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Schmitt, Nina ; Apfelbacher, Andreas; Jäger, Nils; Daschner, Robert; Stenzel, Fabian ; Hornung, Andreas

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**Thermo-chemical conversion of biomass and upgrading to biofuel: The Thermo-Catalytic
Reforming process - A review**

5 Nina Schmitt^a, Andreas Apfelbacher^a, Nils Jäger^a, Robert Daschner^a, Fabian Stenzel^a, Andreas
Hornung^{abc*}

^a Fraunhofer UMSICHT, Institute Branch Sulzbach-Rosenberg, An der Maxhütte 1, 92237 Sulzbach-
Rosenberg, Germany

10 ^b School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, West Midlands,
B15 2TT, United Kingdom

^c Friedrich-Alexander University Erlangen-Nürnberg, Schlossplatz 4,
91054 Erlangen, Germany

15 *Corresponding Andreas Hornung

Phone: +49 (0) 9661/ 908-403

Email: andreas.hornung@umsicht.fraunhofer.de

Abstract

20 Thermo-Catalytic Reforming (TCR[®]) is a promising conversion technology for the production of liquid
bio-fuels. The process is a proven opportunity to convert biological wastes and residues into hydrogen
rich syngas, high quality oil, and char without volatiles. Bio-oil produced from TCR[®] has a high carbon
content, low water content, low oxygen content, and a high heating value; Therefore it is directly
applicable as feed in boilers or as blend in dual fuel engines. A feasible opportunity for using bio-oil in
25 automotive combustion engines is a further upgrade step to bio-fuel by hydrogenation. During this
hydrotreatment heterogeneous atoms like sulphur, nitrogen and oxygen are removed or substituted
through hydrogen. Fraunhofer UMSICHT already produces gasoline and diesel that complies with
European fuel standards EN 228 and EN 590, using different catalysts like NiMo/Al₂O₃, CoMo/Al₂O₃

and Ru/C for the hydrogenation at to 643 K and a constant hydrogen pressure of 14 MPa. Various hydrocarbons and benzene derivatives are verified after hydrotreating.

Keywords: Thermo-Catalytic Reforming, Intermediate Pyrolysis, Biomass, Catalytic Hydrotreating, Biofuel, Bio-oil Upgrading

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1. INTRODUCTION

As environmental protection policies strengthen their grip around fossil fuel harvesting and processing, companies look for new methods to redirect their businesses from the oil field and in the direction of renewable energy and biomass utilization for the decarbonization of their industrial sectors. One area of interest is the production of bio-oils as basis for chemical production or fuel applications. Luckily, bio-oils and biofuels lie within the jurisdiction of political platforms and regulations, because biomass-based fuels recycle carbon from the atmosphere.¹

The most common thermal conversion processes for dry waste biomass or biological residues like gasification, combustion, or pyrolysis are utilization processes. Opposite to coal, the moisture content and oxygen content of biomass are significantly higher. Therefore, the efficiency of thermal treatment is reduced.² However, the different kinds of thermal treatments distinguish themselves in the process conditions and their products: For combustion the presence of oxygen during the treatment is necessary. The so called excess air ratio Lambda λ describes the ratio between the amount of added air and the amount of air necessary for a complete oxidation of the feedstock. Combustion is the complete oxidation with a minimum of $\lambda = 1$. For gasification and pyrolysis λ is below 1 or 0.^{3,4} Combustion generates heat usable for heating and steam production to enable electricity generation.^{5,6} Fuel gas for combustion for heat, and to run engines or turbines for electricity generation are gained through gasification. Besides electricity, hydrogen, methane and carbon monoxide are also produced, and can be further synthesised to Fischer-Tropsch diesel.⁷ Liquids for extracting chemicals and for the use as fuel in combustion engines are produced by pyrolysis. Also synthesis gases and carbon rich solids can be produced by pyrolysis.^{4,8}

Depending on the reaction conditions there are three different kinds of pyrolysis: Slow pyrolysis, intermediate pyrolysis, and fast pyrolysis (Table 1). Product yields depend on heating rate, final

temperature, and residence time in the reaction zone. Therefore, it is possible to guide product yields and composition by changing process conditions.^{9, 11}

Slow pyrolysis has been used for several centuries to produce carbon rich (C = 80 – 90 wt%) coal.¹²

5 During slow pyrolysis the heating value duplicates. For example in one occasion the heating value goes from 16 MJ/kg (waste wood) up to 34 MJ/kg (waste wood solid phase).¹³ Besides a solid phase some liquids like acetic acid and alcohols are also formed.¹⁰

Based on biomass slow pyrolysis conditions, fast pyrolysis was developed. Fast pyrolysis is a breakthrough in bio-oil production, because of the high liquid phase content of 70 – 80 % in reference to dry biomass feedstock.⁴ Heating rates up to 500 K/s, reaction temperatures between 673 K and 823 K,
10 and vapor residence times of 0.5 – 2 seconds are reached while chemical bonds inside the feedstock are broken.¹⁰ The produced gases are rapidly cooled down to stop the decomposition and to avoid high amounts of gas.⁹

Reaction conditions of intermediate pyrolysis are located between slow and fast pyrolysis: Temperatures between 673 – 823 K, reaction times of 240 – 600 s and medium heating rates of 10 – 100 K/s are
15 applied.¹⁰ The thermal decomposition produced by intermediate pyrolysis leads to 25 wt% gas, 25 wt% char and 50 wt% liquid, which easily separates into organic phase and water phase.⁹

In contrast to fast pyrolysis, where only fine powders can be used to enable the fast heat transfer, intermediate pyrolysis is able to handle larger biomass pieces due to lower heat transfer rates. Additionally, the moisture content can be more than three times higher;¹⁴ Therefore various kinds of
20 biomasses can be converted.¹⁰

The TCR[®]-technology provides advantages in relation to established fast pyrolysis technologies regarding the quality of the oil. Besides the oil, additional available products like syngas and char are produced. Therefore, biological residues and wastes can be used for the generation of these bio-products without any conflict to the food production. Due to the composition of the TCR[®]-oil, it can easily be upgraded to
25 generate CO₂-neutral fuels, meeting the EN standards for fossil diesel and gasoline. This review provides an overview about the development, the process itself and current opportunities for applications of the TCR[®]-products.

2. TCR[®]-THERMO-CATALYTIC REFORMING

2.1. History of Fraunhofer UMSICHT's TCR[®]

While the history of pyrolysis began with production of coal, the intermediate pyrolysis was developed recently. Intermediate pyrolysis was first established for the conversion of plastics in Karlsruhe,

5 Germany. After the Haloclean reactor, the Pyroformer reactor was developed; Both are milestones in the research area of intermediate pyrolysis.

2.1.1. Haloclean Pyrolysis Process

The Haloclean concept was developed in the late 1990s and was adapted to biomass. It was the first prototype of an intermediate pyrolysis reactor (Figure 1).

10 The reactor is a rotary kiln including a screw to enable the material transport and to control the residence time. Wheat straw and rice husk are preferred source materials for this reactor.¹⁶⁻¹⁸ Pellets or particles in size up to 25 mm are mixed with stainless steel spheres to ensure the heat transport inside of the rotating reactor. The operation temperature is 323 – 773 K with a residence time of 240 – 480 s. The system reached technical scale (20000 t/a) in 2009.^{10, 14-18} Solid yields of up to 35 % and liquid yields up to 45 %
15 are possible. As a milestone in pyrolysis it is worth mentioning that the shape and size of feed can vary without influencing the performance of the reactor.¹⁰ Typical mass balances for straw pyrolysis at various temperatures are given in Figure 2.

When the temperature increases from 598 K – 673 K, the char yield decreases from 73 – 33.5 wt%. In contrast to the char yield, the gas yield and the oil yield increase. The oil yield can be raised from 18 –
20 34.6 wt%. At 658 K there is the maximum oil (41.6 wt%) yield available. The gas yield enhances from 9 wt% – 31.9 wt% at higher temperatures. The char has a higher heating value of 26 MJ/kg, while the highly phenolic pyrolysis liquid has a higher heating value of 26 MJ/kg.¹⁰

2.1.2. Pyroformer

The Pyroformer combined pyrolysis and hydrogen formation in the same plant for the first time. At the
25 European Bioenergy Research Institute (EBRI) at Aston University in Birmingham, the reactor including

two co-axial rotating screw units (Figure 3) was developed and built to convert waste biomass to solid energy carriers.^{14, 19}

Fresh feedstock is mixed with recycled char and transported through the reactor at 723 K by the inner screw. Afterwards, the outer screw returns parts of the char backwards to be recycled. The recycled char has two advantages: It acts as heat carrier as well as promotor for hydrogen formation. Therefore, higher amounts of H₂, CH₄ and CO are produced and in addition less tar are generated.²⁰ At temperatures between 573 – 823 K feedstock residence times are approximately 120 – 600 s while gas residence times are only a few seconds.²¹⁻²³

The product composition is 40 – 60 % liquids, 12 – 25 % permanent gases and char in the amount between 20 – 48 % depending on the heating rate.²⁰⁻²³ Various feedstocks have been tested in the Pyroformer, for example wood, barely straw, brewers spent grain, de-inking sludge, and sewage sludge.²⁰⁻

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2.2. Fundamentals of Thermo-Catalytic Reforming

The so called Thermo-Catalytic Reforming (TCR[®]) reactor was developed and installed at Fraunhofer UMSICHT branch Sulzbach-Rosenberg, Germany. Just like the Haloclean and the Pyroformer, the main building block of the TCR[®]-reactor is a multi-zone auger reactor. The TCR[®] process combines an intermediate pyrolysis and additional catalytic cracking/reforming of generated products. The residence time of biomass is up to ten minutes while gases leave the reactor after 2 – 10 seconds.¹⁴ The process is heated by external heating bands or heating jackets to ensure steadily increasing temperatures during the process (Figure 4). Before each experiment, the plant is flushed with nitrogen for inertization, as desired for pyrolysis processes. Intermediate pyrolysis operates at standard a pressure and at temperatures of up to 723 K.²⁵ Based on the feeding rate of the inlet screw, the residence time is controlled. Therefore, higher feeding rates lead to shorter residence times.

Right after the reactor, solids are transported and stored in the post-reformer while the gases passes through the char bed. The most promising temperature for reforming is between 773 – 1073 K.²⁵ Neumann et al. figured out that the reforming step is essential for high product qualities.²⁶ Therefore,

experiments are carried out without post-reforming and at 773 – 1023 K as post-reforming temperatures while the temperature in the reactor was 723 K (Table 2).²⁶

Due to further reactions during post reforming, better quality liquids are generated. The carbon content increases, while the oxygen content decreases. A significant difference can be found in the total acid number (TAN). Without reforming the TAN was 23.7 mg_{KOH}/g and after post reforming at 1023 K the TAN decreases to 5.1 mg_{KOH}/g.

To separate non-condensable gases from TCR[®]-liquids, the product is quenched at temperatures of about 273 K while liquids condensate, which is removed immediately. Different reactor and reformer temperatures have been tested. However, it has to be mentioned that the reformer temperature has the biggest influence on the product yields, composition and quality of the oils and gases. Neumann et al. accomplished these experiments under varying reformer temperatures of 773 – 1023 K and determined various product yields.²⁷ Relating to Figure 5 the gas yield is increasing at higher reforming temperatures. As opposed to the increasing gas yield, the liquid yield is decreasing. In addition, the solid content decreases slightly at higher temperatures.

To compare the influence of the temperature range of the TCR[®] post-reforming unit with fast pyrolysis, Scott et al. determined the influence of temperature during fast pyrolysis of cellulose and maple wood in a fluidized bed reactor.²⁸

In TCR[®] the liquid yield decreases slightly from 37 wt% at 773 K to 27 wt% at 973 K. The gas yield behaves inverse to the liquid yield: It increases from 27 wt% (at 773 K) to 44 wt% (at 973 K). The char content slightly decreases at higher temperatures.²⁷

Energy balances are calculated on the basis of mass balances. As an example, an energy balance from the TCR[®] process using digestate feedstock at reforming temperatures of 1023 K is shown in Figure 6. Most of the energy (43 %) is stored in char according to relative high heating value (HHV = 23.9 MJ/kg) and the char yield of 29 wt% (Figure 5). The gas phase amounted to 44 wt% and contains 36 % of the initial energy. Due to the very high higher heating value (HHV = 33.9 MJ/kg), the 6 wt% yield of bio-oil contains 12 % of total energy. The lowest energy content with a heating value of only 2.4 MJ/kg can be found in the aqueous phase. Therefore, this phase (21 wt%) contains merely 0.2 % of energy. Altogether, 91.2 % of the feedstock's energy is transferred to the products.²⁷

Summarizing, the TCR[®]-reactor consists of an intermediate pyrolysis reactor, where the feedstock is decomposed at temperatures of around 723 K and coupled subsequently to a reforming stage (at temperatures between 723 and 1023 K), where the quality of the products is improved. The reforming unit is essential for the success of this process because the product quality and the product yield depend significantly on the reforming process and its temperature.^{26, 27}

2.2.1. Magnitudes of TCR[®]-plants

There are different sizes of TCR[®]-plants at Fraunhofer UMSICHT. For initial feasibility experiments of various feedstocks the TCR[®]2 in pilot plant size is used.²⁹ It has a maximum throughput of 2 kg/h and due to the feed container a maximum overall throughput of 7 litres.³⁰ The feed vessel includes a manual agitator to ensure the supply of the source material to the horizontal auger reactor of 100 mm diameter and 1000 mm length. The reforming unit is a vertically fixed bed reactor of 100 mm diameter and 910 mm height. External heating mantles heat both the reactor and reforming unit electrically, and they are able to resist the high temperatures because they are made of stainless steel.³⁰ The next scale is the continuously operated, electrically heated demo scale TCR[®]30. Feedstock in amounts of 30 kg/h can be put into the reactor, while products are removed during the process. Despite the upscaling factor of 15, the product composition and yield of the phases at similar temperatures stay the same.²⁹

The latest achievement at UMSICHT is the commercial TCR[®]300 (300 kg/h throughput) plant. In contrast to the electrical heating of TCR[®]2 and TCR[®]30, the TCR[®]300-plant is thermally heated by a combustion chamber. Additionally, the plant is constructed in three containers to allow decentralised application.^{29, 31} Due to the size, the heating up of the plant takes a longer time, which means only longer term experiments are economically reasonable. Currently, two TCR[®]500-plants have been constructed within the 'To-Syn-Fuel' and the 'FlexJET' project (Ouadi M (<http://www.flexjetproject.eu>)) funded by the EU.³²

2.2.2. Feedstocks

Various feedstocks were already tested in TCR[®]-plants and have been published like digestate, paper sludge, sewage sludge, wood chips, preconditioned agriculture olive residues, evergreen oak and vine shoots, or even de-inking sludge and municipal solid waste.^{24, 26, 27, 35-36} But there are numerous possible

feedstocks like those presented by Apfelbacher et al. at EUBCE 2016. The difference in the composition of wood chips, olive residues, digestate, municipal solid waste, and sewage sludge are listed in Table 3. There are remarkable differences regarding carbon, nitrogen, oxygen, sulphur, and ash contents resulting in various heating values.³⁴⁻³⁶ Waste biomass or residues are favourable options, in order to avoid a dispute between fuel, chemical or food production.^{29,31} An application of all kinds of biomass with higher heating values (HHV) greater than 8 MJ kg⁻¹ is economically possible.³⁴ However, materials with clearly higher moisture content can be used in the prior art technologies. Water contents of 20 wt% can be converted economically while the maximum technical possible water content is 70 wt% while for fast pyrolysis usually a water content of less than 10 wt% is required.²⁶ Additionally, for fast pyrolysis very high heating rates and very high heat transfer rates at the biomass particle reaction interface are applied requiring finely ground biomass.²⁵ For the TCR[®] larger particles up to 50 mm can be used.

2.2.3. *Liquid separation*

The liquid phase of TCR[®]-plant consists of process water and an organic phase. For a separation of water and oil, the liquid phase is kept in an airtight separating funnel for 14 – 24 h.^{30, 34} The two phases separate due to the unpolatity of the oil and the difference in densities. While using digestate as feedstock, TCR[®]-oil (density at 288 K = 1063 kg·m⁻³) accumulates at the bottom.²⁷ Digestate feedstock consists out of high amounts of non-converted lignocellulosic compounds from the biogas process. From experience, these compounds generate oil with higher densities. In terms of sewage sludge, which is free of lignocellulosic compounds, the bio-oil has therefore a lower density (density at 288 K = 960 kg·m⁻³) and forms the top layer (Figure 7).^{37, 38}

3. PRODUCTS

3.1. TCR[®]-bio-oil

Bio-oil is a desirable product of the TCR[®]-process and the name for the organic phase. It is coloured dark brown, similar to fast pyrolysis oils.³⁹

Table 4 shows oil compositions of different TCR[®]-feedstocks compared to fast pyrolysis oil and biodiesel.

High carbon contents of the TCR[®]-oils are remarkable and so are the high heating values as well as the very low TANs of TCR[®]-oils. Low TANs are required to substitute fossil liquid fuels because they induce wear and corrosion in pipes or engine components. Typical HHV of fast pyrolysis oils are between 16 and 29 MJ/kg.^{43, 44} The low TAN indicates that TCR[®]-oil is free of acids. In comparison to fast pyrolysis oil, the TCR[®]-oils have a low oxygen content and are more similar to biodiesel than to fast pyrolysis oil.

Instead of comparing TCR[®]-oil to fast pyrolysis liquids or biodiesel, it is more interesting to compare it to heavy fuel oil (HFO) (Table 5).

Letho et al. compared wood fast pyrolysis oil to fossil based heavy fuel oil (HFO).⁴⁵ To have a chance for another comparison, digestate based TCR[®]-oil is added to the table. Various authors mentioned a correlation of viscosity, density and LHV to the water content. In literature it is stated, that better oil properties are caused by higher water content.⁴³ This contradiction can be found in fast pyrolysis properties, because low heating values and the high flash points are also caused by it. As fast pyrolysis oils do not sustain combustion, flash point analysis is not possible. In comparison to fast pyrolysis oil, TCR[®]-oil has low water content and a flash point can be measured.²⁷ Due to the low water content, there are some more interesting and unique properties of the TCR[®]-oil like the miscibility with ethanol, biodiesel, vegetable oil, gasoline, diesel and crude oil.^{26, 29} Another unique property is the thermal stability of the homogenous TCR[®]-oil.³⁸ Therefore, 80 wt% of TCR[®]-oil was distilled under atmospheric pressures at 623 K without polymerization and coking, forming a low viscos distillate fraction and a high viscos vacuum oil fraction.^{29, 34, 46} In contrast to TCR[®]-oil, fast pyrolysis oil is more difficult to handle. Due to short gas residence times at fast pyrolysis, there is only incomplete lignin decomposition that leads to inhomogeneous products which exist as aerosols containing true vapors, micron sized droplets and polar molecules bonded with water vapor molecules.⁴ Since fast pyrolysis needs fine grinded material to ensure high heat transfer rates, small particles are partly carried by vapors and accumulate in the oil. Due to the large surface of very small particles ash and solids promote increasing viscosity.^{47, 48} To remove char, ash and alkali metals hot gas filtration is used.^{4, 49}

3.1.1. Storage of bio-oil

Storage stability refers to the ability of a liquid to remain in storage over time without deterioration or forming insoluble substances.⁵⁰ Due to the composition of bio-oil or petroleum derived fossil oil, the storage possibility varies for weeks up to six month.^{51, 52}

Fast pyrolysis oils contain many reactive species like alcohols, aldehydes, ketones, sugars, low molecular lignin fragments (lignin derived phenols), high molecular lignin fragments, extractives, and carboxylic acids.^{51, 52} For example, forestry residue oil is composed of volatile acids (8 – 10 wt%), aldehydes and ketones (10-15 wt%), water (25 – 30 wt%), sugar constitutes (30 – 35wt%), lignin-based constitutes (15 – 20 wt%), and extractives (2 – 6 wt%).⁵³

Since the chemical reaction during fast pyrolysis is stopped by the fast quenching of the products, there are still reactive compounds left which react during heating. As the oil is generated, the viscosity steadily increases due to aging. Higher temperatures, the low pH, and char support these further reactions. Fast pyrolysis oil result in heavy molecular weight tars, sludge, waxes, and multiple phases within short times.⁵⁰ Reactions like esterification, polymerization, acetalization, addition reactions, and condensation reactions take place.^{47, 48, 54, 55} Crude petroleum contains less heteroatoms and olefins, which are crucial for the storage stability of that oil.⁵⁰ Therefore, it is possible to store it for over six months.

Figure 8 describes a typical TCR[®]-oil composition. There is only a low content of heterogeneous atoms. This similar composition of TCR[®]-oil and crude oil is a deciding factor of the good storage ability of the TCR[®]-liquid.^{31, 50}

3.2. Bio-char

Char is generated as a second product from TCR[®]-process. Like mentioned before, the char yield depends on the temperature of the post-reformer. In general, higher temperatures lead to decreased amounts of char.^{27, 56-58} According to Antal et al. the decrease of char correlates to the liberalisation of volatile compounds.^{57, 58}

The obtained biochar from the TCR[®]-process has special properties, like very low hydrogen and oxygen content. The atomic ratio of H:C is between 0.17 and 0.21 and the O:C ratio is between 0.01 and 0.02. The O:C ratio is also an indicator of the stability of the char in the soil. The half-life period of a char with

O:C ratios between 0.2 and 0.6 is > 1000 years.⁵⁹ Therefore, its stability is comparable to hard coal or anthracite (Figure 9) and it is an excellent opportunity for CO₂-sequestration.⁶⁰

The char almost only consists of carbon and ash. However, its composition depends on the input material. For instance sewage sludge has an ash content of about 30 – 50 wt% DM.⁶¹ During the TCR[®]-process the ash content in the char can increase up to more than 70 wt%. In contrast, the ash content of wood with bark is about 0.5 – 2.0 wt% DM.⁶² For this feedstock ash contents from 3 to 10 wt% are obtained in the char. This results in different char qualities. Table 6 shows the composition of TCR[®]-chars made of various feedstocks. The heating values are between that of raw lignite and hard coal.⁶³

Among the analysis of the major components of the char heavy metals and organic pollutants were analyzed, too. As it is shown in Table 7, all components are below the thresholds of the German fertilizer ordinance (DüMV), as well as the limit values of the International Biochar Initiative (IBI) test standards. Some results are even under the detection limit. Furthermore, the nutrients content is concentrated in the char. The phosphorous content in the digestate char sample is more than 7.3 wt% (P₂O₅) for instance. In the char from sewage sludge higher quantities are possible. Concerning this matter, the TCR[®]-char is suitable as a soil improver or raw material for fertilizer production.

Tests have shown that the surface structure and area can be influenced during the second step of the TCR[®]-process. Depending on temperature and residence time the number of fine, meso, and coarse pores as well as the surface area can be influenced. Especially the number of the meso and fine pores (< 0.2 – 10 µm) increase similarly with an increase of the reforming temperature. An additional water injection in the reforming process causes an exorbitant increase of the tight coarse and meso pores (0.2 – 50 µm). A higher percentage of fine pores improves the adsorptive properties of the char. Whereas the meso and coarse pores are mainly responsible for their water holding capacity.⁶⁴ Therefore, the properties of the char can be influenced by the variation of the process parameters whereby different applications are possible.

3.2.1. Application

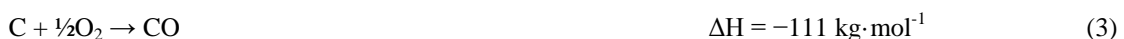
With regard to the properties mentioned above, the biochar can be used as an adsorbent material as well as a soil conditioner or respectively as raw material for fertilizer production. This depends on the

feedstock properties and the used process conditions for the char production. Further applications for biochars are possible. Schmidt described 55 material uses of a biochar.⁶⁵ The best known application, among the one mentioned above, is the use as feed additive and additive for manure treatment in the livestock industry, as soil additive for soil remediation or as a reducing agent in the metallurgical industry. The simplest way is the use as a fuel in incineration or gasification processes.

3.3. TCR[®]-gases

After separation from condensable gases, permanent gas phase is obtained. Like mentioned in the beginning, the gas yields as well as the gas composition depend on the reforming temperature. At higher reforming temperatures the gas yield increases. Due to the reactions occurring during post-reforming the composition of the gas changes. The largest distinction can be found in the decrease of CO₂ and the strong increase of H₂ (Figure 10). In terms of hydrogen production high post reforming temperatures offer the best performance.²⁷

The gas composition is influenced by the post-reforming step. Different reactions like water-gas-shift, cracking, dehydration, or isomerisation take place in the reformer. A collection of these chemical reactions is shown below.



Due to these reactions and the thermal equilibrium, the gas composition at higher temperatures can be explained.

Gas compositions obtained by fast pyrolysis of olive stones show O₂, N₂, CO, CO₂, CH₄, C₂H₄, C₂H₆ and small amounts of H₂ (at higher temperatures).⁶⁶ Like in the TCR[®]-process the gas composition depends strongly on the temperature. Between 573 and 673 K a maximum of CO and CO₂ can be produced, while

CH₄ reaches a maximum at high temperatures of about 873 K. Small amounts of hydrogen (< 10 vol%) are generated at temperatures above 753 K.⁶⁶ Also Domínguez et al. observed higher hydrogen concentrations (~30 vol%) at higher temperatures (1273 K) during the fast pyrolysis of coffee hulls.⁶⁷ The maximum higher heating value reached 12.7 MJ/kg.⁶⁷ However, the influence of temperature can be shown in every research, while the maximum hydrogen contents of 33 vol% can be reached by using fast pyrolysis.⁶⁶⁻⁶⁹

3.3.1. Applications

Due to their composition and the relatively high heating value, TCR[®]-gases can be directly converted at dual fuel engines in a CHP. Due to the high hydrogen content (up to 50 vol%) another option is using included hydrogen for upgrading the TCR[®]-oil.

4. BIO-OIL UPGRADING AND APPLICATIONS

Since the composition of TCR[®]-oil is outstanding, there are other upgrading technologies used than in upgrade of fast pyrolysis liquids applicable. The TCR[®]-oil properties are the following:

- Thermal stability
- Proper phase separation
- Low water content
- Flammability
- Low oxygen, nitrogen & sulphur content
- Low acidity
- High carbon content
- Relatively high higher heating value

In summary, the quality of TCR[®]-oil is very high and comparable to fossil crude oils. Due to the mentioned properties, TCR[®]-oil is feasible to be directly applied as fuel in boilers, combustors, and stationary combined heat and power plants (CHP) engines. However, for superior application further processing is needed. Besides blending with biodiesel for long-term CHP application, another possibility

is the upgrading of bio-oil for direct utilization as transportation fuel or fossil fuel blends. In addition, chemicals like BTX-aromatics can be generated from TCR[®]-oil.^{26, 38, 70}

For fast pyrolysis oils problems like poor volatility, high viscosity and coking, cause problems in application and storage. Regarding the composition standard equipment like boilers, engines, and gas turbines constructed for petroleum fuels have to be modified because of its poor volatility, high viscosity, coking, corrosiveness, and missing flammability. However, to use fast pyrolysis oil in standard applications upgrading is absolutely necessary.⁴³

4.1 Distillation

One of the longest known and important upgrading or separation technologies is distillation. Distillation is one possible way to upgrade TCR[®]-oil. It is only possible, due to the thermal stability of the TCR[®]-oils. Therefore, Conti et al. performed a sequential distillation of paper sludge TCR[®]-oil and separated the liquid into 7 different fractions according to their boiling points (Table 8).³⁴ The distilled fractions are shown in Figure 11 in the comparison to crude TCR[®]-oil. Each distillation fraction has a different composition. The first fraction consists of highly volatile compounds like acetaldehyde, glyoxal, acetone or alcohols [31, 67]. The second fraction (338 – 423 K) is the most abundant yellow colored; It consists of benzene, toluene, xylenes and phenolic compounds.^{34, 71} In the second and third fraction oxygen amounts are about 5 % which is comparable to Christensen et al, who distilled hydrotreated fast pyrolysis oil.⁷² The high boiling point fraction contains naphthalenes and other high-molecular-weight condensed hydrocarbons. The highest amount of oxygen (7.1 %) can be found in the wax-like residue > 623 K.^{34, 71}

4.2 Blending

Blending is an easy and cheap way to use bio-oil directly in diesel engines. Blending includes blending of bio-oils with alcohols, biodiesel or ignition supporter. It is possible due to the similar polarity mixing of the two components. If there are different polarities like polar and non-polar, additional emulators are needed for a homogeneous blend. Fast pyrolysis oils are immiscible with light fuel oil mainly consisting of saturated olefinic and aromatic hydrocarbons (C9-C25). Pure pyrolysis oil does not guarantee a stable

operation and leads to rapid blocking of injection nozzles, which lower the efficiency of the engine. To avoid these problems a modification of the injection system is required. But there have been some positive results from blended oils that ensured stable conditions.^{73,74} The company BTG produced blends from fast pyrolysis oil, ethanol, butanol, and biodiesel in various mixing ratios. These blends have been tested on a 20 kW engine over a time period of 40 h. A stable run was ensured owing to a modification of compression ratio and injection system during the tests.⁷⁵ Another opportunity for completely bio-based fuels is to blend pyrolysis-oil with biodiesel. At Aston University in Birmingham, first experiments with intermediate pyrolysis oil took place. The engines have not been modified for the test runs.^{76,77} TCR[®]-oil blends with biodiesel were tested with ratio of 10, 50 and 75 % TCR[®]-liquid. The ignition experiments demonstrated that TCR[®]-oil blends of up to 50 % showed similar ignition behaviour like pure biodiesel. In terms of a 75 % TCR[®]-oil blend, the ignition was delayed.⁷⁸

4.3 Catalytic Hydrotreating

To generate transportation fuel a removal of sulphur (desulphurization), nitrogen (denitrogenation), and oxygen (deoxygenation) is needed. An established method is hydrotreating, as it is used in fossil oil refineries.⁷⁹ Schmitt et al. calculated the overall hydrogen requirement for the complete upgrading of the TCR[®]-oil and the hydrogen content of the TCR[®]-gas for low and high reforming temperatures and revealed that the hydrogen produced at reforming temperatures of 1023 K offsets the need for the produced oil.⁸⁰ In contrast to most fast pyrolysis oils, which are mainly generated from wood and therefore mainly contain oxygen as hetero atoms. TCR[®]-oil contains additional sulphur and nitrogen because of diverse composition of the raw materials like sewage sludge or digestate. Since nitrogen and sulphur are known for poisoning of isomerization-catalysts the focus of the selection of the upgrading catalyst has to be intensified. Depending on the composition of bio-oil many catalysts and reaction conditions for further processing exist.^{81,82} There are many transition metal catalysts already proved in practice. Mainly used are NiMoS or CoMoS based on Al₂O₃ and also NiWS and CoWS on Al₂O₃. The sulfidic modification of the mentioned catalysts is proved to be the more active variant of catalyst.⁸³ Regarding the activation of the catalyst by sulphurization, contained sulphur is not a significant disadvantage for the catalysts mentioned above. Mo and W act as active sites during the reaction while Ni

and Co promote it. Al_2O_3 offers the support material.⁸⁴ Besides transition metal catalysts also noble metal catalysts like Pt/C, Pd/C, or Ru/C are used.⁸⁵⁻⁹⁰ Noble metals have a very high activity. Ru/C showed a better yield than NiMo/ Al_2O_3 , CoMo/ Al_2O_3 , and other noble metal catalysts.⁸⁵⁻⁸⁸ Unfortunately, noble metals are very expensive which limits their application potential.

5 Due to the high oxygen content of fast pyrolysis oils, the most targeted reaction is hydrodeoxygenation (HDO). During HDO also the water content of the bio-oil is reduced as the oil gets lower in polarity.^{85, 91, 92} A complete deoxygenation of fast pyrolysis oil results in a very small amount of oil and high amount of water.⁹² Consequently, there is a trade-off between the product quality and product yield.⁹³

10 However, hydrotreating induces also hydrocracking, hydrodesulphurization (HDS) and, in case nitrogen appears in bio-oil, hydrodenitrogenation (HDN).⁸⁶

To avoid fast intoxication of the catalyst a two-step process including mild (stabilization step) and deep HDO is typically practiced with fast pyrolysis oil. Therefore, the first HDO takes place at lower temperatures and pressures. During mild HDO water is removed and C=C-double bonds are hydrated so that less coke is produced.^{87, 94-97} The catalyst-lifetime during hydrotreating is less than 100 h.⁹³

15 There are far less experiments about hydrotreating of TCR[®]-bio-oil. Neumann et al. used bio-oil from digestate to generate high quality products. In a trickle bed reactor at temperatures up to 643 K and constant hydrogen pressure of 14 MPa, the catalyst load (liquid hourly space velocity) was 0.6 h^{-1} . A sulphided NiMo/ Al_2O_3 catalyst was used. After hydrotreating, the color of the generated product was clear and low viscos. The ultimate analysis of hydrotreated TCR[®]-oil is shown in Table 9.^{29, 33, 78} It has
20 outstanding quality and is similar to standard fossil transportation fuels.

Further experiments tested various catalysts like H-ZSM-5, NiMo/ Al_2O_3 , CoMo/ Al_2O_3 , and Ru/C in a batch reactor at hydrogen pressures up to 17 MPa and 653 K.³⁸ While H-ZSM-5 does not have any influence, the other catalysts were able to remove nearly all heterogeneous atoms. Due to that removal, the carbon content in the product increases to around 85 wt% and the color also changes to bright yellow
25 (NiMo/ Al_2O_3) and clear (CoMo/ Al_2O_3 , Ru/C) depending on the catalyst.^{38, 98} A GC/MS spectrum of TCR[®]-oil consists of BTX-aromatics, alkanes, and cycloalkanes.^{29, 98, 99} Hydrotreated TCR[®]-oil can be fractionated into gasoline meeting EN 228 standard and diesel meeting EN 590 standard [28, 91].^{29, 99} Ensuing first engine tests of gasoline fraction at an engine test bench with a 1.6 dm^3 4 cylinder

turbocharged EU5 gasoline engine subsequently demonstrated lower emissions compared to E5 gasoline.³³

5. CONCLUSION

5 Thermo-Catalytic Reforming offers a novel method to produce high quality products from various kinds of biomass. Hydrogen rich gas ($H_2 < 50$ vol%), low oxygen and low water containing oil, and volatile free char is generated. Their quantity and quality depend on the post-reforming temperature. The hydrogen rich gas can be used in dual fuel engine, as synthesis gas, or for the hydrogenation of the TCR[®]-oil. TCR[®]-char is an adorable feed for combustion, acts as carbon storage or is possible to be upgraded to
10 active carbon, because of its high surface. Bio-oil has promising properties like low water content, flammability, low oxygen content, and high carbon content. Due to its thermal stability, it is distillable and is applicable for thermal processes like e.g. hydration. Its full miscibility with crude oil supports its implementation to petroleum refineries. As a blend with biodiesel or fossil diesel it can be directly applied to a diesel engine. Successful upgrading has already been proven in a continuous trickle bed reactor using
15 activated NiMo/Al₂O₃ as catalyst. After distillation of the upgraded TCR[®]-oil into a gasoline and diesel fraction, the properties are observed to also meet the fossil fuel standards EN 228 and EN 590. Engine tests in an engine test bench with a 1.6 dm³ 4 cylinder turbocharged E5 gasoline engine were performed successfully.

6. PERSPECTIVES

20 Within the current started EU project 'To-Syn-Fuel' a large scale biorefinery including a TCR[®]500 and direct large scale hydrotreatment implementing the utilization of TCR[®]-hydrogen is constructed.³² Additionally, further adaptations of TCR[®]-char such as catalytic applications or the utilisation as activated carbon are investigated.

25 7. ACKNOWLEDGEMENTS

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Table 1: Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood ^{9,10}

Mode	Conditions ¹⁰	Liquid ⁹	Solid ⁹	Gas ⁹
Fast	673 – 823 K, heating rates up to 500 K/s, short residence time 0.5 – 2 s	75 %	12 % char	13 %
Intermediate	673 – 823 K, heating rates 10 – 100 K/s, solid residence time 240 – 600 s	50 % in 2 phases	25 % char	25 %
Carbonisation (Slow)	~673 K, heating rates up to 50 K/s, solid residence times hours to weeks	30 %	35 % char	35 %
Gasification	~1023 – 1173 K	5 %	10 % char	85 %

Table 2: Influence of reforming temperatures on the TCR[®]-oil composition²⁶

Ultimate Analysis	Unit	No Reforming	773 K	1023 K
C	wt%	75.1	78.0	79.6
H	wt%	7.6	8.3	7.0
N	wt%	4.9	5.2	5.2
S	wt%	1.2	1.2	1.1
O*	wt%	10.6	7.0	7.0
Proximate analysis				
H ₂ O	wt%	< 2	< 2	< 2
Ash	wt%	0.6	0.2	0.1
Measured HHV	MJ/kg	34.4	36.7	35.2
Total Acid Number	mg _{KOH} /g	23.7	8.8	5.1

*calculated by difference

Table 3: Composition of different kinds of feedstock

Ultimate Analysis*	Unit	Wood Chips³⁴	Digestate³⁴	Olive Residues³⁵	Municipal Solid Waste³⁶	Sewage Sludge³⁴
C	wt%	45.0	34.8	44.9	43.1	23.3
H	wt%	6.4	4.3	6.5	6.1	4.3
N	wt%	0.3	1.9	0.4	1.0	3.6
S	wt%	0.1	0.4	0.1	0.3	0.9
O**	wt%	47.7	43.8	46.0	31.4	19.7
Proximate analysis***						
H₂O	wt%	8.0	11.0	8.7	10.0	9.7
Ash	wt%	0.6	14.8	2.2	18.1	46.5
HHV	MJ/kg	17.8	16.9	19.3	18.3	10.0

*Moisture Ash Free Basis; **Calculated by Difference; ***Dry Basis

Table 4: TCR[®]-oil compositions produced from various feedstocks at 973 K reforming temperature compared to fast pyrolysis oil and biodiesel

Ultimate Analysis*	Unit	TCR [®]	TCR [®]	TCR [®]	Fast	
		Sewage Sludge ³⁴	Digestate ³⁴	Wood Chips ³⁴	Pyrolysis (Wood) ⁴⁰	Biodiesel ⁴¹
C	wt%	77.4	75.8	73.2	54.2	77.2
H	wt%	7.7	7.4	8.0	6.9	13.2
N	wt%	9.6	6.0	1.5	0	0.1
S	wt%	0.8	1.9	0.3	0	< 0.1
O**	wt%	4.5	8.9	17.0	38.9	9.4
Proximate Analysis***						
H₂O	wt%	1.7	3.9	9.5	12.8	< 0.1
Ash	wt%	< 0.05	< 0.05	< 0.05	0.4	< 0.1
HHV	MJ/kg	35.6	35.6	35.3	20.1	39.3
Total Acid Number (TAN)	mg _{KOH} /g	4.6	4.9	5.4	111-200 ⁴²	2

*Moisture Ash Free Basis; ** Calculated by Difference; ***Dry Basis

Table 5: Physical properties of wood fast pyrolysis oils, mineral oils, and TCR[®]-oil^{27, 45}

Analysis	Fast Pyrolysis (wood)⁴⁵	HFO 180/420⁴⁵	Digestate TCR[®]-oil²⁷
Water [wt%]	20-30	~0	1.7
Nitrogen [wt%]	<0.4	0.4	2.2
Sulfur [wt%]	<0.05	1.0	0.6
Stability	Unstable*	Stable	Stable ³⁴
Viscosity (317 K) [cSt]	15-35**	180/420 max.	40.0
Density (288 K) [kg/dm³]	1.10-1.30**	0.99/0.995 max.	1.063
Flash Point [°C]	40-110***	65 min.	> 45
LHV [MJ/kg]	13-18**	40.6 min.	32.5
Distillability	Non-distillable	Distillable	Distillable ³⁴

*Polymerizes when heated and for prolonged periods of time.

**Depends on water content

***Flash point method unsuitable for fast pyrolysis oils. They do not sustain combustion.

Table 6: Chemical composition of TCR[®]-chars from sewage sludge, digestate, brewer spent grain, and wood (analysed by external laboratory) (Stenzel F, unpublished)

Ultimate Analysis	Unit	Sewage Sludge	Digestate	Brewer Spent Grain	Wood
C	wt%	22.2	64.0	72.6	89.8
H	wt%	0.9	1.0	0.1	2.2
N	wt%	2.0	1.4	4.6	0.3
S	wt%	1.0	0.5	0.4	0.1
O*	wt-%	0.0	0.7	4.9	4.5
Ash	wt-%	74.4	32.0	17.5	3.1
LHV	MJ/kg	8.2	23.0	26.0	34.4

Table 7: Analysis of a TCR[®]-char from digestate compared to the thresholds of the German Fertilizer Ordinance and the IBI test standards (Stenzel F, unpublished)

	Unit	DüMV	IBI Test Cat. B	TCR[®]-char
Arsenic	mg/kg dm	40	12 – 100	< 0.8
Cadmium	mg/kg dm	1.5	1.4 – 39	< 0.2
Chromium	mg/kg dm	300	64 – 1200	5
Chromium(VI)	mg/kg dm	2	n.a.	n.a.
Copper	mg/kg dm	900	63 – 1500	68
Lead	mg/kg dm	150	70 – 500	< 2
Mercury	mg/kg dm	1	1 – 17	< 0.07
Nickel	mg/kg dm	80	47 – 600	3
Zinc	mg/kg dm	5000	200 – 7000	300
Thallium	mg/kg dm	1	n.a.	< 0.2
Dioxin / PCB	ng WHO-TEQ	30	9 / 200 – 500	< 1

< – below the detection limit

dm – dry matter

n.a. – not applied

DüMV – German Fertilizer Ordinance

IBI – International Biochar Initiative

5

Table 8: Distilled fractions from paper sludge TCR[®]-oil. The values in brackets indicate products distribution with respect to elemental composition of bio-oil.³⁴

Fraction (K)	Yield [%]	N [%]	C [%]	H [%]	S [%]	O [%] [*]
1 < 338	2.1	1.7 (2 %)	86.4 (2 %)	10.1 (2 %)	0.9 (2 %)	0.9 (1 %)
2 338-423	18.0	1.6 (14 %)	84.9 (18 %)	9.2 (18 %)	0.6 (12 %)	3.7 (18 %)
3 423-473	12.5	2.4 (14 %)	83.1 (12 %)	8.7 (12 %)	0.5 (7 %)	5.3 (18 %)
4 473-523	13.3	2.8 (18 %)	84.1 (14 %)	8.5 (13 %)	0.7 (11 %)	3.9 (14 %)
5 523-573	3.4	2.8 (5 %)	87.1 (4 %)	8.3 (3 %)	0.7 (23 %)	1.1 (1 %)
6 573-623	11.2	2.3 (12 %)	87.8 (12 %)	8.2 (10 %)	0.6 (7 %)	1.1 (3 %)
7 > 623	18.7	2.2 (20 %)	79.8 (18 %)	9.3 (19 %)	1.5 (31 %)	7.1 (36 %)

^{*}Calculated by Difference

Table 9: Ultimate analysis and properties of hydrotreated TCR[®]-bio-oil from digestate³³

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	DIN EN ISO 20884
O*	wt%	< 0.8	
Physical Properties			
H₂O	mg/kg	30	DIN EN ISO 12937
LHV	MJ/kg	42.3	DIN 51900-2
TAN	mg _{KOH} /g	< 0.1	DIN EN 14104
Flash point	K	< 253	DIN EN ISO 3679
Density	kg/m ³	815.7	DIN EN ISO 12185
Viscosity (313 K)	mm/s ²	0.97	DIN EN ISO 3104
Copper corrosion	rating	Class 1	DIN EN ISO 2160

*Calculated by Difference