

Microwave spectroscopy for pyrolytic bio-slurries

Arndt Göller
GM
hf sensor GmbH
Leipzig, Germany
sales@hf-sensor.de

Björn Jungstand
R&D
hf sensor GmbH
Leipzig, Germany
sales@hf-sensor.de

Nicolaus Dahmen
IKFT
KIT
Eggenstein-Leopoldshafen,
Germany
nicolaus.dahmen@kit.edu

Klaus Raffelt
IKFT
KIT
Eggenstein-Leopoldshafen,
Germany
klaus.raffelt@kit.edu

Abstract— The elemental composition of bio-slurry as intermediate for renewable fuel production in the bioliq® process of the Karlsruhe Institute of Technology, its water content and heating value have to be controlled carefully to regulate the gasification process and to adjust the gasification products. The continuous knowledge of the bio-slurry composition is very important for this. Microwave spectroscopic measuring methods in connection with a multivariate data analysis to data evaluation are, however, well suited for solving such measuring tasks. This was the motivation to evaluate the use of microwave spectroscopy techniques for following up the properties of bio-slurry in the bioliq® process. Two different microwave spectroscopic measuring systems were tested in this application. A large number of test measurements was carried out, with good results.

Keywords - microwave, spectroscopy, renewable fuels, biocrude oil, bioliq®, bio-slurry, multivariate data analysis, PLSR

I. INTRODUCTION

Renewable fuels are an important aspect of the political strategy for energy security and lowering green house gas emissions. The bioliq® process from KIT (Karlsruhe Institute of Technology, Germany) has been developed in order to produce hydrocarbon based drop-in fuels from agricultural residues like wheat straw, corn residues, sugar cane bagasse, etc. [2]. Thin-walled biomass is converted at 500°C into biocrude oil and char powder and then into a liquid-like suspension. This bio-slurry serves as a densified intermediate for storage and transport. It consists up to 90% of the original biomass energy. Downstream it can be gasified in an industrial large-scale entrained flow gasifier and liquefied in the reactors of a conventional oil refinery.

The pyrolytic biocrude oil obtained by flash pyrolysis has poor fuel characteristics compared to gasoline. The heating value is only 40–50% of conventional fuels due to the high oxygen and water content. It contains a plenty of oxygenated small molecules (carboxylic acids, ketones, alcohols, aldehydes, phenol derivatives), phenol-based oligomers

(pyrolytic lignine) and water [2]. It shows low chemical stability due to aldol reactions and esterifications. The ageing products are unpolar dimers or oligomers and water, by which the aged biocrude tends to separate into a polar aqueous phase and an oily medium polar phase. To overcome spontaneous phase separation the bioliq® process takes use of a staged cooling from the pyrolysis temperature of 500°C onto a first condensation level of 85 – 100 °C (oily phase) and a second level of 20 – 40 °C (aqueous phase). The water content of the pyrolytic condensate is essential for the whole process chain, but reacts very sensitive on fluctuating process parameters and must therefore be controlled continuously and in real time.

Bio-slurry is prepared by mixing biocrude oil and char powder and can be used for storage and transport from the pyrolysis plant to the gasifier and oil refinery. Elemental composition, water content and heating value have to be controlled carefully to regulate the gasification process and to adjust the gasification products, mainly the ratio of carbon monoxide and hydrogen. Without continuous knowledge of the feed composition it is impossible to carry out a defined gasification reaction. Actually the slurry composition is measured by periodic sampling and measuring by Karl-Fischer titration, elemental analysis and bomb calorimetry during experiments in the bioliq® demonstration plant. This is time-consuming and too expensive for a commercial process in industrial scale and the motivation to evaluate the use of microwave spectroscopy techniques for following up the properties of bio-slurry in the bioliq® process. As a rough estimate, the complex bio-slurry composition can be simplified by 3 compounds: Water, biochar and a mixture of medium polar organic liquid. In so far, the goal of this preliminary study is to estimate if water and biochar content could be quantified by microwave techniques, and as a consequence also the organic part of the liquid biocrude.

As liquids were chosen 4 biocrudes which show in particular differences in polarity and water content (see table 1). In the first condensation step of the bioliq® process, at around 90°C an organic condensate is produced which is chemically instable during storage (ageing) and separates into a heavy phase (C) with a high oligomeric content, and a light

phase (B) with much sugar content. At a temperature of 20 – 40 °C the low volatiles are condensed, and an aqueous phase (A) of high polarity is formed. Whereas these 3 biocrudes are produced in the bioliq® process, as a fourth biocrude the organic condensate of the Degussa process (D) was used, which is a commercial by-product of charcoal production.

TABLE 1: TYPICAL COMPOSITIONS OF BIOCRUDES FROM FAST PYROLYSIS (A, B, C) AND SLOW PYROLYSIS (D) MEASURED BY GAS CHROMATOGRAPHY, ROUNDED TO THE NEXT INTEGER OR IN CASE OF SMALL VALUES TO 0.5 OR ZERO. THE NON-DETECTABLES REPRESENT APPROXIMATELY OLIGOMERES, WHICH CANNOT PASS THE CHROMATOGRAPHIC COLUMN.

composition in weight-%	A	B	C	D
water	80	37	22	18
acetic acid	5	5	4	5
propionic acid	0.5	1	1	0.5
hydroxyacetaldehyd	0	4	3	1
methanol	2	0	0	0
acetol	4	5	3	1
furan derivatives	1	2	2	4
phenol derivatives	0.5	3	7	15
sugars	0	9	4	13
non detectables	4	28	49	34

The organic matrix of wheat straw biochar is relatively unipolar due to its low oxygen content, but the charcoal consists of up to 40% inorganic oxides like SiO₂, K₂O, CaO, KCl. In this study, we investigated the biocrudes B and C with and without charcoal, and biocrude D without charcoal.

II. MICROWAVE SPECTROSCOPIC SENSORS FOR PYROLYTIC BIO-SLURRIES

The dry substance (DS) or dry matter content or more general the concentration of ingredients as well as of intermediate and end products is an important parameter in many processes in the industry, agriculture, power generation and in the production of biofuels. The strong correlation of DS content with various other process parameters and process requirements like the pumpability of a medium, wear protection for pumps and agitators, gas production rate in biogas plants, organic degradation, tracking of processes and enhancement of process safety permits with continuous recording of DS content a greatly improved process control. Even today DS sampling is carried out manually and randomly, whereby the results are often only available after a few days. This is a great opportunity for the establishment and use of microwave DS sensors with the right features like easy installation, user friendliness and serviceability and standardized calibration routines.

There are also applications where in multicomponent mixtures the water content and other material parameters are of special interest. The acquisition of two or more of such parameters is impossible by use of just one parameter measuring method, no matter what physical basis.

Microwave spectroscopic measuring methods in connection with a multivariate approach to data evaluation are, however, well suited for solving such measuring tasks. The MWTS T microwave measuring systems developed by hf sensor for recording scalar spectra of microwave

transmission and reflection in a pipe measuring cell and MWTS PP SPEC for purely reflective microwave spectroscopic measurements have been used in various of such applications in recent years [7, 8].

The electronics of the scalar transmission measuring system is split into two units, that are read out together with a control unit, called MOIST CONTROL.

The transmitter realizes the generation of microwave signal and measurement of transmission power. A frequency range from 2 to 3 GHz is covered by an integrated PLL/VCO combination. A reproducible and spectrally very pure microwave signal is generated by this PLL based signal source in combination with a TCXO. Setting the frequency is carried out over the digital interface of the PLL synthesizer. The transmitting power has to be adjustable in order to enable adaption to the measuring cell. Moreover it has to be temperature stable over a wide temperature range. Both these requirements are met by a temperature compensated automatic gain control AGC with adjustable set point. The measurement of the transmitting power is done in one channel of the integrated reflectometer.

The receiver contains two components for power measurement, one for linear power measurement by use of a diode detector and one for logarithmic power measurement by means of a LOGAMP. The logarithmic power measurement component covers a very wide power range. The linear power measurement unit enables much higher resolution, but needs precise adaption to the power range required and is also temperature compensated. The received signal must be preamplified by round 40 dB in two amplifier stages because of the high attenuation over the measuring distance in the measuring cell, which is in the order -60 to -85 dB.

The analog signals of both power measurement units are filtered, amplified and digitized by two high precision 16 Bit AD-Converters with precision voltage references in order to achieve highest accuracy and stability. Digital signal processing is carried out in both units with a standard digital component from commercial process moisture and an DS sensors of hf sensor.

The measurement is started in the control unit, which also carries out the processing and evaluation of measured spectral data. The measuring and calibration methods have been newly developed for the intended multivariate analysis of complete microwave spectra. Fig. 1 shows the block diagram of the complete measuring system.

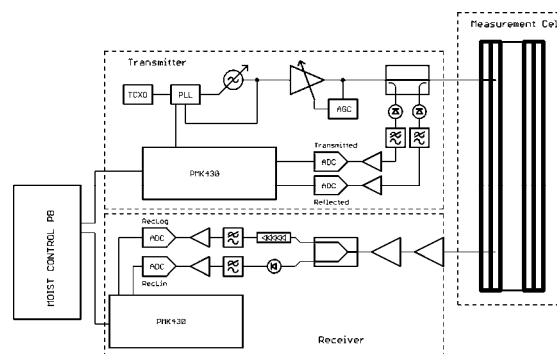


Fig. 1 Block diagram of complete measuring system MWTS T

The technical requirements to the microwave measuring cell in this application were very hard. It should be mountable in a stainless steel high pressure pipe system with inner diameter DN25 or DN30 and withstand maximum pressure of 80 Bar and temperatures of up to 100°C. Another challenge was that the small inner diameter of the pipes would lead to a “waveguide below cutoff” construction with no microwave propagation possible, but only evanescent field modes when filled with air. The filling with biofuels containing a certain amount of water in normal operation mode changes this problem to another one. If the water content of the biofuels varies over a broad range a transition from cutoff case to wave propagation case could happen, associated with completely different microwave behavior for different levels of water or DS content.

Therefore an outer pipe with 40 mm inner diameter was chosen for the principal construction of the microwave measuring cell. Using this diameter the cutoff problem can be avoided in normal operation mode. The measuring cell consists of an outer pipe DN40 made from stainless steel and high wall thickness and an inner pipe made from a high performance plastic material. This inner pipe also serves to accommodate the coupling elements, which in this case are pin-shaped.

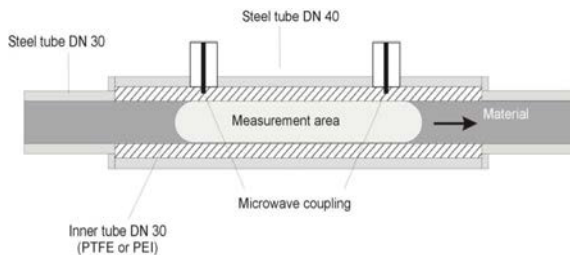


Fig. 2 High pressure measuring cell with microwave coupling elements

This sensor construction – shown in fig. 2 – can be integrated in a pipe system with DN30. It can be operated both in reflection mode and in transmission mode. The measuring section has 100 mm length, the transmission measurement is carried out along the measuring path between the coupling pins.

With this special measuring system complete scalar microwave spectra are recorded for measurements using microwave spectroscopy. The effect of individual substance influences on areas of the spectrum are different. The evaluation is carried out by reading one or more parameters from the spectrum (e.g. in the case of a resonance phenomenon) and doing the subsequent statistical evaluation of these parameters or all points of the spectrum using multivariate methods.

The advantages of this measurement method are that the influences of different effects can be separated. The statistical reliability is significantly higher than with non-spectroscopic evaluation. The following Fig. 3 shows the MWTS T microwave spectroscopic measuring system for the combined reflection / transmission measurement in pyrolysis slurries. As designed the measurement system can be integrated in a DN30 pipe system with pipe expansions to DN40 at both ends of the measuring pipe section. The microwaves are coupled in via an inner plastic pipe, where the coupling pins end in blind holes. Direct contact of the coupling devices with the medium is thus excluded.



Fig. 3. MWTS T microwave spectroscopic measuring cell for combined reflection / transmission measurement

III. MICROWAVE SPECTROSCOPIC MEASUREMENTS

With the measuring system, microwave spectroscopic measurements were successfully carried out at KIT, from which information on the water and solids content in pyrolytic slurries could be derived. The recorded microwave spectra were evaluated using the PLSR (partial least square regression) method.

In multivariate evaluation, a large set of input data is mapped onto one or a few target variables. This mapping is done using statistical methods. It is analyzed which of the input data or which combination of input data has a high correlation to the target variables. On the basis of this data, a prediction or calibration model can be calculated. The PLSR is such an evaluation model. The optimization of the evaluation is done on the basis of some statistical error variables (e.g. maximum absolute error, RMSE,...) with adjustable weighting. In order to increase the significance of this model, cross-validation is used in the calculation of the models. In the present evaluations, 60% of the measurements were used for calibration and 40% of the measurement data for validation. The cross-validation is supplemented by a grouping of the measurement data. This grouping ensures that the cross-validation always covers the entire data range of the target variable.

First a calibration model with a corresponding parameter set was developed based on the measurement data of five materials. For each material, several spectra at constant material temperature were used to compensate inhomogeneities of the material. Fig. 4 shows an example of the spectra of these five materials.

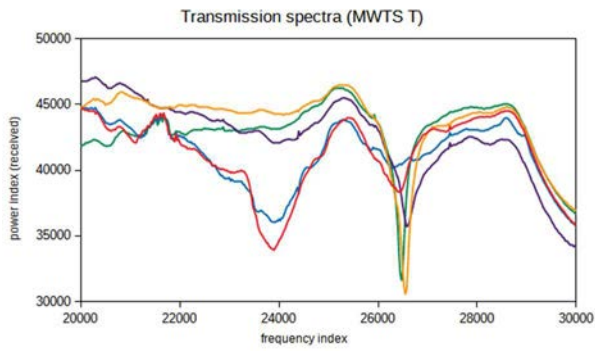


Fig. 4. Microwave transmission spectra of bio-slurries. Red line: phase C; blue line: phase C with 15% charcoal. yellow line: phase B; green line: phase B with 15% charcoal; violet line: phase D.

The application of the optimal calibration model to the measured spectra of the pyrolytic bioliq slurry resulted, as shown in Fig. 5, in a very good correspondence between calculated values and reference values (the water content was measured by Karl-Fischer titration).

The following errors result for the determination of the water content by PLSR:

maximum absolute error: 0.17% water content
 RSME: 0.09% water content

For the char content one obtains:

maximum absolute error: 0.11% char content
 RSME: 0.07% char content

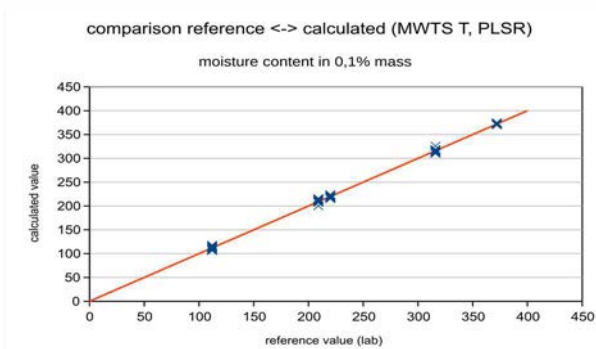


Fig. 5. Comparison of reference vs. calculated for water content of bio-slurry using MWTS T.

The biocrude from the Degussa process (phase D) was included in the PLSR model, although its spectrum (violet line in Fig. 4) showed a slightly different form than the others. A reason can be the much higher content of phenolics and sugars (see tab. 1), which was not included as a parameter in the model, but can be included in future studies.

Furthermore, measurements to determine the temperature behavior were recorded at a later point in time. The errors remained sufficiently small over the entire variation in the temperature range. The transmission data in particular seem to be well suited to depicting both the char and water content. However, it applies here that the PLSR is only suitable to a limited extent for depicting the influence of temperature.

In addition, the purely reflective microwave spectroscopic measuring system MWTS PP SPEC can be mounted on a sight glass fitting and was adapted to the special requirements of the bioliq® project.

For DS measurements reflective microwave sensors can be used (Fig. 6). The principle construction of microwave reflection sensing heads is simple. They contain a microwave source, a circulator or a reflectometer and some microwave detectors.

Using reflection methods low power electromagnetic energy is transmitted by a microwave applicator into the material. Both transmitted wave and reflected wave are separated and measured. The reflection coefficient is the ratio of reflected and transmitted wave:

$$\Gamma = \frac{u_{\text{reflected}}}{u_{\text{transmitted}}} \quad (1)$$

Since (1) is a ratio, the measurement is independent from power level. The amplitude of reflected wave depends on the dielectric properties of the material under test (MUT) and so far from water or DS content.

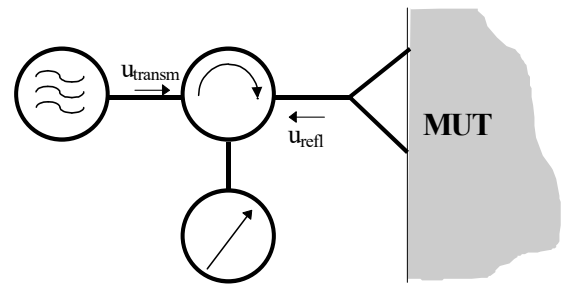


Fig. 6 Principle of microwave reflection measurement

Microwave applicators especially optimized for DS measurements can be mounted from outside with dielectric coupling elements at vessels and pipes without direct media contact. The microwave radiation penetrates the material under test through the dielectric coupling window or sight glass and captures a representative sample volume. The penetration depth of microwaves into the material is up to 8 cm and therefore much higher than that of infrared optical measuring systems, reaching only penetration depths in the millimeter range. Another advantage is that due to the high frequency measurements are not influenced by varying PH values or by the conductivity of the material.

In numerous industrial applications the continuous surveillance of DS content of aqueous media is required within hermetically sealed piping systems. Those components have to be free of dead space and media contact especially for applications in the food and pharmaceutical industry. In such applications microwave DS sensors can be combined with common sight glasses like from the series VARINLINE®. A particularly big advantage of this configuration is that no changes are necessary at those parts of the sight glass fitting which are in contact with the medium. This way the type approvals of the manufacturers with regard to hygiene or food regulations are retained.



Fig. 7 Microwave DS sensor MWTS PP mounted at a sight glass VARINLINE®

Based on this configuration the new reflective microwave spectroscopic measuring system MWTS PP SPEC was designed and adapted to the special requirements of the bioliq® project. To improve the recording of such spectroscopic measurements a new control unit and a new PC software were developed.

Various measurements took place in the IKFT (KIT) technical center. The aim was to test the suitability of a MWTS PP 200 SPEC on a sight glass fitting (DN50) for the simultaneous determination of the water and char content of bio-slurry.

The light fraction (B), the heavy fraction (C), ground char powder and two mixed samples were available as starting materials. Five spectra were recorded for each material.

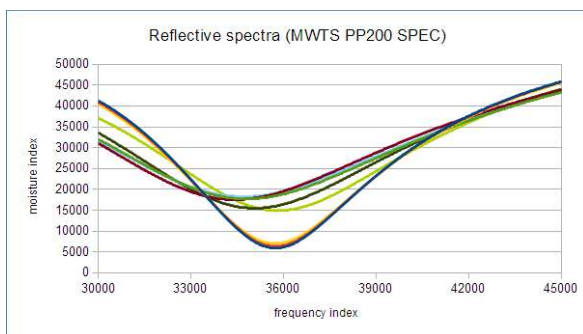


Fig. 8 Typical reflective spectra for bio-slurry.

A total of twelve different material mixtures were used in the tests. One was discarded because of segregation. In the following evaluations, only the eight mixtures that contained char were used. A spectrum of each of these eight mixtures is shown in figure 8.

The measurement data is evaluated in the form of a calibration for the char or water content. This calibration is carried out using PLSR. A group-based pre-classification of the measurement data and cross-validation are used for this.

For the evaluation, this calibration is applied to the measurement data and then the errors (deviations between the laboratory value and the calculated value) are calculated. The maximum absolute error and the RMSE of this calibration are determined from this.

For the determination of the water content by PLSR, the following errors result:

maximum absolute error: 0.22% water content
 RSME: 0.11% water content

For the char content one obtains:

maximum absolute error: 0.60% char content
 RSME: 0.33% char content

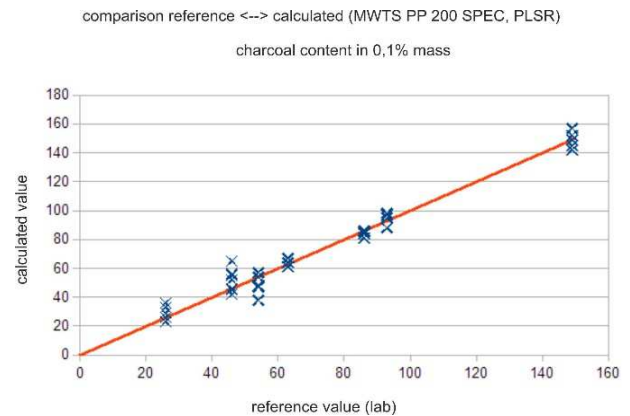


Fig. 9 Comparison reference vs. calculated for bio-slurry with 7 different char contents using MWTS T.

If the data of the material mixtures without char are included in the evaluation, the errors increase. However, since there are no slurries without coke content in the bioliq® process, this can be neglected.

The effects of temperature are very important, but have not yet been sufficiently investigated. However, initial measurements show that compensation of the temperature using PLSR will not be sufficient. Further measurements on the temperature influence are planned in a newly constructed test bench for both types of microwave spectroscopic sensors.

IV. CONCLUSIONS

In general, the results of the measurements with both types of microwave spectroscopic measuring systems on pyrolysis slurries can be described as very good. The application of the optimal calibration model to the measured spectra of the pyrolytic bioliq® slurry resulted in a very good correspondence between calculated values and reference values.

Temperature variations have high impact on the measurements, but have not yet been sufficiently investigated. For this, a complete test bench is currently under construction and will be used for future measurements.

Both measuring system types have shown their high potential for the investigation of water content and other material parameters in aqueous multicomponent mixtures.

REFERENCES

- [1] S. Czernik, D.K. Johnson, S. Black, "Stability of wood fast pyrolysis oil," *Biomass Bioenergy* 1994, 7, pp. 187–192.
- [2] N. Dahmen, J. Abeln, E. Mark, Th. Kolb, H. Leibold, J. Sauer, D. Stapf and B. Zimmerlin, "The bioliq process for producing synthetic transportation fuels," *WIREs Energy Environ* 2016. doi: 10.1002/wene.236, pp. 1 – 10.

- [3] A. Göller, „Biogasanlagen – Bilanzierung von Feststoffströmen mit Mikrowellen-TS-Sensorik“. Internationale Konferenz des IBBK ‚Fortschritt beim Biogas‘, Stuttgart: (19. - 21.09.2007). Tagungsband-Poster (IBBK), S. 47ff. [Posterbeitrag]
- [4] T. Nacke, A. Barthel, „Inline-Mikrowellen-Prozesssensorik zur Bestimmung des Trockenmasseanteils im Biogaserfermenter“ Gülzower Fachgespräche, Messen, Steuern, Regeln bei der Biogaserzeugung, Bd. 27, S. 32-57
- [5] T. Nacke, A. Barthel, „Online-Massebilanzierung der Prozesssubstrate und Gaserträge als Basis für eine automatisierte Prozessführung von Biogasanlagen“. VDI-Konferenz Prozessmesstechnik an Biogasanlagen 2011, Düsseldorf, Tagungsunterlagen
- [6] A. Göller, S. Vogelei, T. Nacke, „Mikrowellen-TS-Sensorik für Biogassubstrate – praktische Einsatzfälle“. VDI-Konferenz Prozessmesstechnik an Biogasanlagen 2012, Fulda, 09.-10.10.2012, Tagungsunterlagen
- [7] A. Göller, B. Jungstand, „Mikrowellen-TS-Messung in wässrigen Flüssigkeiten,“ 3. Fachseminar des FA MTHz, Mikrowellen- und Terahertzprüftechnik in der Praxis; 5. April 2017, Würzburg, Vortrag 4
- [8] A. Göller, B. Jungstand, „Mikrowellenspektroskopische TS-Sensorik für die kombinierte Bestimmung von Feststoff- und Wassergehalten in Mehrstoffgemischen“, Berichtsband zur 9. CMM-Tagung „Innovative Feuchtemessung in Forschung und Praxis“, 20. September 2017, Karlsruhe, S. 157 -

Repository KITopen

Dies ist ein Postprint/begutachtetes Manuskript.

Empfohlene Zitierung:

Graf, F.; Sauerschell, S.; Prabhakaran, P.; Bajohr, S.; Slama, J.; Stapf, D.; Kolb, T.
[Sektorenkopplung mit Gas im Rahmen des BMBF-Vorhabens SEKO – Teil 2: Gasfachliche Untersuchungen.](#)
2020. Energie-, Wasser-Praxis.
doi: [10.5445/IR/1000126820](https://doi.org/10.5445/IR/1000126820)

Zitierung der Originalveröffentlichung:

Graf, F.; Sauerschell, S.; Prabhakaran, P.; Bajohr, S.; Slama, J.; Stapf, D.; Kolb, T.
[Sektorenkopplung mit Gas im Rahmen des BMBF-Vorhabens SEKO – Teil 2: Gasfachliche Untersuchungen.](#)
2020. Energie-, Wasser-Praxis, (10), 43–49

Lizenzinformationen: [KITopen-Lizenz](#)