbon sources, can play an important role in the production of motor and heating fuels as well as of organic starting materials for chemical synthesis. The biomass of all kinds must therefore be used efficiently.

Biogenic fuels can – even in the short term – replace a portion of the fossil energy sources and thereby make a contribution to the reduction of CO_2 emissions. The aspects mentioned above, together with existing legal and economic requirements, are contributing to increased political and economic pressure to search for solutions. For example, the European Union (EU) requires in its Biogenic Fuel Guidelines that the present proportion of biogenic motor fuels be increased from 2 % of the total consumption in the year 2005 to 5.75 % by the year 2010. The goal for the year 2005 was met, and even surpassed, using the biofuels of the first generation: Biodiesel, plant oils and bioethanol. Their raw materials, vegetable oils, sugar or starch, are produced from rape, wheat or sugar beets.

A still greater potential for reduction of CO_2 emissions is shown by the fully synthetic biogenic fuels of the second generation, also known as BTL fuels (Biomass-To-Liquids). They can be produced using a broad palette of possible raw materials and employing whole plants. These can be agricultural and forest residues such as straw, waste forest wood, or all the other dry biomass, including energy-yield plants. BTL fuels have the advantage that they are purer and more environmentally friendly than petroleum-based fuels. Furthermore, they can be adjusted to meet special requirements, for example from the automobile manufacturers, and the ever stricter exhaust emission norms. With the distribution infrastructure which is in place today, they can be directly utilized, requiring no new engine technology, and they permit the same vehicle operating ranges as petroleum-based motor fuels.

Obstacles to the Use of the Biomass

In comparison to the use of fossil energy carriers, the production of synthesis gas from the biomass is more complex

INTERNET

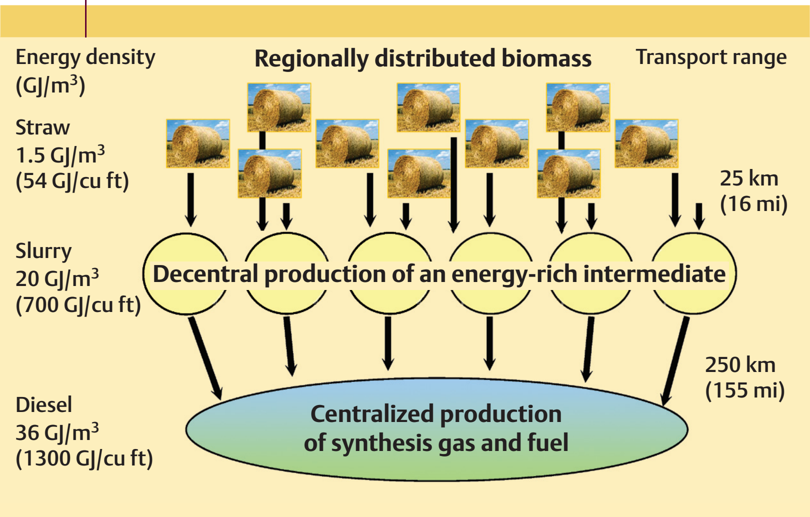
Forschungszentrum (Research Centre) Karlsruhe
www.fzk.de/bioliq

European Biofuel Platform
www.biofuelstp.eu

Agency for Renewable Raw Material
www.btl-plattform.de

Renewable Energy. Edited by R. Wengenmayr, Th. Bührke. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. ISBN 978-3-527-40804-7

FIG. 1 | CONCEPT

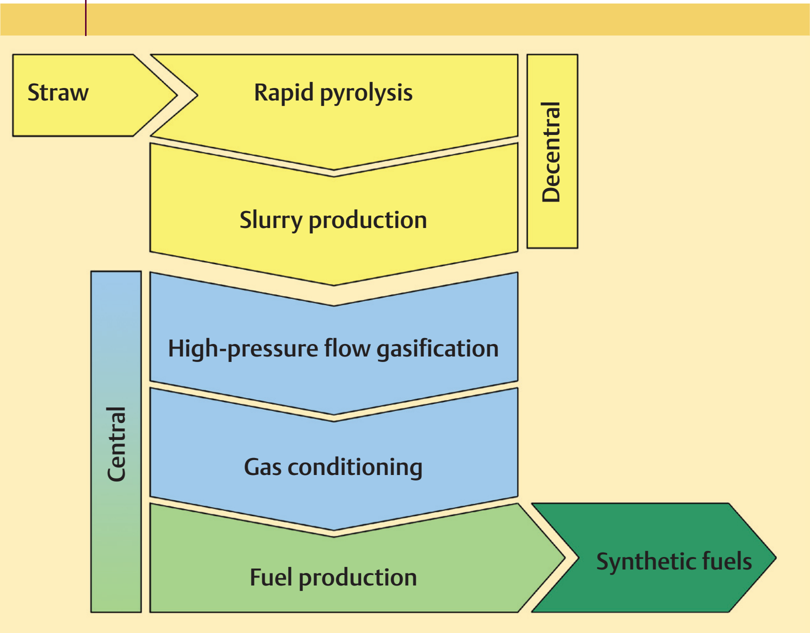


The decentral-centrally deployable bio-slurry gasification concept envisages the production of an energy-rich intermediate, which can be economically transported over longer distances, and which then is converted to synthesis gas and fuels in large, centralized installations.

and more expensive. For the technical application of biomass fuels on a large scale, several hurdles exist.

For one thing, the biomass accumulates over large areas and therefore has to be collected and transported often over long distances. In particular, less valuable biomass such as straw or forest wood residues have a low volumetric energy density (baled straw ca. 2 GJ/m^3 (70 GJ/cu ft), in comparison to 36 GJ/m^3 (1300 GJ/cu ft) for diesel fuel). Here, the question arises as to the distances over which it is economically and energetically feasible to transport these materials.

FIG. 2 | PROCESS STEPS



The steps of the bioliq®-process.

In addition, there is a large variety of potentially usable biomass materials. The processes used must guarantee the utilization of the largest possible bandwidth of raw materials. Biomass furthermore consists of heterogeneous solid fuels with to some extent differing chemical compositions; and solid fuels in principle require a greater processing effort.

Making use of already established technologies, e.g. for the processing of fossil-fuel raw materials, helps to shorten the development phase and reduce risks. In particular, the high ash content of many biomass materials causes problems for thermochemical processes, for example due to corrosion or agglutination and blockages of the apparatus. ‘Ash content’ refers here to the proportion of salts and minerals present.

Motor-fuel synthesis requires a tar-free, low-methane synthesis gas at high pressures of 30 to 80 bar (0.04-0.11 torr), and the extensive elimination of trace impurities which would act as catalyst poisons. On the other hand, this facilitates or even simply allows meeting the stricter exhaust emission norms when the fuel is burned.

Biomass materials, with their average chemical composition of $C_6H_9O_4$, yield on gasification a C/H ratio near to one, which is insufficient for the production of hydrocarbons. This requires an additional process step, the water-gas shift reaction, in which through addition of water, a part of the CO is converted into hydrogen and CO_2. This leads however to poor carbon efficiency. In the long term, it will be expedient to fill the additional hydrogen requirements by utilizing other renewable energy sources.

The biomass is taken from the biosphere, and this must in the long term be done in an ecologically compatible manner. Furthermore, the use of the biomass also has socio-economic aspects, since the new role for arable lands, grasslands and forests as providers or processors of energy-yield raw materials requires the establishment of new logistics, income and labor structures and must not lead to an irreparable loss of food-producing areas.

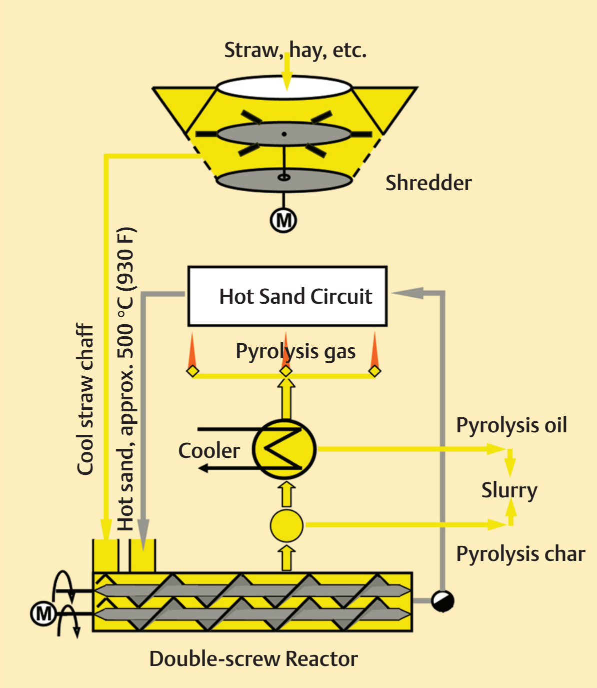
The Karlsruhe bioliq® Process

At the Karlsruhe Research Center (Karlsruhe, Germany), we have developed a biomass-to-liquid process intended to overcome these logistical and technical hurdles. The emphasis of our process lies in the use of relatively inexpensive, thus far mostly wasted biomass residues. The Karlsruhe synthetic motor fuel is produced by a process involving several steps, the bioliq® process (Figures 1 and 2).

The process steps in the bioliq® Process

1. Rapid pyrolysis: In a first step, the decentrally accumulated biomass is converted through rapid pyrolysis into pyrolysis oil and pyrolysis char (see the infobox ”Pyrolysis“, p. 64). The air-dried biomass is chopped up and mixed with hot sand, which serves as heating agent, at ambient pressure and under exclusion of air in a double-screw mixing reactor for rapid pyrolysis (Figure 3). The heating, the

FIG. 3 | RAPID PYROLYSIS



Schematic of the rapid pyrolysis process, which uses a double-screw mixing reactor to produce pyrolysis oil and pyrolysis char, the precursors of bio-slurry.

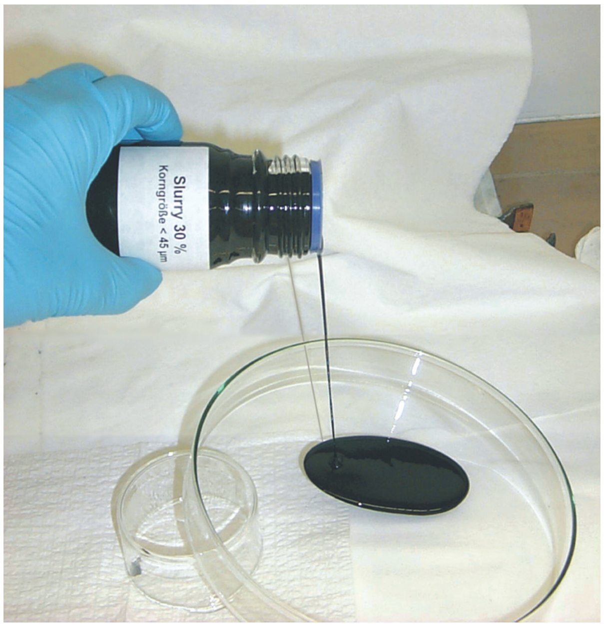


Fig. 4 ***The products of the biomass pyrolysis are used to prepare an energy-rich, free-flowing intermediate: bio-slurry.***

actual pyrolytic conversion of the biomass particles at about 500 °C (930 F), and the condensation of the resulting pyrolysis vapors all take place within seconds. Depending on the operating parameters of the reactor and the biomass employed, 40-70 % of an organic condensate (pyrolysis oil) and 15-40 % pyrolysis char are obtained. The remaining product is a non-condensable pyrolysis gas, whose heat of combustion can be used for heating the sand or for drying and preheating of the input materials. The mixing reactor used here was developed about 40 years ago by the industry as a 'sand cracker' for the rapid pyrolysis of various refinery products [1].

2. Slurry production: The brittle and highly porous pyrolysis char is mixed with the pyrolysis oil to give a suspension, called bio-slurry (Figure 4). For this process, the size distribution of the char particles is important. Only when their size is sufficiently small is the resulting slurry stable over long periods of time and can be converted rapidly by the following gasification step. The energy density of the slurry relative to its volume is more than an order of magnitude higher than that of dry straw, and this is an advantage for its transport. Rapid pyrolysis is required at this point in order to obtain the ideal mixing ratio of pyrolysis condensates to pyrolysis char for the preparation of the bio-slurry. This is in turn necessary for a complete utilization of both components.

3. Entrained flow gasification: The bio-slurry is atomised with hot oxygen in a pressurized entrained flow gasifier and is converted at over 1,200 °C (2,200 F) to a tar-free and methane-poor crude synthesis gas. This flow gasification apparatus originally has been developed for gasification of Central German salty lignite. It is especially well suited for an ash-rich biomass [2]. This is due to a cooling screen onto which the ash precipitates as molten slag and then drains out of the reactor (Figure 5).

The suitability of this type of gasifier was demonstrated in – so far – four test series using different bio-slurries and operating parameters with the 3-5 MW pilot gasifier plant at the Future Energy company in Freiberg. Bio-slurries with up to 33 wt.-% of char were tested, from which a practically tar-free, methane-poor (< 0.1 vol.-%) synthesis gas was obtained. It consists of 43-50 vol.-% carbon monoxide, 20-30 vol.-% hydrogen, and 15-18 vol.-% CO_2. Gasification takes place under a pressure which is dependent on the synthesis to follow. This avoids costly compression of the synthesis gas. Thus, Fischer-Tropsch syntheses require pressures up to 30 bar (0.04 torr), while the methanol or dimethyl-ether synthesis requires up to 80 bar (0.11 torr).

4. Gas purification and conditioning: Before use in a chemical synthesis, the crude synthesis gas must be purified from particles, alkali salts, H_2S, COS, CS_2, HCl, NH_3, and HCN, according to the requirements of the synthesis to follow. This prevents poisoning of the catalysts used for the following synthesis step.

5. Synthesis: The conversion of synthesis gas into motor fuels on a large scale is an established technology. For example, the Sasol company uses the Fischer-Tropsch synthesis to produce more than six million tons of fuel from anthracite coal annually. In this manner, about seven tons of air-dried straw can be used to prepare a ton of synthet-

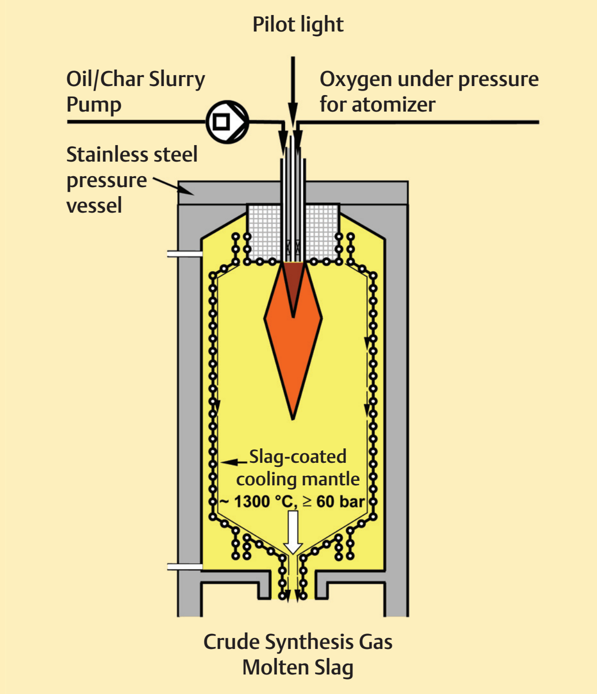
PYROLYSIS

Pyrolysis (from the Greek: *pyr*, fire; and *lysis*, dissolution) refers to the thermal decomposition of chemical compounds under oxygen exclusion. In this process, depending on the temperature and the processing time, char, liquid condensates (pyrolysis oils) and flammable gases are formed. In rapid pyrolysis, a high yield of liquid products is obtained. This occurs during very short reaction times of a few seconds. This rapid heating for short times is achieved by use of a heat transfer agent such as hot sand, which is mixed intensively in special reactors with the pyrolysis reactants.

ic fuel. Nearly 50 % of the energy originally contained in the biomass remains in the liquid end product. As by-products, heat and electric power can be produced, and they completely meet the energy requirements of the overall process.

Methanol production, with the order of many millions of tons per year, is likewise an established process technology. Methanol is on the one hand an intermediate for a methanol-to-gasoline process. It is however also directly usable itself as a motor fuel. It is used for the synthesis of the anti-knock compound MTBE (methyl tertiary-butyl ether), for the production of rape methylester, and of biodiesel through esterification of rape oil, as well as being an input fuel for high-temperature fuel cells.

FIG. 5 | THE FLOW GASIFIER



Schematic drawing of the high-pressure entrained flow gasifier, in which the bio-slurry is converted to synthesis gas using pure oxygen at temperatures above 1200 °C.

The Current State of Development

Our work up to now in Karlsruhe demonstrates that even bio-slurries with a high char content resulting from biomass pyrolysis products using pure oxygen in a flow gasifier at high pressures can be completely and safely converted into a tar-free synthesis gas. This process is suitable for practically all materials which yield a sufficiently stable condensate for suspending the char powder after rapid pyrolysis.

Now that the technical feasibility of the process has in principle been demonstrated by experiments with our own and with industrial equipment, the overall process is being further developed as rapidly as possible. For this purpose, we are currently setting up a pilot plant at the Karlsruhe Research Center within the framework of a public grant and with industrial cooperation partners. It will have a biomass throughput of 500 kg/h (approx. 1,100 lb), and is intended to demonstrate and further develop the process, to show the practicability of the procedures applied, to prepare for scaling-up to a commercially relevant size, and to allow the compilation of reliable cost estimates. The first of three constructional phases, the phase of biomass milling, rapid pyrolysis and continuous mixing of the bio-slurry, was authorized and begun in 2005. The pyrolysis plant is operated together with the German firm Lurgi AG, Frankfurt (Main), since 2007. As the next step, the construction of the gasifier and the fuel synthesis plant will follow also in cooperation with Lurgi.

Costs and Development Potential

The Karlsruhe Biomass-to-Liquid process is particularly suited to the requirements of the widely distributed biomass production from agriculture: The rapid pyrolysis and production of the bio-slurry is carried out at a large number of decentrally located plants. They provide the decisive enhancement in energy density needed for further economical transport of the raw materials. The gasification and the following steps of gas conditioning and synthesis can then be performed at a large central installation of a size which makes it commercially cost-effective, and which is supplied by road or rail transport with the bio-slurry raw material.

In a possible scenario, about 40 rapid-pyrolysis installations, each with a capacity of 200 thousand tons of bio-slurry annually, could be set up to supply a central gasification and fuel production plant with a capacity of a million tons of fuel. Then, at a price of 70 Euro (approx. 100 $) per ton for the air-dried starting material, a production price of less than one Euro per kg (less than one $/lb) of fuel could be realized. With integration of the gasifier into an equipment network of the chemical industry, the diversification of the usable products can also be broadened. Along with the option of the utilization of biomass as a source of carbon, necessary in the long term, economically favorable processes could also be developed in the near future.

The focus for the process development is currently on low-grade biomass, which thus far has not been used at all, such as surplus grain straw, barn straw or waste wood. The use of solid wood is not seen as a fruitful solution in the long term. Even though this less problematic starting material might permit the technical realization of the process to be attained more rapidly, it can be expected that the demand for solid wood will increase due to its uses in construction, for cellulose production, and for decentral and household heat and energy production.

The use of entire plants appears to be still more expedient, for example of grain plants or specifically cultivated energy-yield plants. The accompanying systems analysis research [3] leads us to expect an annual production of about 5 million tons of synthetic motor fuel just from the use of waste forest wood and surplus straw, together about 30 million tons of dry material. This corresponds to roughly 10 % of the current consumption of petrol and diesel fuels in Germany.

According to estimates by the Agency for Sustainable Raw Materials (FNR), by the year 2015 a fraction of biogenic motor fuels of 25 % of the overall consumption is possible. Combined with other biochemical and physicochemical processes, a still higher-quality utilization of the biomass in the sense of a biomass refinery should be feasible. Similarly to today‘s petroleum refineries, it would use a broad spectrum of raw materials to produce a variety of basic chemical materials and fine chemicals, which would result in a clear-cut reduction of the consumption of fossil materials by the chemical industry.

Acknowledgments

We thank the Ministry for Nutrition and Agriculture in Baden-Württemberg (MLR), the German Federal Ministry for Nutrition, Agriculture and Consumer Protection (BMELV), the Agency for Sustainable Raw Materials (FNR), and the European Commission via support of the EU project Renew for their continued support and financing.

Summary

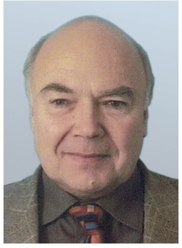
Synthetic fuels from the biomass can provide an important contribution to a renewable energy economy. The Karlsruhe BTL concept bioliq® aims at bringing decentral production in line with centralized processing on an industrial scale. To this end, thermochemical methods are employed: rapid pyrolysis for the production of a readily transportable, energy-rich intermediate product, and entrained-flow gasification to yield synthesis gas and to process it further into the desired fuels. The bioliq process was distinguished with the BlueSky Award by the UN Organization UNIDO in 2006.

References

[1] R.W. Rammler; Oil & Gas Journal, 1981, Nov.9, 291.
[2] M. Schingnitz et al., Fuel Processing Technology 1987,16, 289.
[3] R. L. Espinoza et al., Applied Catalysis A: General 1999, 186, 13 und 41.

About the Authors

Nicolaus Dahmen studied chemistry at the Ruhr University in Bochum, obtained his doctoral degree in 1992 and moved in the same year to the Karlsruhe Research Center. There, he is now concerned with the thermo-chemical transformation of biomass into hydrogen and synthesis gas. As project leader, he is responsible for the construction of the bioliq® pilot plant in Karlsruhe.



Eckhard Dinjus began his studies of chemistry in 1963 at the Friedrich Schiller University in Jena and completed his doctorate there in 1973. In 1989, he obtained the Habilitation, and thereafter he was leader of the Research group "CO_2 chemistry" in the Max-Planck Society. Since 1996, he has been director of the Institute for Technical Chemistry at the Karlsruhe Research Center, and he occupies the chair of the same name at the University of Heidelberg.

Edmund Henrich studied chemistry at the Universities of Mainz and Heidelberg. He received his doctorate in Heidelberg in 1971 and the Habilitation in 1993 in the field of radiochemistry. He has worked at the Karlsruhe Research Center since 1974, and as Division Leader of the Institute for Technical Chemistry there, he is responsible for R and D activities relating to the Karlsruhe BTL process. Since 2005, he has been extraordinary professor at the University of Heidelberg.

Contact:
Dr. Nicolaus Dahmen, Dr. Eckhardt Dinjus,
Dr. Edmund Henrich, Forschungszentrum Karlsruhe,
Institut für Technische Chemie,
PO box 3640, D-76021 Karlsruhe, Germany.
Nicolaus.Dahmen@itc-cpv.fzk.de