

State of the Art of the Bioliq[®] Process for Synthetic Biofuels Production

Nicolaus Dahmen,^a Eckhard Dinjus,^a Thomas Kolb,^b Ulrich Arnold,^a Hans Leibold,^b and Ralph Stahl^a

^a Karlsruhe Institute of Technology (KIT), Institute for Catalysis Research and Technology, 76021 Karlsruhe, Germany; nicolaus.dahmen@kit.edu (for correspondence)

^b Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

Published online 4 April 2012 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/ep.10624

Synthetic fuels from biomass (also referred to as BTL, biomass to liquids) may contribute to the future motor fuel consumption to a considerable extent. To overcome the logistical hurdles connected with the industrial use of large quantities of biomass, the de-central-centralized bioliq[®] concept has been developed. It is based on a regional pretreatment of biomass for energy densification by fast pyrolysis. The intermediate referred to as biosyncrude allows for economic long-range transportation. Collected from a number of those plants, the biosyncrude is converted into synthesis gas, which is cleaned, conditioned, and further converted to fuels or chemicals in an industrial plant complex of reasonable size. Gasification is performed in a high-pressure entrained flow gasifier at pressures adjusted to those of the subsequently following chemical syntheses. For increased fuel flexibility and conversion of ash rich feed materials, the gasifier is equipped with a cooling screen operated in slagging mode. At Karlsruhe Institute of Technology (KIT), a pilot plant has been erected for process demonstration along the whole process chain. The two MW_{th} fast pyrolysis plant is already in operation since 2009; the five MW_{th} gasifier, the hot gas cleaning section, and a gasoline synthesis via dimethylether are to be finished in 2011. Commissioning of that plant complex will follow in 2012. The technology applied in the bioliq[®] process chain and on the state of construction of the pilot plant is presented. © 2012 American Institute of Chemical Engineers Environ Prog, 31: 176–181, 2012

Keywords: synthetic biofuels, fast pyrolysis, gasification, hot gas cleaning, synthesis gas

INTRODUCTION

Compared to alternative motor fuels and drive concepts liquid hydrocarbon fuels still exhibit the highest energy density and will largely contribute to private, public, and freight transportation within the next decades. In regard to resource conservation and CO₂ emission reduction targets, the use of biomass as the only renewable carbon source is to be explored and developed for its contribution in this field. Due to the expected competition to food and feed production, biofuels of the first generation are limited in their potential share of the world's motor fuel consumption. The bioliq[®] project aims at the large scale production of synthetic biofuels from any kind of dry biomass including purpose grown crops, for example, from short rotation plantations as well as residues from agriculture, forestry, and certain types of or-

ganic waste [1, 2]. The concept has been designed in a way to overcome the problems met when low grade, residual biomass will be used to a large extent as required in a BTL process. Like in gas (GTL) or coal to liquids (CTL) plants, the complex technology of syngas production, its cleaning and conditioning, as well as the subsequently following syntheses require industrial size due to economies of scale considerations. Biomass such as straw, hay, residual wood, and so forth usually exhibit low volumetric energetic densities, thus limiting collection area and transportation distances. In the bioliq[®] process, biomass is pretreated in regionally distributed fast pyrolysis plants for energy densification (Figure 1).

The products, pyrolysis char and liquid condensates, are mixed to form stable, transportable, and flowable slurries also referred to as biosyncrude. Thus, biomass is energetically concentrated by a factor of up to 15 in the case of wheat straw allowing for economic transport over long distances [3, 4]. In an industrial plant complex of reasonable size, the biosyncrude is gasified in an entrained flow gasifier at a pressure slightly above that of the following fuel synthesis to avoid energy consuming syngas compression.

THE BIOLIQ[®] PILOT PLANT

On KIT's site, a pilot plant according to the bioliq[®] concept has been constructed for process demonstration, to obtain reliable mass and energy balances, for gaining practical experience, and to allow for reasonable cost estimates as a basis for further scaling up of the process. A scheme of the installed facilities and of the process steps is depicted in Figures 2 and 3, respectively. The fast pyrolysis pilot plant is equipped with a twin-screw reactor in combination with a pneumatic heat carrier loop with sand as the heat carrier medium as the main technical features (Figure 4). The plant with feed capacity of 500 kg h⁻¹ (two MW_{th}) of air dried biomass is already in operation. The straw, reduced in size by a two stage-cutting mill to particles smaller than 10 mm, is pneumatically transferred into a silo. Withdrawn by a mass flow-controlling auger, the material is elevated to a feed hopper via two slide valves applying an inert nitrogen atmosphere. Finally, the material is fed to the twin-screw reactor by a screw conveyor. In the reactor, the straw is mixed with a 10-fold excess of hot sand at around 500°C. Within 1 m of reactor length (corresponding to ca. 3 sec of gas retention time) hot vapors and char escape via the reactor's top, while the sand is dropped down to be reheated to about 600°C and transferred to the sand bunker by hot flue gas generated by natural gas combustion. Commercially, the noncondensable pyrolysis gas would be applied to the burner system. It

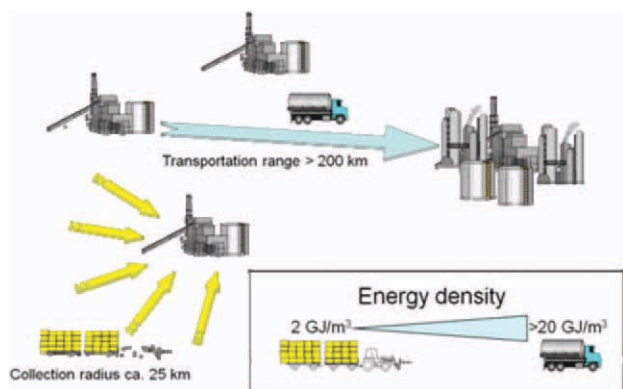


Figure 1. The bioliq[®] process concept. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

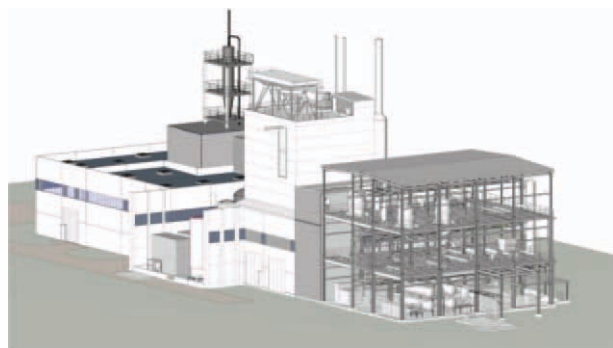


Figure 2. Scheme of the bioliq[®] pilot plant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consists of mainly CO₂ (ca. 50 vol %) and CO (35 vol %). The minor constituents H₂, CH₄, and C₂–C₅ alkanes and alkenes contribute about half to the higher heating value of about 9 MJ/kg. Under optimized conditions, this has been estimated to be sufficient to provide the heat required for heating up and pyrolysis of the biomass. In addition, some char contained in the recirculating sand is burned by adjusting the oxygen content in the lift pipe to control the heat demand in an optimal way. An enrichment of char in the heat carrier loop has not been observed in the operation campaigns conducted so far. The flue gas escapes the sand bunker; fines are removed by a cyclone and a hot gas filter. Currently, the flue and pyrolysis gas are burnt in a flare. The char from the product gas leaving the reactor is separated by a hot gas cyclone; afterwards the hot vapors are condensed in two steps: the tar condensate is obtained in a quench by injection of recirculating, cooled off condensate. An electrostatic precipitator prevents aerosols from carrying over into the next condenser, where the aqueous condensate is obtained also by recirculating of already cooled off material. The two-staged condensation takes into account, that pyrolysis oils, in particular those of nonwoody biomass, tend to spontaneous or delayed phase separation with increasing water content. Therefore, the two condensates are already separated in the process. Each of the two liquid phases shows some ageing [5], which do not lead to a significant change in the properties of the subsequently formed biosyn-crude.

In the first operation period, the heat carrier loop with internal char combustion was successfully tested. Since 2010, four pyrolysis campaigns were carried out with straw as the feed material. In total, around 1000 h operation of the heat carrier loop and 200 h of straw pyrolysis of have been accumulated. Regarding the products distribution and yield, the results from bench scale experiment were verified. At a maximum throughput of 500 kg h⁻¹ straw (11 wt % humidity; 5 wt % ash), a preliminary mass balance was determined yielding 24 wt % of solids (char plus ash), 23 wt % of tar condensate containing 5.3 wt % of water, 32 wt % of aqueous condensate consisting of up to 70 wt % of water, and 21 wt % of noncondensable pyrolysis gas. The loss of sand due to abra-

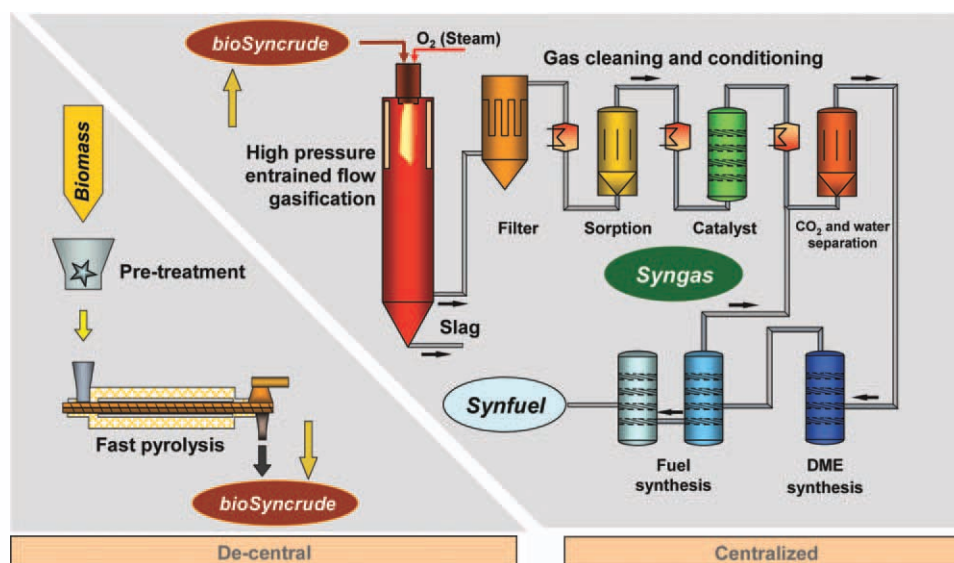


Figure 3. Bioliq[®] process concept. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

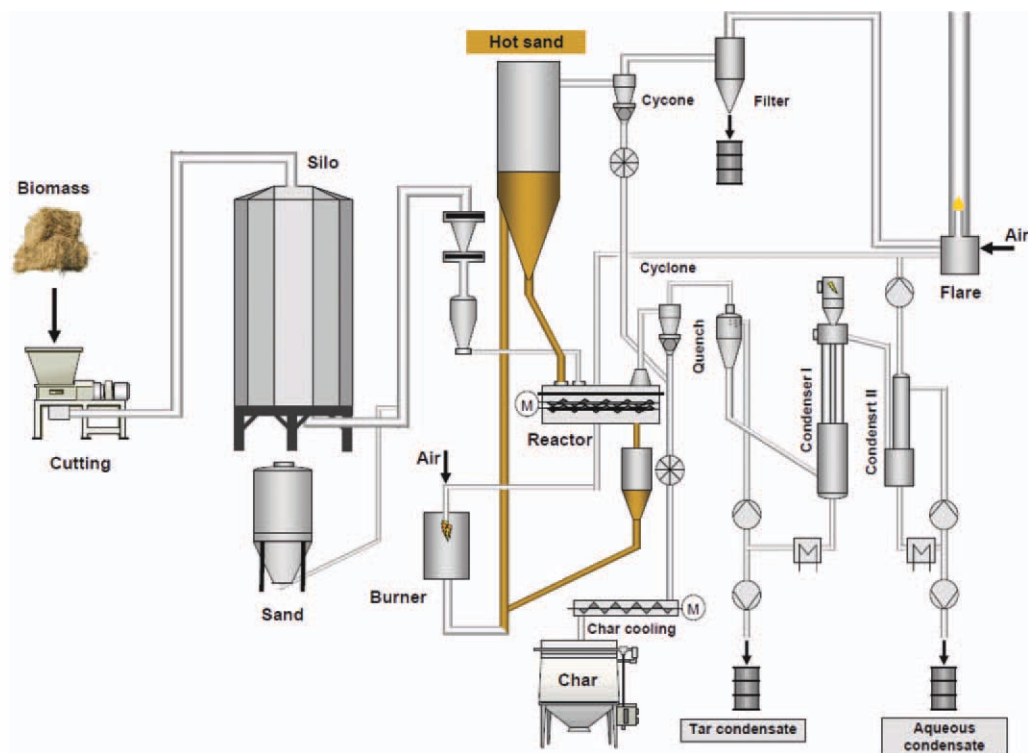


Figure 4. Fast pyrolysis process scheme. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

sion was determined to be below 1% related to the feed mass flow rate during stationary operation at feed rates of 400–500 kg/h. Here, the sand loss typically amounts to 3 kg/h.

The biosyncrude is prepared from the liquid and solid pyrolysis products by colloidal mixing ranging from tar condensate based slurries to aqueous slurries containing up to 40 wt % of char [6]. Slurries with small char particles in a size range of few 10 μm , mixed into the relatively viscous tar phase remain homogeneous for month. Char particles suspended in the aqueous condensate with its low, water-like viscosity tend to sedimentation in the course of hours. Sedimentation can be prevented by addition of a gelling agent (starch; lignin). Alternatively, remixing of those slurries is possible, for example, immediately prior to gasifier feeding. In Figure 5, gasification results of different slurries varying in chemical composition are presented, obtained from experiments at the 3–5 MW_{th} pilot gasifier of Future Energy (today Siemens Fuel Gasification Technologies) in Freiberg, Germany, conducted in the years 2002–2005. For production of the diverse feed materials, colloidal mixers have been used; processing condensates and chars from wood pyrolysis and char from straw prepared by intermediate pyrolysis. To simulate the slag behavior of straw ash, about 3 wt % straw ash from straw combustion as well as some KCl have been added.

The high-pressure entrained flow gasifier at KIT was designed for five MW_{th} fuel capacity, blown by oxygen and steam as gasification agents (Figure 6). The larger thermal capacity compared to the pyrolysis plant is due to the scale-up ability of the pilot plant, requiring a certain minimum size for reliable design of larger plants. The slagging reactor is equipped with an internal cooling screen, particularly suited for the conversion of ash rich feeds and fast start up and shut down procedures. Two reactor inlets have been constructed for alternative use at 40 or 80 bar operation. At the

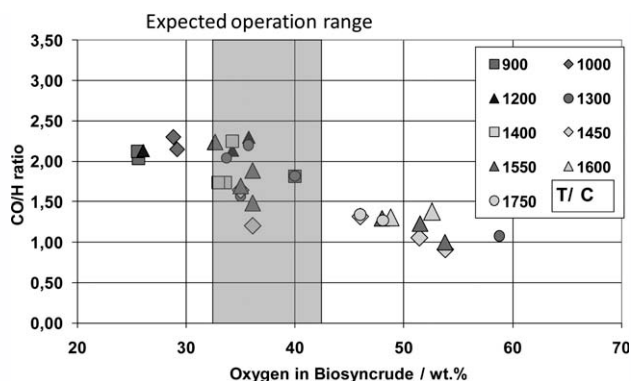


Figure 5. Freiberg gasification results with different feed materials varying in oxygen content.

lower pressure, access for measuring devices is given by appropriate apertures allowing for characterization of fluid dynamics and reaction properties by inline detection devices. Two syngas cooling designs can be realized in the pilot gasifier: A dip tube forcing the gas to pass a bulk quench water zone and an alternative allowing for removal of hot syngas up to 800°C, where the product gas is cooled using a system of nozzles that inject cooling water. The minerals sloughing down into the quench water reservoir are removed as solid slag.

From the gasifier, 700 $\text{Nm}^3 \text{h}^{-1}$ (ca. two MW_{th}) are separated from the raw gas stream. The residual gas is flared off or is available for other use. The separated raw synthesis gas is purified and conditioned by a high temperature-high pressure hot gas cleaning system, operating at the gasifier pres-

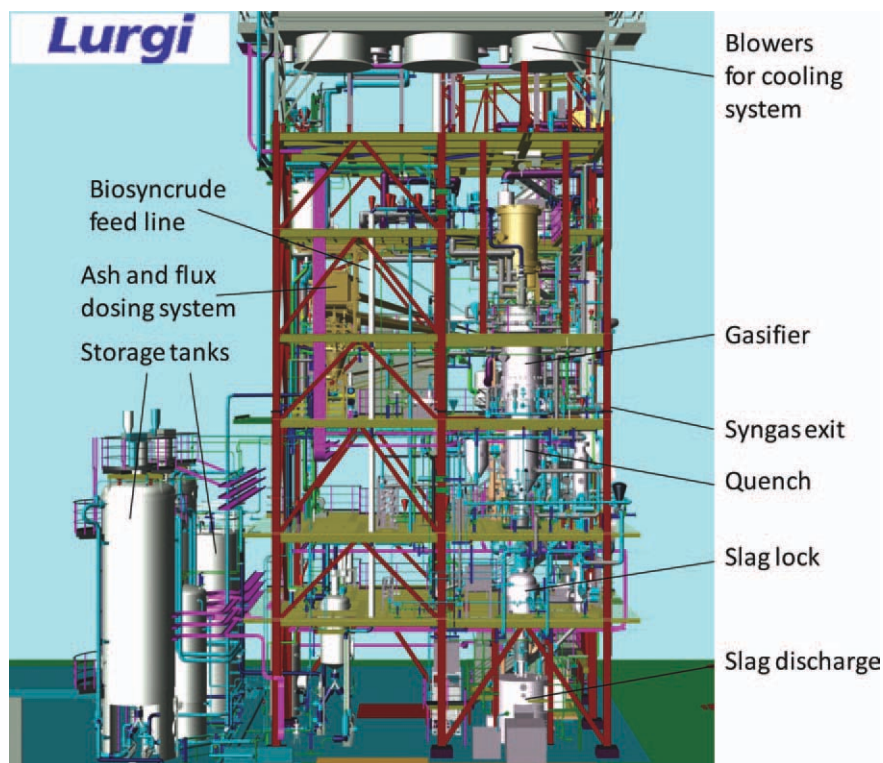


Figure 6. Construction scheme of the gasifier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

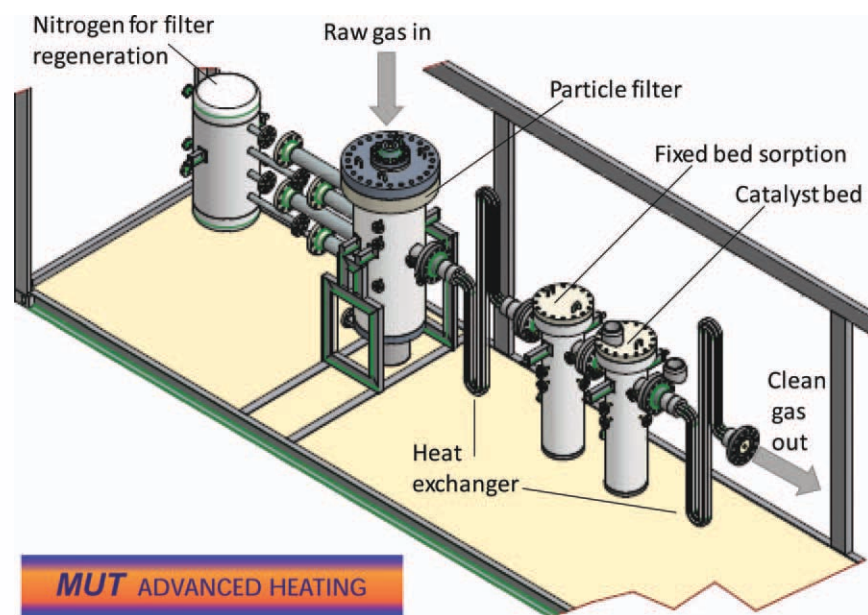


Figure 7. Gas cleaning section. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tures (80 and 40 bar, respectively) (Figure 7). Particulates are removed in an innovative hot gas filter to particle contents of $<1 \text{ mg/Nm}^3$ with horizontal arrangement of ceramic filter elements and KIT own technology for recleaning (at 800°C). Filtering is followed by a two-stage fixed bed sorption (at $>500^\circ\text{C}$) for HCl, H_2S , COS, and alkaline removal down to values below 0.1 mg/Nm^3 with mineral sorbents and a catalytic converter for decomposition of ammonia, HCN, and organic

trace compounds (at $>500^\circ\text{C}$). From the hot gas cleaning, energy savings are expected from improved heat integration by optimization of the operation temperatures of syngas removal from the gasifier and the gas cleaning and synthesis steps [7].

Prior to the DME synthesis, water and carbon dioxide are separated. For CO_2 removal, a conventional liquid solvent is used. The purified synthesis gas is then converted to DME by a one-step synthesis process in a bed of a mixed catalyst for

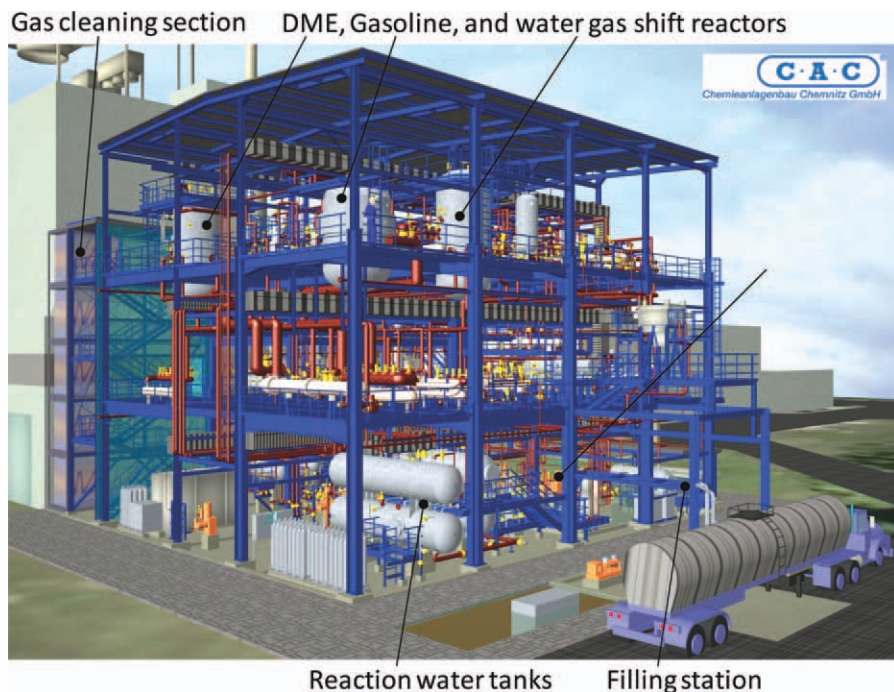


Figure 8. Construction scheme of the synthesis plant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methanol formation and dehydration (at 250–300°C, ca. 60 bar). In addition, the water gas shift reaction occurs. DME can directly be obtained from CO/H₂ ratios of around unity, which are expected in the case of biomass gasification. However, it was found in forerunning studies, that the selectivity toward DME is not influenced by the syngas composition. The reaction mixture enters the gasoline reactor, where methanol and DME are nearly completely converted into gasoline of high octane numbers (at 350–400°C and 25 bar). A ZSM-5 zeolite-type of catalyst is used here. In all reactors, a new, heat pipe based system is used for heat removal, providing nearly isothermal conditions in the catalyst bed and improved process control. After product separation at low temperatures, unreacted gas is recycled to the DME reactor. The water phase is used as process water, while the raw gasoline phase is distilled to yield the final gasoline product along with some heavy and light products that are disposed, but would be used by internal processes in a commercial plant. The synthesis pilot plant is shown in Figure 8.

PILOT PLANT OPERATION AND DEVELOPMENT

The pilot plants for gasification, gas cleaning, and synthesis were completed mechanically by the end of 2011. After functional testing, the complex will be commissioned in 2012. For operations, typically carried out in campaigns of a few weeks, a staff of qualified personnel is available. Around 1500 h of operation per year are targeted.

The erection, operation, and further development of the pilot plants are carried out in cooperation with partners from industry. Lurgi GmbH, Frankfurt, is the partner for fast pyrolysis and gasification, MAT Mischanlagentechnik GmbH, Immenstadt, for biosyncrude preparation and storage, MUT Advanced Heating GmbH, Jena, for gas cleaning, and Chemietechnik Chemnitz GmbH for synthesis.

Beyond pilot plant construction and operation a comprehensive associated research and development program has been initiated at KIT to improve the fundamental understand-

ing but also to optimize and further develop the underlying process steps such as fast pyrolysis [8] or gasification [9] and the overall process chain. Special attention is paid to the further development of synthesis processes.

The methanol/DME based route to gasoline was chosen for two reasons: First, gasoline production via methanol/DME directly leads to a motor fuel with high selectivity [10]. By-products usually are used by process internal recycling. This on the one hand simplifies operation of the relatively small pilot plant, which in the now realized first plant configuration focuses on the demonstration of the bioliq[®] process chain. However, about commercial biosynfuel production, it will be of importance also to provide ways for selective fuels production in addition to the refinery type Fischer-Tropsch synthesis providing a broad product spectrum with complex market interactions. Therefore, the recent research also aims at the selective production e.g. of alkylate gasoline, kerosene, or tailor-made-fuels for new or optimized combustion engines via methanol. Second and on a longer term, the methanol routes opens up options for synthesis of oxygen containing products not only for the fuel but also for the chemistry sector. The production of pure hydrocarbon leads to a low energy and carbon efficiency regarding the highly oxygen containing biogenic feed material. The production of oxygenates as fuels, fuel additives, and chemicals, leaving at least a certain proportion of oxygen in the target molecules, would increase the effectiveness of the overall process. The more so because biofuels in the near future are expected to hold only a certain share of the total fuel consumption, potentially leading to a nondesirable number of fuel blends. Therefore, the production of oxygenated additives could be a more value-added alternative compared to the production of the hydrocarbon component of a fuel.

ACKNOWLEDGMENTS

For financial support for the erection of the bioliq[®] pilot plant the Federal Ministry of Food, Agriculture and Consumer Protection, the state of Baden-Württemberg as well as

the European Regional Development Fund is gratefully acknowledged.

LITERATURE CITED

1. Dahmen, N., Dinjus, E., & Henrich, E. (2008). Synthetic fuels from biomass. In R. Wengenmayr, & T. Bürke (Eds.), *Renewable Energy-Sustainable Energy Concepts for the Future* (pp. 64–65), Weinheim: Wiley-VCH.
2. Henrich, E., Dahmen, N., & Dinjus, E. (2009). Cost estimate for biosynfuel production via biosyncrude gasification, *Biofuels, Bioproducts and Biorefining*, 3, 28–41.
3. Dahmen, N., & Dinjus, E. (2010). The bioliq process—concept, technology and state of development, *Motor-technische Zeitschrift MTZ*, 71, 864–868.
4. Leible, L., Kälber, S., & Kappler, G. (2008). Energiebereitstellung aus Stroh und Waldrestholz, *BWK*, 60, 56–62.
5. Oasmaa, A., Korhonen, J., & Kuoppala, E. (2011). An Approach for stability measurements of wood based fast pyrolysis bio-oils, *Energy Fuels*, 25, 3307–3313.
6. Raffelt, K., Dahmen, N., Dinjus, E., Henrich, E., Kornmayer, C., Stahl, R., & Steinhardt, J. (2007). Aspects of Bio-slurry production from pyrolyzed wheat straw. *Proceedings of the 15th European Biomass Conference and Exhibition*, Berlin: ETA Florence and WIP Munich.
7. Leibold, H., & Seifert, H. (2010). Energetische Aspekte bei der Heißgasreinigung von biomassebasierten Synthesegasen. In K.J. Thome-Kozmiensky (Ed.), *Erneuerbare Energien* (Volume 4, pp. 95–107). Berlin: TK Verlag.
8. Kornmayer, C., Dinjus, E., Henrich, E., Weirich, F., & Reimert, R. (2008). Verfahrenstechnische Betrachtungen zur Schnellpyrolyse von Lignocellulose im Lurgi-Ruhrgas-Doppelschnecken-Mischreaktor. *Proceedings of DGMK-Fachbereichstagung, Energetische Nutzung von Biomassen*, Velen VIII (pp. 215–222). Velen.
9. Seifert, H., Kolb, T., & Leibold, H. (2009). Syngas aus Biomasse – Flugstromvergasung und Gasreinigung. In K.J. Thome-Kozmiensky (Ed.), *Kraftwerkstechnik: Sichere und nachhaltige Energieversorgung* (pp. 123–132). Neuruppin: TK Verlag.
10. Dinjus, E., Arnold, U., Dahmen, N., Höfer, R., & Wach, W. (2009). Green Fuels—Sustainable Solutions for Transportation. In R. Höfer (Ed.), *Sustainable solutions for modern economies*, *RCS Green Chemistry No. 4* (pp. 125–163). London: RCS Publishing.