

COMBINED HEAT AND POWER GENERATION FROM SOLID BIOMASS DERIVED BIOLIQUIDS AND SYNGAS BY TCR®- UPGRADE OF TCR-LIQUIDS BY HYDRODEOXYGENATION

Andreas Hornung^{1,2,3}, Andreas Apfelbacher¹, Johannes Neumann¹, Nils Jäger¹, Nina Schmitt¹, Robert Daschner¹

¹ Fraunhofer UMSICHT, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany

² Università di Bologna

³ Friedrich-Alexander Universität Erlangen-Nürnberg and University of Birmingham

ABSTRACT: Bioenergy plays a significant role for the future energy supply and energy transition. Thus it is essential to expand the applicability of biofuels. Especially residue biomass is in the focus of academic and commercial research. A promising conversion technology for the production of liquid and gaseous fuels for combined heat and power (CHP) from residual biomass is the Thermo-Catalytic Reforming process (TCR®). At the EU BC&E 2016 positive results have been presented for the operation of a demo-scale combined heat and power diesel engine with bio-oil from this pyrolysis and reforming process. Main advantage of liquid biofuel from this process is the direct applicability in an internal combustion engine which is problematic for common fast pyrolysis oils. The liquid product of the TCR® process showed remarkably properties like a low TAN number, low viscosity, high heating value and as an unique and essential property for CHP application thermal stability. The CHP engines were run on several gas TCR®-liquid mixtures. To meet the targeted high efficiency at an input of 80% gaseous and 20% liquid fuel, minor optimisations were required by means of injection timing and exhaust gas recirculation. In this context performance, emission characteristics and efficiency were measured and compared for different settings and operation points. The Thermo-Catalytic Reforming process is a key component of the Biobattery concept developed within the framework of the Center for Energy Storage (CES).

Keywords: CHP conversion, Thermo-catalytic reforming,

1. INTRODUCTION

Bioenergy plays an important role in the future energy supply scenario [1-3]. Thus, it is essential to expand the types of bio-feedstocks with a specific focus on fuels produced from biomass residues with the aim to convert the fuels generated on internal combustion engines for combined heat and power production [4].

The usage of dedicated energy crops is connected to the land use competition for food production [5]. Therefore the utilization of agricultural/industrial waste such as straw, digestate, sewage sludge can represent the favoured strategies for the bioenergy sector. These uncritical feedstocks play a significant role in the thermo-catalytic reforming technology (TCR®). Several bioenergy conversion processes have been developed including biochemical (enzymatic conversion, fermentation, anaerobic digestion) [6-8] and thermochemical process (e.g. pyrolysis, gasification, hydrothermal liquefaction) [4, 9, 10].

Pyrolysis is a thermochemical process able to convert woody and non-woody biomass providing a liquid fuel (bio-oil), a likely substitute of heavy oil, a gaseous fuel (syngas) and a solid material (char) for several applications, especially soil applications, such as soil amendment or agent for soil remediation [11]

It can be distinguished three different kind of pyrolysis process (fast, intermediate and slow) depending on the temperatures, heating rates and vapour residence times which are applied.

Above-mentioned process parameters cause significant difference in terms of product distribution and quality of solids, non-condensable gas and liquids (aqueous and organic) [4].

Intermediate pyrolysis operates at relatively moderate temperatures (400-500°C) and heating rates (minutes) in the complete absence of oxygen, with vapour residence times in range of seconds. This moderate heating rate induced the formation of pyrolysis liquids with very low tar content in comparison to other pyrolysis technologies.

But even with intermediate pyrolysis, the liquids generated were not suitable for long term CHP application. The combination of intermediate pyrolysis with an integrated reforming stage – the TCR® process – opens the door for a new generation of liquid and gaseous products having the required properties for CHP application.

2. MATERIALS AND METHOD

2.1 Raw materials

The sewage sludge for the TCR®-experiments was supplied from a wastewater treatment plant in Bavaria. The chemical properties of sewage sludge depend on the catchment area of the wastewater treatment plant and the used technology as well as seasonal fluctuation. The sewage sludge was dried and had a diameter of 1 to 10 mm, with a granulate structure and a moisture content of 9.7 wt% on average.

2.2 Experimental setup

The TCR® reactor is installed at the site of Fraunhofer UMSICHT, Institute Branch Sulzbach-Rosenberg, Germany. The whole system is a continuous operating reactor with a capacity of 30 kg of biomass per hour. The reactor consists of a feeding unit with a sluice system, the TCR® reactor (screw reactor and reformer stage), condensation unit existing out of a shell and tube heat exchanger and a quench system and a continuous char extraction screw including char storage. Online gas analytics are carried out by a calibrated pyrolysis gas detection system (Gas-analyzer MGA 12). The measurement principle of the gas analyzer is based on an infrared photometer (CO, CO₂, and CH₄), an electrochemical cell (O₂) and a thermal conductivity detector (H₂). The calorific value of the gas was measured with an online gas-calorimeter from Union Instruments CWD 2005.

The TCR® reactor consists of two major units. In the

first unit, intermediate pyrolysis occurs at temperature of 400 to 450°C. The heating rate of the feedstock was around 1°K/s (Fig.1).

The inner diameter of the screw reactor is around 200 mm; the length of the reactor around 2200 mm. The feedstock is conveyed through the reactor by means of a screw and enters the post reforming reactor in the second stage (700°C).



Figure 2: Conceptual drawing of a TCR[®] plant and of the products gas, oil and char

In this second unit -the reforming stage- the pyrolysis vapours are converted into a hydrogen-rich syngas and organic biphasic liquid fraction (bio-oil and aqueous phase) with improved fuel physical and chemical properties (Fig. 2)



Figure 2: TCR[®] 30 plant at Fraunhofer UMSICHT

The quality of the TCR[®]-oil and the TCR[®]-gases are improved to such a grade, that both are suitable for an application on internal combustion engines like CHPs.

The engines test of the TCR[®]-oil and TCR[®]-gas were carried out on a 20kW_{el} Kubota compression ignition engine with indirect injection system and modification for dual fuel use (gas regulation valve). The liquid used was a blend of up to 75 % TCR[®]-oil and 25 % biodiesel. The combustion behavior of the TCR[®]-gas was tested in ratio of 67% TCR[®]-oil 33% biodiesel blend. The gas was added with a ratio of approximately 66 % in terms of the energy input into the internal combustion engine.



Figure 3: CHP unit for 20kW_{el}

3 RESULTS AND DISCUSSION

3.1 Mass- and energy balances

The mass- and energy balances of thermo-catalytic reforming process with post reforming temperature of 700 °C for sewage sludge as feedstock is shown in figure 4. With sewage sludge consisting of high amounts of minerals a high yield of ash (38%) in the products was observed. Further 10% was collected as char. Process water has an estimated yield of 23 %. Further 12% of the product was TCR[®]-oil and 17 % was TCR[®]-gas. In terms of the energy balance, the situation looks completely different. With the TCR[®]-oil accounting for 35 % and the TCR[®]-gas accounting for 25 % of the energy, the CHP compatible compounds summed up to 60 % of the energy of the feedstock. The solid product -the char- contained 35 % of the energy.

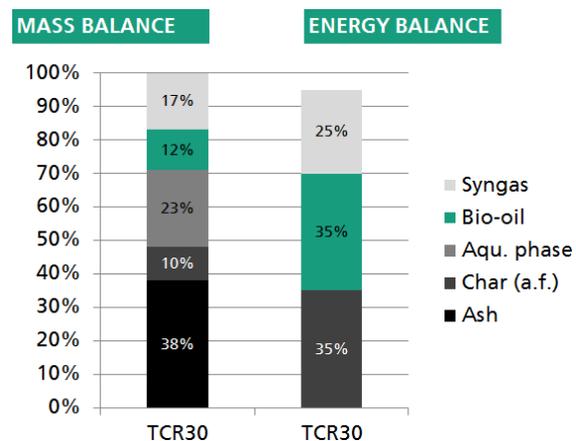


Figure 4: Mass- and energy balance for sewage sludge

3.2 Quality of the CHP compatible products.

Liquids and gases generated by thermochemical processes like gasification or pyrolysis must fulfill certain requirements to be applicable to internal combustion

engines. Properties like a low total acid number (TAN), high heating value, low viscosity, low water content and especially the thermal stability are essential for liquids to be compatible to conversion on internal combustion engines. A further requirement of the liquids is that they are free of tars and particles. In literature one can find several attempts of converting liquids generated by pyrolysis on internal combustion engines. Most of these attempts failed or have been stopped, as the liquids were destroying the injection systems, springs or the valves of the engines due to corrosion and blockage.

Figure 5 shows the TCR[®]-oil and selected analytical data for the liquid. TCR[®]-oils. It exhibits typically low water concentration, due to their lower polarity compared to other pyrolysis liquids. The reforming stage carried out at 750 °C causes the degradation of oxo-compounds in the pyrolysis vapours. The condensed TCR[®]-oils, therefore show lower oxo-compounds causing a lower polarity of the oils. This lower polarity makes the TCR[®]-oil less soluble for water and leads to a good phase separation. In addition, due to the very low water content, and the lower concentration of oxo-compounds, the TCR[®]-oil shows a very high lower heating value of 34 MJ/kg (for comparison: diesel: 42 MJ/kg, conventional flash pyrolysis oils: 16 MJ/kg [13]). A further result of the low water and oxo-compounds is the relatively low oxygen content in the TCR[®]-oils being with a number of nine approximately five times lower compared to other pyrolysis liquids [13]. A further point of importance is the Total Acid Number (TAN) of the liquids. In order to avoid corrosion of the injection system of a CHP, TAN values lower than 10 mg KOH/g are required. The TCR[®]-liquids show TAN values in a range of 3 to 5 mg KOH/g oil (for comparison: vegetable oi: 2 mg KOH/g oil, conventional pyrolysis oils: 70 to 100 mg KOH/g oil [14]). Regarding the viscosity of the TCR[®]-oil the analytics show, the values are in the range of conventional diesel (2.0 mm²/s to 4.5 mm²/s) [15]. Beside the problematic of corrosion, viscosity, and heating value, one essential property required for CHP application of fuels is the thermal stability in a temperature range up to 350 °C. Atmospheric distillation experiments have demonstrated that the TCR[®]-liquids are distillable where approximately 80% of the compounds are distillable in the temperature range till 350 °C - 20% remained as heavy oil. This thermal stability is unique for pyrolysis liquids, but essential for the application on internal combustion engines, as the injection system of the engines can exhibit temperatures even higher than 350 °C. If the liquids were not thermal stable, coking of the liquids in the injection system would happen and destroy the engines. Experiences like this have been described in literature for the application of not thermal stable liquids engine [16].

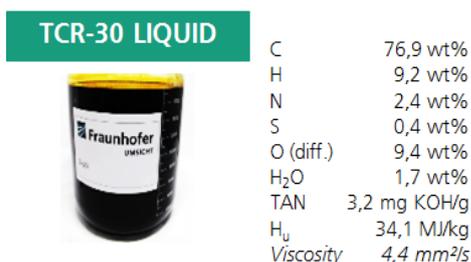


Figure 5: Selected analytical data for TCR[®]-oil

4. CONVERSION OF LIQUIDS AND GASES ON CHP ENGINES

The TCR[®]-oils were tested on a CHP engine as describe in Fig. 3. For the investigation TCR[®]-oil blends with biodiesel were tested with ratio of 10, 50 and 75% TCR[®]-liquid (Fig. 6). The ignition experiments demonstrated that TCR[®]-oil blends of up to 50 % showed a similar ignition behavior like pure biodiesel. In terms of a 75% TCR[®]-oil blend, the ignition was delayed. This was caused by a higher content of naphtha compounds (lower boiling compounds) in the TCR[®]-liquid. The negative effect could be eliminated by an earlier ignition point.

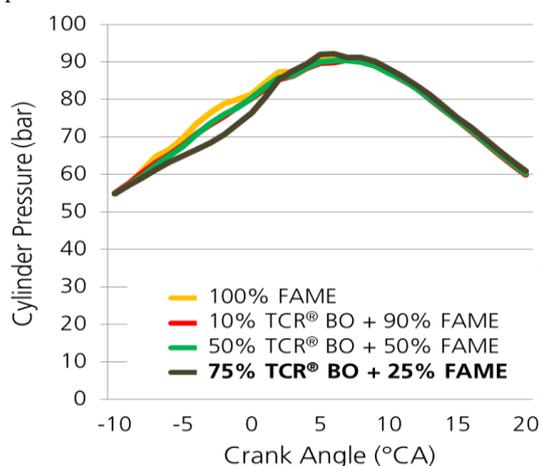


Figure 6: Ignition test with TCR[®]-oilblends

The same ignition tests were carried out with TCR[®]-oil biodiesel blend and TCR[®]-gas. The ratio is shown in Fig. 7. These investigations showed that the addition of TCR[®]-gas had a positive influence on the ignition behavior of the TCR[®]-oil biodiesel blend (Fig. 7)

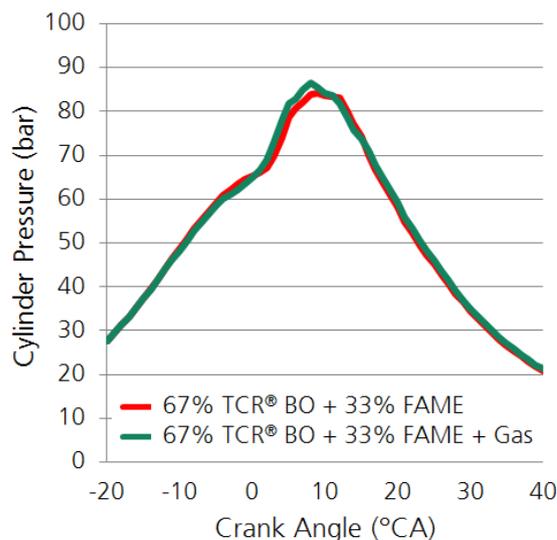


Figure 7: Ignition tests of TCR[®]-oil-biodiesel blends and gas mixtures

4 UPGRADE OF TCR-OILS BY HDO

The bio-oil from sewage sludge was generated using the TCR 30 reactor at 400 °C intermediate pyrolysis temperature and 700 °C post reforming temperature. The TCR bio-oil was hydrodeoxygenated by an external provider in a laboratory reactor with a continuously trickle bed reactor and a catalyst bed volume of around 100 cm³. The experiment was carried out with a typical industrial refining catalyst (NiMo-Al₂O₃) for hydrodeoxygenation. The experimental setup used by the external provider is shown in Figure 8.

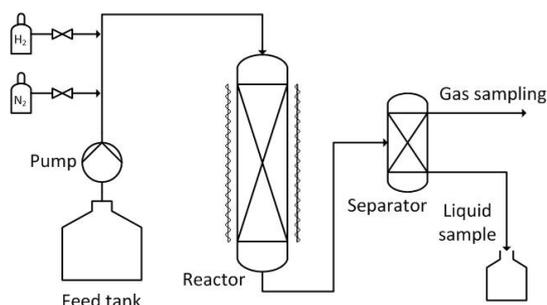


Figure 8: Schematic flowsheet of the hydrodeoxygenation reactor

The temperature increased in the reactor from 230 °C at the beginning to 370°C at the bottom of the catalyst bed. The heating was controlled by five heating sleeves and the temperatures were kept constant. This non-isothermal operation was chosen due to the expected highly exothermal reactions during the bio-oil hydration and to avoid catalyst damaging temperatures. The liquid hourly space velocity (LHSV – Reactant Liquid Flow Rate/Reactor Volume) for the hydrodeoxygenation was set to 0.6 h⁻¹. An amount of 1500 litre H₂ per litre bio-oil was added. The reactor pressure was kept constant during the upgrading process at 14 MPa. The product was separated into liquid and process gas after the reactor by means of a high pressure separator.

For the analysis of the HDO process gas a Micro-GC was used. The difference in the gas composition to 100 % was estimated to be NH₃, as this could not be detected by the Micro-GC. The amount of reaction water was measured after separating the water phase from the oil phase via gravity settling and decantation. The crude TCR and HDO bio-oil were analysed by an external certified petrochemical analysis laboratory. The applied standard test methods are given next to the analysis results.

The properties of the crude bio-oil are shown in Table 1. The most outstanding properties of the TCR bio-oil are its low oxygen content of 7.0 wt%, the low water content of 2.2 wt% and the low total acid number (TAN) of 2.1 mg KOH/g. The lower heating value of the TCR bio-oil was found to be 34.0 MJ/kg. Furthermore the low viscosity of 4.43 mm²/s is comparable to common biofuel like biodiesel (3.5–5 mm²/s according to EN 14214; 1.9–6.0 mm²/s according to ASTM D6751). The TCR bio-oil was derived from digestate having high nitrogen and sulphur content. As a result of the feedstock composition the bio-oil contains quite high amounts of nitrogen and sulphur. Therefore, higher hydrogen consumption during HDO is expected, as NH₃ and H₂S will be generated.

Table 2: Ultimate analysis and properties of the TCR® bio-oil

Ultimate analysis	Unit	Value	Test method
C	wt%	77.6	DIN 51732
H	wt%	8.0	DIN 51732
N	wt%	4.6	DIN 51732
S	wt%	0.6	DIN 51399-2
O (by difference)	wt%	7.0	

Physical properties	Unit	Value	Test method
H ₂ O	wt%	2.2	DIN 51777-1
LHV	MJ/kg	34.0	DIN 51900-2
Flash point	°C	47.0	DINEN ISO 3679
Density (15 °C)	kg/m ³	1014.4	DINENISO12185
Viscosity (40 °C)	mm ² /s	4.43	DINEN ISO 3104
TAN	mg KOH/g	2.1	DIN EN 14104
Copper corrosion	rating	Class 1	DINENISO 2160

The hydrodeoxygenated TCR bio-oil is shown in Figure 9. As it can be seen the HDO oil is a clear, bright, fully transparent and low viscous liquid.



Figure 9: TCR bio-oil after hydrodeoxygenation

The ultimate analysis of the hydrodeoxygenated TCR bio-oil is shown in Table 2. The produced HDO oil is low in sulphur (101 mg/kg) and nitrogen (below detection limit) and has an oxygen content lower than 0.8 wt% calculated by difference. Compared to the analysis of the crude TCR bio-oil in Table 1, more than 98 wt% of nitrogen and sulphur were removed during the hydrodeoxygenation. The water content after the hydrodeoxygenation was measured as 0.003 wt% compared to 2.2 wt% in the crude TCR bio-oil. The LHV increased from 34.0 MJ/kg to 42.3 MJ/kg and is comparable to standard fossil fuels like gasoline and diesel. The TAN was reduced from 2.1 mg KOH/g down to 0 mg KOH/g. The density decreased from 1014.4 kg/m³ to 815.7 kg/m³ and the viscosity decreased from 4.43 to 0.97 mm²/s as well. Overall the properties of the HDO TCR bio-oil are comparable to a mixture of fossil fuels consisting out of gasoline, kerosene and diesel.

Table 3: Ultimate analysis and properties of the HDO TCR bio-oil

Ultimate analysis	Unit	Value	Test method
C	wt%	86.2	DIN 51732
H	wt%	13.0	DIN 51732
N	wt%	< 0.1	DIN 51732
S	mg/kg	101	DINENISO20884

O (by difference) wt% < 0.8

Physical properties	Unit	Value	Test method
H ₂ O	mg/kg	30	DINENISO12937
LHV	MJ/kg	42.3	DIN 51900-2
TAN	mg KOH/g	0.0	DIN EN 14104
Flash point	°C	< -20	DINEN ISO 3679
Density (15 °C)	kg/m ³	815.7	DINENISO12185
Viscosity (40 °C)	mm/s ²	0.97	DINEN SO 3104
Copper corrosion	rating	Class 1	DINEN ISO 2160

The product yields and balance for the hydrodeoxygenation process is shown in Figure 10. The required hydrogen for the HDO reaction was calculated to be 6.62 g per 100 g of TCR oil. Approximately 83 wt% of the TCR bio-oil was converted to liquid hydrodeoxygenated fuel. The generation of gaseous hydrocarbons results from cracking processes during the HDO process or could be related to the molecular structure of the TCR bio-oil (e.g. ethers). Ammonia and Hydrogensulfid and are formed by the hydrogenation of nitrogen and sulphur. The H₂S balance shows a significant gap between the TCR bio-oil composition and the detected amount of H₂S gas. It is assumed that a reasonable amount of H₂S was solved within the process water. Additionally, sulphur depositions were found within the liquid sample containment, which are not included in the mass balance.

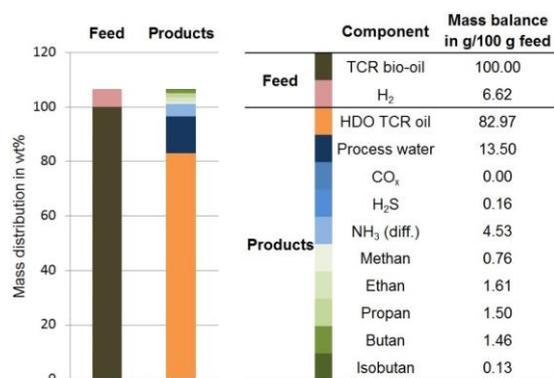


Figure 10: Balance of the TCR bio-oil hydrodeoxygenation

The total hydrodeoxygenation experiment took approximately six days. Overall about 8 litres of TCR oil were hydrated. The activity of the catalyst was tested before and after the experiment with plant oil and gas oil as reference substances. While the conversion of plant oil to alkanes worked as expected before and after the experiment, the desulphurisation effectivity of gas oil dropped from 98.5% to 94%. Reasons for the deactivation of the catalyst could be coking by unsaturated bio-oil compounds, inhibition by nitrogen compounds at catalytically active centres or catalyst sintering caused by relatively high temperatures. As shown in Figure 10, the product yield after HDO of the TCR bio-oil was almost 83 wt%. Compared to other HDO pyrolysis oils from literature the yield is very high. Furthermore the HDO TCR bio-oil has an oxygen content lower than 0.8 wt%, which is significant lower compared to other HDO pyrolysis oils. The hydrodeoxygenated TCR oil is distillable. The distillation of the HDO liquid resulted in a petrol fraction (approx. 40%) and a diesel

and a kerosene fraction. Analytic test of the diesel and petrol fraction have shown, that these fraction fulfill almost all standards of the required DIN fuel norms.

5 CONCLUSION

The novel TCR[®]-technology produces a thermal stable liquid with high heating value, low viscosity and very low total acid number [17, 18]. Due to these unique properties these liquids are suitable for the conversion on internal combustion engines to heat and electrical power.

Blends of the TCR[®]-liquid with biodiesel and with the TCR[®]-gas were carried out on a 20 kW_{el} CHP plant demonstrating the applicability of these products.

The Engine performance was assessed for different mixtures of liquid and gaseous TCR[®]-fuels as well as for different loads. By lowering the amount of liquid fuel an increase in ignition delay was observed due to a reduced fuel-air-mixing. This delay was successfully compensated by an earlier start of injection. Knocking from the high hydrogen concentration was avoided by exhaust gas recirculation and oxygen reduction in the intake air.

High quality biofuel from solid biomass was produced by hydrodeoxygenation of TCR bio-oil. The TCR bio-oil from sewage sludge showed an oxygen content of 7.0 wt%, a water content of 2.2 wt%, a total acid number of 2.1 mg KOH/g and a LHV of 34.0 MJ/kg.

The O/C and H/C ratios of the crude TCR bio-oil are comparable to those of already hydrodeoxygenated fast pyrolysis oils known from literature. This high quality of the crude TCR bio-oil was further improved by hydrodeoxygenation. The hydrogenated TCR bio-oil meets an outstanding quality and is in many parameters comparable to standard fossil transportation fuels, for example the LHV of 42.3 MJ/kg is in the range of gasoline and diesel fuel. The hydrodeoxygenation of TCR bio-oil is a promising way of producing solid biomass based high grade biofuels. Analytics have demonstrated, that it is possible for the diesel and petrol fraction to fulfill the required fuel norms, so that it is possible to run standard car engines on these fractions.

6 REFERENCES

- [1] E. Hauser, F. Baur, F. Noll, Beitrag der Bioenergie zur Energiewende, Institut für ZukunftsEnergieSysteme (2014).
- [2] BDEW Bundesverband der Energie- und Wasserwirtschaft e.V., Erneuerbare Energien und das EEG: Zahlen, Fakten, Grafiken (2014).
- [3] P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresource Technology (83) (2002) p. 37–46.
- [4] Hornung A, Transformation of biomass, Theory to practice. 1st ed. Chichester, UK: John Wiley & Sons Ltd. (2014).
- [5] Rathmann, R., Szklo, A., Schaeffer, R. (2010). Land use competition for production of food and liquid biofuels: An analysis of the arguments in the current debate. Renewable Energy, 35, 14-22.
- [6] Jørgensen, H., Kristensen, J. B., Felby, C. (2007). Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities. Biofuels, Bioproducts and Biorefining, 1, 119-134.

- [7] Lin, Y., Tanaka, S. (2006). Ethanol fermentation from biomass resources: current state and prospects. *Applied microbiology and biotechnology*, 69, 627-642.
- [8] Molino, A., Nanna, F., Ding, Y., Bikson, B., Braccio, G. (2013). Biomethane production by anaerobic digestion of organic waste. *Fuel*, 103, 1003-1009.
- [9] Czernik, S., Bridgwater, A. V. (2004). Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, 18(2), 590-598.
- [10] Goyal, H. B., Seal, D., Saxena, R. C. (2008). Bio-fuels from thermochemical conversion of renewable resources: a review. *Renewable and sustainable energy reviews*, 12, 504-517.
- [11] Lehmann, J. and Joseph, S. (2009). Biochar for environmental management: An introduction. In: J. Lehmann and S. Joseph, editors, *Biochar for environmental management: Science and technology*. Earthscan, London., 1-12.
- [12] Ouadi, M., Brammer, J. G., Yang, Y., Hornung, A., Kay, M. (2013). The intermediate pyrolysis of deinking sludge to produce a sustainable liquid fuel. *Journal of analytical and applied pyrolysis*, 102, 24-32.
- [13] <http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis>.
- [14] Oasmaa A, Peacocke GVC (2010) Properties and fuel use of biomass derived fast pyrolysis liquids, VTT Technical Research Centre of Finland, VTT publication 450.
- [15] ARAL, *Dieselmotoren Anforderungen, Qualität, Perspektiven*, 4.aktualisierte Auflage, Mai 2010.
- [16] Dietrich Meier, Stefan Schöll und Susanne Hoffmann; *Arbeitsbericht des Instituts für Holzchemie und chemische Technologie des Holzes*, Mai 2007.
- [17] J. Neumann, S. Binder, A. Apfelbacher, J.R. Gasson, P.R. Garcia, A. Hornung: *J. Anal. Applied Pyrol.* 113, pp. 137-142, 2015.
- [18] J. Neumann, J. Meyer, M. Ouadi, A. Apfelbacher, S. Binder, A. Hornung: *Waste Management* 47, pp. 141-148, 2016.

7. ACNOWLEDGEMENT

The authors would like to thank the Bavarian State Ministry of Economic Affairs, Infrastructure, Transport and Technology for the financial support of the project. The project was conducted in the framework of the Center for Energy Storage.

