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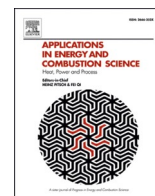
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Thermo-Catalytic Reforming (TCR)–An important link between waste management and renewable fuels as part of the energy transition

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ABSTRACT

The significant progress in energy demands and limited fossil fuel sources, together with environmental concerns, have enforced the study of green, renewable, and sustainable energy sources. Biomass and its residues can be converted into valued fuels and chemicals through advanced thermal conversion technologies. Pyrolysis has been used for a long time for charcoal formation, while intermediate and fast pyrolysis technologies have become of considerable interest in recent years. This substantial interest is because these processes provide different bio-products (synthesis gas, bio-oil and biochar), which can be used directly in numerous applications or as a sustainable energy carrier. This paper investigates an overview of the fundamentals of Thermo-Catalytic Reforming (TCR) technology which is a novel intermediate pyrolysis process combined with a post catalytic reforming unit. This study also identifies the TCR process's features and advantages compared to other pyrolysis technologies, followed by a technical scale unit and the transfer of intermediates in final products. Finally, the treatment of effluents, heat management and implementation of such technologies are discussed. This paper shows how a continuous pyrolysis/reforming plant has been developed and established based on targeted reactor design and in conjunction with preventing major effluent streams, which could have a major impact on the technology's commercial success. Along with two major European projects (To-Syn-Fuel and GreenFlexJET), the TCR technology shall help to overcome the dependency on fossil crude oil and fuels.

1. Introduction

One of the core sectors of renewable resources is bioresources. The fossil fuel-based energy transition to sustainable alternatives to meet the increasing demand for fuels, energy, and chemicals is a significant challenge facing industrial progress. The world's energy consumption since the 1990s and predicted needs for future decades are shown in Fig. 1. This figure shows that the world's energy consumption has amplified from the 1990s towards the 2020s, and that will increase further in the future considerably. Much of the world's energy consumption happens between non-OECD nations (outside the Organization for Economic Cooperation and Development) because of the solid economic growth and expanding population [1,2]. Nowadays, the

sustainable biomass feedstock growth for the production of biofuels and biochemicals is significantly considered worldwide, with extensive work being conducted to convert academic and scientific improvements into profitable reality [2–4]. Researchers have been looking for new ways to avoid emissions during the production of chemicals, fuels, heat, and power. To reduce CO₂ emissions, an important step is the replacement of fossil oil [5,6].

The main approaches to transform lignocellulosic waste biomass into valuable chemicals and energy carriers are pyrolysis and gasification [7]. However, biological approaches (such as anaerobic digestion) cannot effectively break down lignocellulosic waste biomass due to the complexity of lignocellulosic biomass structure and so are limited to mainly cellulosic biomass such as food and agricultural waste [8, 9].

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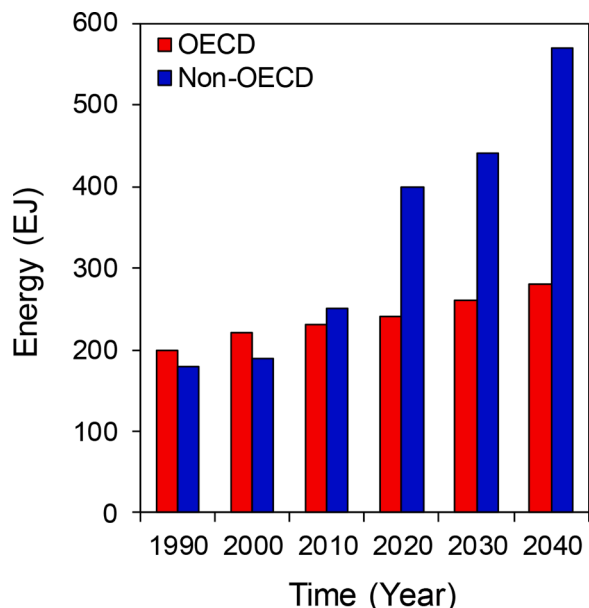


Fig. 1. The world energy consumption between 1990 and 2040. Reproduced with permission from ref. [2], Copyright © 2021, Springer Nature.

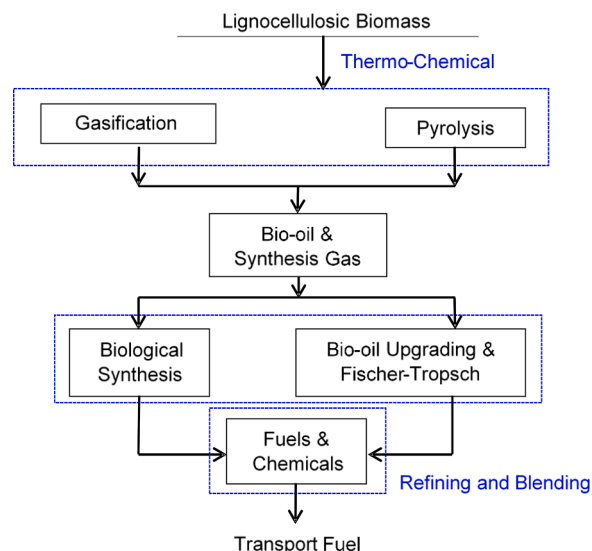
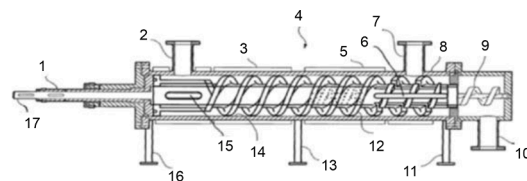


Fig. 2. Thermo-chemical processes for conversion of biomass to chemicals and fuels. Reproduced with permission from ref. [2], Copyright © 2021, Springer Nature.

Fig. 2 represents the main conversion procedures currently applied for the production of chemicals and transport fuels, and this article mainly focuses on pyrolysis technologies.

Biomass pyrolysis is biomass decomposition via heating in no presence of oxygen. Pyrolysis is an endothermic process. The pyrolysis temperature range is from 300 °C to 800 °C [10,11]. Pyrolysis is divided into various classes, which are slow, intermediate and fast pyrolysis [12]. Residence time is a crucial factor in the biomass pyrolysis process. The solid residence time is hours and minutes for slow and intermediate pyrolysis, respectively. However, the solid residence time for fast pyrolysis is very short, less than 5 seconds [13]. Slow pyrolysis favours charcoal production, while intermediate and fast pyrolysis (shorter solid residence times) favour gas and liquid production [13,14].

This article's originality is the novel Thermo-Catalytic Reforming (TCR) technology that can process any kind of problematic waste



1. External screw shaft; 2. feed inlet pipe; 3, 4, 5 and 8. electrical heating bands; 6. external screw slot; 7. gas outlet pipe; 9. internal screw; 10. solid drop out pipe; 11, 13 and 16. supports; 12 and 14. external screw; 15. external screw slot; 17. internal screw shaft.

Fig. 3. Pyroformer reactor. Reproduced with permission from ref. [21], Copyright © 2013, Elsevier.

biomass, and this technology is developed by Fraunhofer UMSICHT, Germany. TCR is intermediate pyrolysis combined with post catalytic reforming to convert waste biomass to valuable bio-oil, syngas, and biochar. Instead of forest wood or energy crops from agricultural land, sewage sludge, biogas digestate, deinking sludge, or livestock manure can be utilized to produce valuable biofuels through TCR [15,16]. This technology is new and can be complementary to gasification and anaerobic digestion (AD) processes. In terms of gasification, the TCR technology can provide solid biochar from problematic feeds (woody and non-woody feeds) to produce tar-free syngas [17,18]. In terms of anaerobic digestion, the economic frame can be optimized as the solid residue fraction from anaerobic digestion can be processed through TCR (as a feed) to produce valuable biofuels [19]. In this article, the development and scale-up of the TCR technology are investigated in detail as part of the To-Syn-Fuel and GreenFlexJET projects. Furthermore, a comparison between TCR and other technologies is discussed.

2. Development of the pyroformer and Thermo-Catalytic Reforming (TCR)

2.1. Pyroformer

Pyroformer (Fig. 3) is an intermediate pyrolysis unit that is patented by A. Hornung and A. Apfelbacher. This unit was one of the first intermediate pyrolyzer units after the Haloclean rotary kiln reactor (cycled-spheres reactor) [20]. Pyroformer is fundamentally an auger screw system inclosing a carbon steel compartment (horizontal position) containing two co-axial rotating screws [20]. This unit operates at a pressure of up to 10 bar. Its heating system is external via heating bands. The design is suitable for treating high ash content biomass and maximizing the contact time between pyrolysis biochar and organic vapours [21].

In the Pyroformer system, the internal screw moves a mix of fresh biomass and recycled char fraction, heated at typical pyrolysis temperatures [22]. The temperature range of intermediate pyrolysis is between 350 and 450 °C, with a product distribution of typically 25 (wt%) gas, 25 (wt%) char and 50 (wt%) liquid [10]. The external screw transports the pyrolysis char back to the inlet zone, improving the heat transfer of the biomass [23]. The biochar layer controls the heating rate in the reactor and protects the feedstock from very high temperatures, avoiding fast pyrolysis reactions [24]. The feedstock is converted into biochar, volatile gases and vapours. The remaining pyrolysis char (which is not recycled in the system) leaves in the solid drop out pipe of the Pyroformer, and the pyrolysis gas-phase goes through the gas outlet pipe [21].

The innovation of this unit is the effect of biochar recycling that makes an additional catalytic impact through the system. Biochar is a carbon-rich material and has a high porosity structure. Biochar is a promising alternative to replace conventional solid carbon-based catalysts, which are environmentally unfriendly and expensive. The metals present in the ash, which are bound to the char, such as Ca, Fe, Al etc, are catalysts in their right [25,26]. Furthermore, the biochar physico-chemical properties can be adjusted via base/acid treatment or

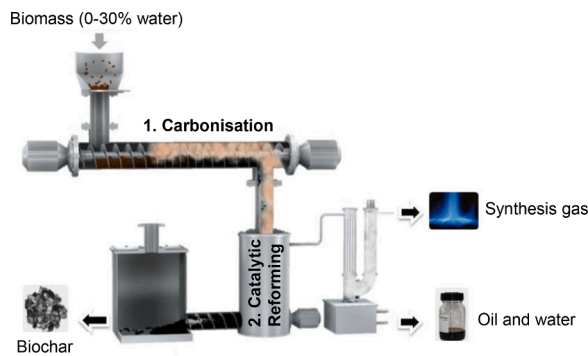


Fig. 4. Illustration of the Thermo-Catalytic Reforming reactor. Reproduced with permission from ref. [31], Copyright © 2019, American Chemical Society.

carbonization [27,28]. As a result, biochar is a suitable candidate for catalytic applications.

This catalytic impact enhanced the bio-oil quality compared with the bio-oil of fast pyrolysis because of oil formation with less water content, lower molecular weight, less heavy tar formation, and also using biochar improved syngas yields and thus producing a significantly higher heating value biofuels [29]. A real advantage of this new concept, compared to other catalytic approaches in pyrolysis or reforming, is that the char is used as catalysts. The biochar is formed based on incoming feed during the process, and no contamination, fouling and deactivation are happening. Furthermore, the reactor can be driven constant over time to prevent these major problems of other catalytic processes.

2.2. Thermo-Catalytic Reforming (TCR)

TCR novelty is about joining the intermediate pyrolysis (that was developed from the Pyroformer unit) with post catalytic reforming (treatment) as shown in Fig. 4. TCR was designed and developed by A. Hornung and Fraunhofer UMSICHT to make biofuels and valuable chemicals from waste materials [19]. TCR process flow diagram (PFD) is shown in Fig. 5. TCR system has two crucial steps that are: 1) intermediate pyrolysis at mild temperatures that feedstock thermal heating occurs in the absence of oxygen, and 2) reforming (treatment) step at elevated temperatures that vapour catalytic cracking happens to enhance the formation of syngas and organic vapours with superior

physicochemical properties [22, 30].

The intermediate pyrolysis step occurs at 400-500 °C in an auger reactor with solid residence times between 5 and 10 minutes in the TCR technology [32,33]. Biochar is being shaped during the intermediate biomass pyrolysis in the auger reactor, and then it is collected in the reforming reactor (fixed bed reactor). Finally, the reforming treatment is performed between biochar and produced vapours, thus creating a catalytic effect in all products and improving their physicochemical properties [34,35].

The temperature of the post reformer is between 500 and 700 °C [18]. The higher post reformer temperature forms a higher yield of syngas. The upgraded vapours are then condensed and make three different products, which are a bio-oil fraction (6-11 wt%), an aqueous phase (21-26 wt%), and syngas fraction (27-44 wt%). The remarkable compounds of syngas are hydrogen (55 vol% maximum) and then carbon dioxide (35 vol% maximum), carbon monoxide (25 vol% maximum), methane and some other hydrocarbons [34].

TCR products can be utilized in various applications from diverse areas. For instance, bio-oil can be mixed with gasoline and diesel to be used in engines, the gas fraction can create heat and power through CHP (combined heat and power), and char can be applied in gasification and combustion processes and as a soil conditioner or fertilizer [36]. TCR is a

Table 1
Bio-oil characteristics from pyrolysis of woody biomass.

| Properties | Fast pyrolysis [13,39,43] | TCR [44,45] |
|-----------------------------------|---------------------------|-------------|
| <u>Mass balance</u> | | |
| Bio-oil (wt%) | 60 | 7.0 |
| Water content (wt%) | 15 | 14 |
| Char (wt%) | 12 | 21 |
| Gas (wt%) | 13 | 58 |
| <u>Bio-oil</u> | | |
| Moisture content (wt%) | 15-30 | 6-8.4 |
| Viscosity (mm ² /s) | 40-100 | 12.1-36.5 |
| Acid number (mg KOH/g) | 88-126 | 9.3-30.1 |
| HHV (MJ/kg) | 16-19 | 32.8-35.5 |
| <u>Bio-oil elemental analysis</u> | | |
| C (wt%) | 54-58 | 72.2-78.6 |
| H (wt%) | 5.5-7.0 | 7.0-7.4 |
| N (wt%) | 0-0.2 | 2.2-2.6 |
| O (wt%) | 35-40 | 11.4-17.9 |
| Ash (wt%) | 0-0.2 | 0-0.05 |

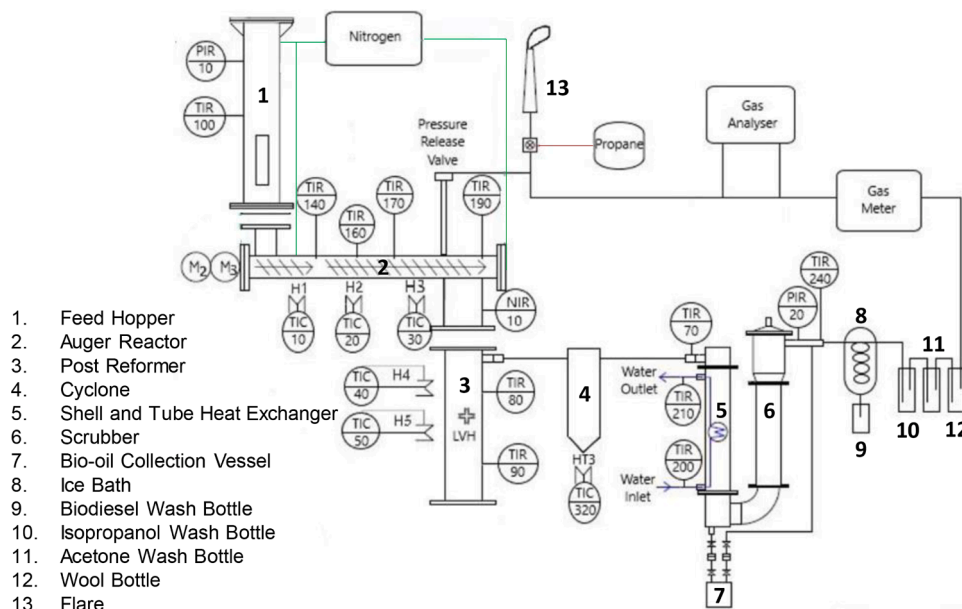


Fig. 5. TCR process flow diagram (PFD). Reproduced with permission from ref. [15], Copyright © 2020, Elsevier.

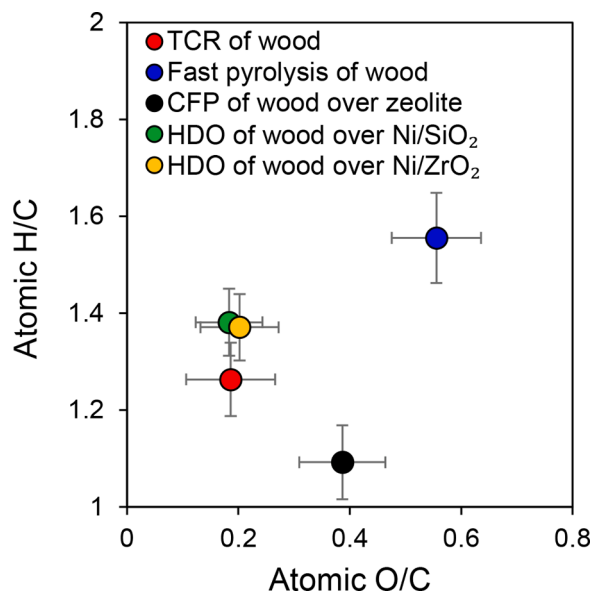


Fig. 6. Diagram of Van Krevelen for bio-oil from the TCR of wood [44,45], fast pyrolysis of wood [13,39], catalytic fast pyrolysis (CFP) of biomass over zeolite [43] and hydrotreated bio-oil from wood fast pyrolysis over Ni-based catalysts [50].

safe technology functioning without using externally sourced solvents, chemical products, or catalysts, and it operates at atmospheric pressure [37]. Also, its flexibility in terms of plant control delivers a great diversity of value-added products such as an enhanced quality bio-oil which is easy to store and transport, energy-dense and stable biochar with similar structures to anthracitic coal and syngas rich in hydrogen [19,38]. Another benefit of this technology is the efficient design that can transform most of the introduced energy from the original feedstock [37].

2.2.1. Comparison between other technologies and TCR

Table 1 displays the characteristics of the bio-oil formed from a woody biomass fast pyrolysis and TCR. The fast pyrolysis bio-oil has many drawbacks, which are as follows [39–41]:

- A high oxygen content with a complex mixture of compounds,
- It has a low higher heating value,
- It is strongly corrosive,
- A high acid number,
- It has poor chemical stability, and its phase can be changed with time.

TCR technology can form TCR-oil with superior physicochemical fuel properties compared with the fast pyrolysis bio-oil. TCR crude oil is low in oxygen content (11.4–17.9 wt%), low in acidity (9.3–30.1 mg KOH/g), and higher heating value (32.8–35.5 MJ/kg) that is in contrast with the fast pyrolysis bio-oil properties (Table 1). It is worth mentioning that TCR does not produce extra N content (wt%). However, it depends on the initial N content (wt%) coming from the specific lignocellulosic biomass which was processed. N content (wt%) of lignocellulosic of different biomass is reported to be varied between 0.0 (wt%) and 5.20 (wt%) [42]. Moreover, the TCR bio-oil phase splits simply from the water phase and has a very high calorific value that is completely miscible with conventional fossil fuels and crude oil [23,39]. The application of TCR-oil blended with biodiesel has been already successfully proven and studied in a diesel engine [34]. However, further upgrading will be required to comply with European fuel standards, EN 228 and EN 590 for gasoline and diesel [17].

There is no need for wide pretreatment stages or costly precious

metals or zeolites catalysts to be applied in the reactor [15,46,47]. TCR technology is well suited to all ranges of waste organic feedstocks that are high in ash and moisture contents such as sewage sludge, paper sludge, anaerobic digestate, municipal solid waste, and others [18,48]. Furthermore, TCR forms a considerable amount of green hydrogen that can be purified and separated for hydrotreatment of the TCR bio-oil and crude oil in a petroleum refinery [38].

TCR biochar is an outstanding fuel source for gasification as it forms tar-free syngas, which can be applied as an additional source of H₂. The important benefit of utilizing this approach is that it decreases demand for externally sourced hydrogen for refining, which further increases the sustainable and economic credentials. Moreover, the H₂ yields can be maximized by injection of steam (TCR aqueous phase) into the TCR unit, which improves a water gas shift reaction [22,38]. This is in contrast to fast pyrolysis, which requires an external source of H₂ to enhance the bio-oil properties [49]. In applying ash-rich feeds and a gasification temperature of about 800 °C, the remaining ash can simply be applied for phosphorous recovery [26].

The Van Krevelen diagram displays the H/C and O/C ratios for different technologies (Fig. 6). The H/C and O/C of TCR bio-oil from woody biomass were 1.27 and 0.19, respectively [44,45]. However, the fast pyrolysis bio-oil from woody biomass has significantly higher H/C (1.56) and O/C (0.56) values than TCR bio-oil properties [13,39]. Also, catalytic fast pyrolysis (CFP) of lignocellulosic biomass over zeolite catalyst has ratios of H/C (1.09) and O/C (0.39) [43], which are not as favourable as the TCR ratios. Finally, the H/C and O/C of hydrotreated bio-oils from fast pyrolysis of woody biomass over Ni-based catalysts are moderately different from the TCR values [50]. As a result, TCR proved significant enhancement in bio-oil stability and properties characteristics without using any external catalysts.

2.3. Hydrogenation

The hydrogenation of TCR-oil makes it possible to produce hydrogenated oil, which can be distilled to produce raw gasoline and EN-conform diesel. The Hydrogenation of the TCR-oil removes heteroatoms like sulphur, nitrogen and oxygen and saturates C-C double bonds. The hydrogenation of sulphur components leads to H₂S, nitrogen components to NH₃ and oxygen components to water. Active catalysts for the hydrogenation are Co-Mo, and Ni-Mo supported on Al₂O₃ and zeolites.

The catalyst has to be activated with H₂S to convert the oxide state to the active sulphidic state. To reach a unique bio-fuel quality meeting European standards like EN 228 and EN 590 for common gasoline and diesel, the removal of heteroatoms like sulfur, nitrogen, and oxygen from TCR-oil is required. In former research, the crude TCR-oil was hydrogenated in a 500 ml batch reactor, and different catalysts (NiMo/Al₂O₃, CoMo/Al₂O₃, Ru/C, and ZSM-5) were tested under high temperatures (up to 380 °C) and high pressures (up to 170 bar) for 20 hours. They showed different properties and offered promising results. In the former research work, the Ru/C catalyst showed the best results; however, that catalyst was the most expensive one.

The results from the batch reactor have been transferred to a continuous flow reactor, which was used for the hydrogenation of the TCR-oil. The continuous flow reactor consists of three reactors, and activation of NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts with dimethyl disulfide (DMDS) was investigated. The pretreatment of the catalysts with DMDS under the pressure of up to 35 bar and temperature of up to 280 °C under hydrogen led to the decomposition of DMDS to hydrogen sulfide (H₂S). The H₂S converted the oxide species of the catalysts into the more reactive sulfide species.

Compared with the Ru/C catalyst, the NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts offered nearly the same results. The amount of oxygen and sulfur could be removed nearly to zero, viscosity was reduced, and the color of the hydrogenated TCR-oil changed from black to slightly yellowish (Fig. 7). In addition to that, the high heating value increased



Fig. 7. TCR-oil, hydrogenated TCR-oil, TCR-diesel and TCR-gasoline.

Table 2

Elemental composition of hydrogenated TCR-oils produced by different catalysts.

| Catalyst | C (wt %) | H (wt %) | N (wt %) | S (wt %) | O (wt %) | HHV (MJ/kg) |
|-----------------------------------------|----------|----------|----------|----------|----------|-------------|
| CoMo/ Al ₂ O ₃ | 85.8 | 13.0 | 1.3 | <0.01 | <0.01 | 45.2 |
| NiMo/ Al ₂ O ₃ | 86.4 | 12.7 | 0.8 | <0.01 | <0.01 | 45.0 |
| Ru/C | 85.4 | 14.0 | 0.6 | <0.01 | <0.01 | 46.3 |

up to around 46.3 MJ/kg (Table 2). The biofuels produced by the hydrogenation of TCR-oil comply with European standards like EN228 and EN590 for common gasoline and diesel.

2.4. Treatment of the aqueous phase

Next to research on the main TCR products, char, oil and gas, intensive research is done on the characterization, valorization, and the purification of the evolving aqueous phase to enhance the technology's overall economics. Regardless of the applied thermochemical conversion technology, the production of an aqueous phase will be inevitable if biomass is used.

The quantity and the chemical composition of the aqueous phase depend on the thermochemical conversion technology and the used feedstock. However, all produced aqueous phases are rich in various organics, challenging to treat and costly to dispose of [51]. Due to this, the aqueous phase is, up to now, at least a financial bottleneck for the industrialization of these technologies.

2.4.1. Chemical composition of the aqueous phase

The chemical composition of the aqueous phase from thermochemical conversion technologies consists of water-soluble organics, inorganics and water. Also, suspended solids (tar, ash) may be present if no filtration of the gas or aqueous phase itself is done. The concentration of dissolved organic compounds is high, and the total organic carbon (TOC) is generally much higher for dry conversion technologies than for wet conversion technologies.

The quantity of the aqueous phase generally depends on the conversion technology and the moisture of the feedstock. The ratio of the chemical oxygen demand (COD) to the TOC is, according to Leng et al. [52,53], about 3:1. In literature, COD values of 50–100 g/l for wet conversion technologies and more than 100 g/l up to several hundred grams per liter can be found for dry technologies [52–55]. On the other hand, the nitrogen content in the aqueous phases ranges from several to a dozen grams per liter and is mainly governed by the degree of decomposition of proteins in biomass such as manure, sewage sludge and microalgae [56].

2.4.2. Valorisation strategy of the TCR aqueous phase from sewage sludge

In the case of dry conversion technologies and, therefore, high concentrations of persistent and inhibitory compounds in the aqueous phase, new innovative strategies have to be developed [57]. Table 3

Table 3

Main properties of the TCR aqueous phase from sewage sludge.

| Main properties | Unit | Value |
|------------------------------------------------------------------------------|-------|-------------|
| Chemical oxygen demand (COD) | g/l | 34.3 – 43.9 |
| Total organic carbon (TOC) | g/l | 14.6 – 20.5 |
| Total inorganic carbon (TIC) | g/l | 12.2 – 18.8 |
| Total nitrogen bound (TNb) | g/l | 38.6 – 58.7 |
| Ammonium/Ammonia nitrogen (NH ₄ ⁺ /NH ₃)-N | g/l | 30.6 – 43.2 |
| pH | - | 9.3–9.7 |
| Electrical conductivity | mS/cm | 102–128 |

shows exemplarily aqueous phase characteristics from sewage sludge treatment.

The phase separation of the TCR-condensate into bio-oil and aqueous phase, which is an important precondition for the valorization, happens self-contained due to the polarity and density difference of the liquids. Other wet or dry thermochemical conversion technologies will need further equipment for the separation putting additional economic stress on the production of biofuels [51]. In the considered biorefinery scenario, the aqueous phase, which contributes about 20 wt% of the initial feed (on a dry basis), is used to provide a portion of the hydrogen needed to upgrade the produced bio-oil. Also, valuable products like chalk and ammonium sulfate are produced.

In the first step of the valorization route for the aqueous phase, the organics are reduced via an electrooxidation process. Unlike in conventional electrolysis cells, special boron-doped diamond electrodes are used. Due to this, instead of producing oxygen at the anode, hydroxyl radicals are produced, which oxidize the organics in the aqueous phase [58]. The main advantages of this process are that (a) the oxidation takes place non-selectively no matter the composition of the organic compound, (b) complete oxidation of the organics can be reached (c) no chemicals have to be added to keep the reaction running and (d) the simultaneous production of hydrogen [58].

In case the electricity used in the process comes from renewable energies, the electrooxidation can even be operated climate-neutral [59]. The process requires a specific charge of 3.4 Ah/g_{COD} at maximum efficiency. With this, about 1.4 liter H₂ is sufficient for the hydrogenation of 1.8 g bio-oil [60]. According to the aqueous phase properties (Table 3), sewage sludge TCR with an average COD of about 40.5 g/l and an aqueous phase to a bio-oil ratio of 2:1, close to 15% of the evolving evolution bio-oil can be hydrogenated using the hydrogen produced during the electrooxidation treatment of the aqueous phase [57].

In a second step, the inorganic carbon, which is the reason for the high electrical conductivity of the aqueous phase, is reduced. At the same time, the aqueous phase's pH is increased to shift the NH₄⁺/NH₃ equilibrium to NH₃. For this, calcium hydroxide is used. Calcium carbonate, a valuable soil additive, will precipitate during the treatment and thus can be recaptured. To eliminate the inorganic carbon from 1 liter of the mentioned TCR aqueous phase from sewage sludge, about 97 mg Ca(OH)₂ is needed, while about 130 mg CaCO₃ is formed. Alternatively, if the regained calcium carbonate is stored underground, about 57 g CO₂ is actively removed from the atmosphere for each liter aqueous phase treated.

In a third step, ammonia, the precursor of various chemical compounds such as fertilizer, can be recovered. For this, the aqueous phase is heated up to about 60–70 °C. The ammonia is then stripped via air and subsequently recaptured using sulfuric acid, generating about 174 g (NH₄)₂SO₄. In the last step, the purified aqueous phase can be discharged into the municipal sewage water system and post-treated in a conventional wastewater treatment plant. Therefore, the presented purification strategy for the aqueous phase opens up the chance to regain valuable products of the aqueous phase and, at the same time, improve the overall efficiency of the presented biorefinery by providing hydrogen for the upgrading process of the bio-oil.

As mentioned above, the valorization strategy is very closely linked

Table 4

Material name, formula, melting temperature (T_m), and enthalpy of fusion (Δh_m), measured in a differential scanning calorimeter (DSC 204 F1 Phoenix, Netzsch) at 1 K/min.

| Material | Formula | T_m (°C) | Δh_m (J/g) |
|--------------|----------------------|------------|--------------------|
| Xylitol | $C_5H_{12}O_5$ | 93.1 | 232.6 |
| D-Sorbitol | $C_6H_{14}O_6$ | 98.3 | 189.5 |
| Erythritol | $C_4H_{10}O_4$ | 119.1 | 332.8 |
| Isomalt | $C_{12}H_{24}O_{11}$ | 141.4 | 113.8 |
| Maltitol | $C_{12}H_{24}O_{11}$ | 148.7 | 163.2 |
| D-Mannitol | $C_6H_{14}O_6$ | 165.7 | 275.4 |
| Dulcitol | $C_6H_{14}O_6$ | 187.3 | 341.8 |
| Myo-Inositol | $C_6H_{12}O_6$ | 224.4 | 256.7 |

to the used thermochemical conversion process, the used feedstock and the targeted product of the biorefinery. However, electrooxidation with boron-doped diamonds opens up the possibility of reducing inhibitory and persistent organic compounds in the aqueous phases produced by such conversion technologies.

2.5. Managing energy flow at low and medium temperature

For the development of modern processes, energy efficiency is one important aspect to ensure competitiveness within the market. High-temperature processes often offer the unused potential for the reuse of waste heat. Therefore, the use of waste heat is a decent way to improve the energy efficiency and sustainability of the TCR process. During the TCR process, waste heat at about 200 °C is generated, which can be used for drying the feedstock. The heat storage allows heat to be used in a greater variety of processes, as it overcomes the dependency on time. Large scale drying processes are state of the art technology. Depending on the existing waste heat and the needed temperature levels, different drying processes exist. Solar drying can be used if there is enough space. A combination of solar drying and waste heat usage can be used in a temperature range around 70 to 80 °C. With waste heat between 80 to 150 °C temperature, belt dryers or paddle dryers can be used. Fluidized bed dryers, thin-film dryers or tumble dryers can be used with waste heat at temperatures above 150 °C [61]. In combination with the TCR, a hybrid process working at 70 – 90 °C using a solar dryer together with waste heat from the TCR has a high potential. This waste heat is at a much higher temperature level. Hence, the drying process is much faster.

To stabilize this system, the use of heat storage systems is favorable. Latent heat storage offers great potential due to its high energy density. Different phase change materials (PCM) can be used to meet the needs of the two temperature levels. In general, PCMs should have a high energy density and a suitable melting temperature. Besides this, cycle stability is vital to ensure a long lifetime of the whole storage system. PCMs should also be non-toxic, non-flammable and environmentally friendly, as well as low-cost and highly available [62]. One material class is especially promising in terms of solar drying in combination with the utilization of waste heat. The melting temperature of sugar alcohols is spread over the whole temperature range of 70 °C to 230 °C, and they offer high energy densities. Since they are used as food additives and in the pharmaceutical industry, they are also highly available at a reasonable price. Some especially interesting sugar alcohols in terms of their use as PCM can be found in Table 4.

To use the PCM in the drying process, the PCM needs to fit the desired temperature range. To store waste heat from the TCR at a temperature level of 200 °C, D-Mannitol and especially Dulcitol, due to its high melting enthalpy, are favorable. On the other hand, lower temperatures are needed to store thermal energy for the hybrid drying process; since the application has temperatures of 90 °C, the melting point needs to be below.

While the melting point of Xylitol is only slightly above the desired temperature, Erythritol offers a very high enthalpy of fusion, but the



Fig. 8. Auger reactor, combustion chamber, and post-reformer of the TCR-500 plant.

melting temperature is too high. Hence, both materials cannot be used as single materials. The eutectic mixture of both of them, on the other hand, matches the needed criteria. Sugar alcohols are considered single eutectics. Eutectic mixtures do have a lower temperature than the single material, but the enthalpy is between the ones of the pure material. Therefore, the combination of Erythritol and Xylitol offers the best properties for the application. The mixture consists of 77 wt% of Xylitol and 23 wt% of Erythritol.

The melting temperature of the eutectic mixture is 83.4 °C, and the enthalpy of fusion is 244.5 J/g. Since the melting also happens in one narrow peak, no separation of the two materials is happening. Since the melting temperature is below 90 °C, it is suitable for the application. The enthalpy is also higher than the one of pure Xylitol. In conclusion, the mixture has the perfect properties to store the thermal energy provided during the daytime in combination with waste heat.

The eutectic mixture, as well as Dulcitol, offer a high potential to combine latent heat storage with the feedstock drying of the TCR process. By doing so, sunlight and waste heat can be used for the drying process, and the use of fossil fuels can be reduced or even substituted. The advantage of combining solar thermal energy with the use of waste heat is the higher temperatures, which also lead to faster drying, and therefore, higher throughputs can be generated. In total, the overall energy efficiency of the process is rising.

3. Scale-up of TCR technology

The most recent step in TCR development is part of the Horizon 2020 projects To-Syn-Fuel (www.tosynfuel.eu) and GreenFlexJET (www.greenflexjetproject.eu). In both projects, the operational capacity of the plant is designed for 500 kg per hour of solid organic wastes with a water content of less than 20% in order to produce green fuels as well as green gasoline, jet and diesel [63,64]. The unit is heated by the flue gas from a gas combustion system. The main purpose of this unit is the long-term operation of a pre-commercial demonstrator [63]. This is the actual step of development before the technology reaches a fully commercial scale. This unit was commissioned in July 2021 and shall be operated for more than 4000 h within the To-Syn-Fuel project for the production of more than 200,000 liters of bio-crude oil from sewage sludge.

For the up-scale operational parameters, such as residence time, temperature and heating rate, the TCR processes were successfully transferred from the lab and pilot-scale to the 500 kg/h plant scale. Trials with sewage sludge were carried out for the evaluation of parameter sets from the industrial-scale unit. The whole process was established and automatized. The gaseous and liquid TCR products were characterized and used for further purposes like CHP application or



Fig. 9. Hot gas filter and condensation stage of the product gas train of the TCR-500 plant.

biofuel for internal combustion engines. The heating system was completely re-designed for optimized heat transfer and minimum heat energy demand.

3.1. TCR-500 demonstrator

The TCR-500 is a thermal heated plant to convert 500 kg/h of dried biomass into high-quality products named TCR bio-oil (approx. 50 l/h), TCR-syngas (approx. 100 Nm³/h), and TCR-biochar (approx. 250 kg/h). The TCR-500 (Fig. 8) consists of two reactor stages, which are the auger reactor and the post reformer, and a combustion chamber with a heat gas distributor, as well as a product gas train that consists of a hot gas cleaning system, a condensation stage, and a scrubber. A feeding system feeds the TCR plant with sewage sludge, and a char extraction system removes the carbonisate.

The first reactor stage is the auger reactor. The auger itself is approx. 8.6 m long, has a diameter of 0.76 m and operates with a rotational speed of 4 – 5 rpm. While the retention time of 8 – 10 min, the feedstock is heated to approx. 450 °C and converted into char and vapours.

The second reactor stage is the so-called post reformer that heats up

the char and vapours to approx. 650 °C, and the catalytic reforming takes place. The char operates as a catalyst, which leads to high hydrogen content of up to 40 vol% in the TCR-syngas. Furthermore, the cracking of long hydrocarbon chains due to the high temperatures avoids tar issues within the product gas treatment system. The reduction of acids in the gas stream leads to low total acid numbers (TAN) of the TCR bio-oil. This is important to meet the requirements for biofuels. TCR-500 results are comparable to those from the bench and pilot scale.

The combustion chamber burns propane and the resulting flue gas with approx. 900 °C provides the heat to heat up the post reformer and the auger reactor. A flue gas distributor distributes the flue gas to the post reformer and the auger reactor in a way that both components are operating at set temperatures.

Downstream the post reformer, the two-stage hot gas cleaning system removes dust from the vapours (Fig. 9). The first stage is a multi-cyclone that removes coarse particles. In the second stage, two parallel-operated ceramic fibre bag filters clean the gas from fine particles. If one of the filters is fully loaded with dust, the vapour flow switches to the second filter. The recovery of the first filter is possible due to a jet impulse cleaning with nitrogen.

The dust-free vapours are then flowing through a gas cooler that reduces the gas temperature to approx. 20 – 35 °C, and the TCR bio-oil and process water are separated from the TCR-syngas. A gravimetric separator separates the bio-oil and process water from each other (Fig. 9). A scrubber cleans the syngas from H₂S and NH₃ with an iron chloride solution. The H₂S is removed to protect the components downstream of the TCR-500 from corrosion. The NH₃ is removed to reduce NO_x emission during the combustion process of the TCR syngas. The final stage of the TCR-500 is an electrostatic precipitator to remove aerosols from the gas stream.

The feeding system feeds the auger reactor with dried sewage sludge (water content approx. 10 – 15%). A chain conveyor transports the biomass from feed storage to a sluice system, ensuring that the TCR-500 plant stays inertised. Downstream the sluice system, a calibrated dosing screw feeds the auger reactor with 500 kg/h of the dried sewage sludge. Downstream the post reformer, the char extraction screw with a jacket and inner tube cooling system transports the carbonisate to a chain conveyor and cools the char to temperatures lower than 90 °C. Finally, the chain conveyor transports the char to the storage silo.

How can we get the maximum output out of bioenergy plants? One of

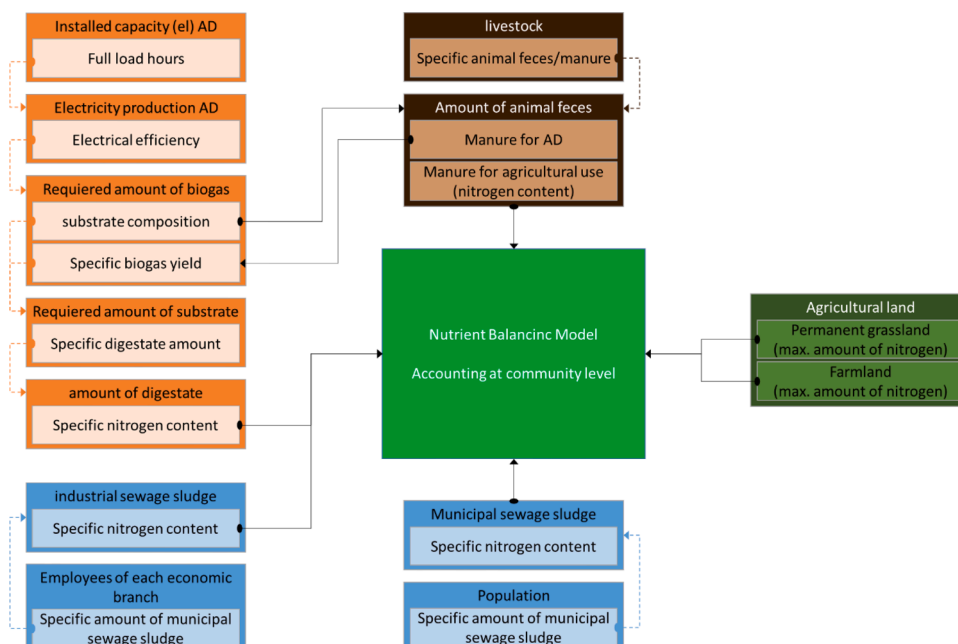


Fig. 10. Schematic representation of the information flow of the nutrient balancing model used for this study.

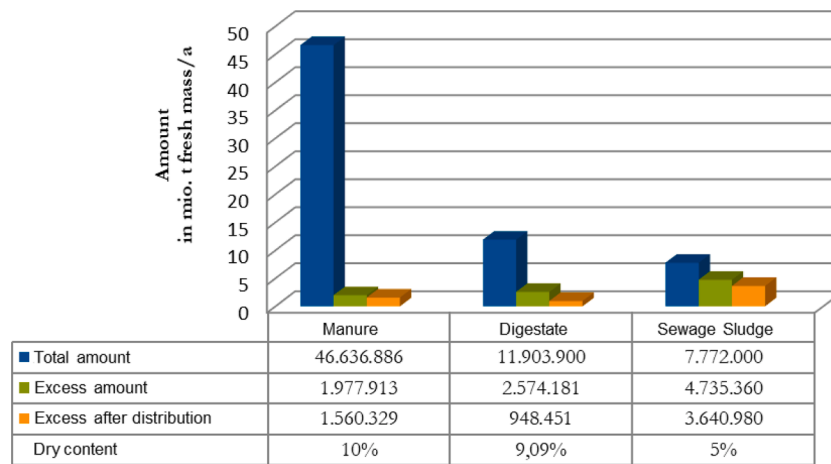


Fig. 11. Comparison of the quantities of liquid manure, digestate and sewage sludge for Bavaria according to the nutrient balancing model (blue: the community-internal quantities, green: excess quantities without distribution, orange: excess quantities after distribution).

the most challenging aspects of process control is to handle varying fuel qualities. The heterogeneity of biogenic fuels and especially biogenic residues limits fuel flexibility. Varying water and ash content, particle size and particle size distribution are challenging for biomass utilization in general and biomass combustion in special. Plant operators invest a lot in fuel quality management and fuel pretreatment, researchers aim at defining fuel standards, and plant manufacturers try to optimize fuel flexibility with systems that are more robust or specialized technology.

Technologies to detect online fuel characteristics are key to a more fuel-flexible operation enabling plants to react to changing fuel qualities. Regarding the syngas fuel, portable syngas analyzer such as Gasboard-3100P can be used to measure synthesis gases. Regarding bio-oil, online GC × GC-MS, including FID and TCD detections, are essential to characterize the bio-oil fuel but are a costly instrument and also cannot measure physical fuel properties such as total acid number, viscosity, density, water content, flash point etc. Therefore, the most economical approach at the moment is to condense the oil and analyze all properties offline. However, research and industry are following many different approaches for different applications. Being part of process control, online fuel characterization could help to optimize bioenergy processes.

3.2. Implementation of TCR as an example for the state of Bavaria in Germany

For the successful implementation of new technology, it is essential to know about the applicability and demand of markets. Fraunhofer UMSICHT did intense analysis for this purpose. Based on a nutrient balancing model (Fig. 10), the quantities of liquid manure, digestate and sewage sludge occurring in Bavaria were determined.

Taking into account the available agricultural land, fertilizer limits, and, on average, reasonable transport distances of 10 km, excess quantities understanding is important for energetic use (Fig. 11). The most significant proportion of the quantities of liquid manure produced is cattle manure with approx. 88.5% and pig manure accounts for approx. 11%. Due to an applied distribution hierarchy and the dominant amount of cattle manure, the excess from manure before and after distribution into neighbouring communities corresponds almost entirely to cattle manure.

These excess quantities lead to an energetic potential of 1,245,426,872 GWh. This potential results from the respective calorific values of the material flow. For sewage sludge, 11 MJ/kg for dry material (DM) [65] is applied; for digestate it is calculated with 17.59 MJ/kg DM [66]. The calorific value for manure is determined using the method from Thrän et al. [67, 68]. The calorific values used are shown in Fig. 12.

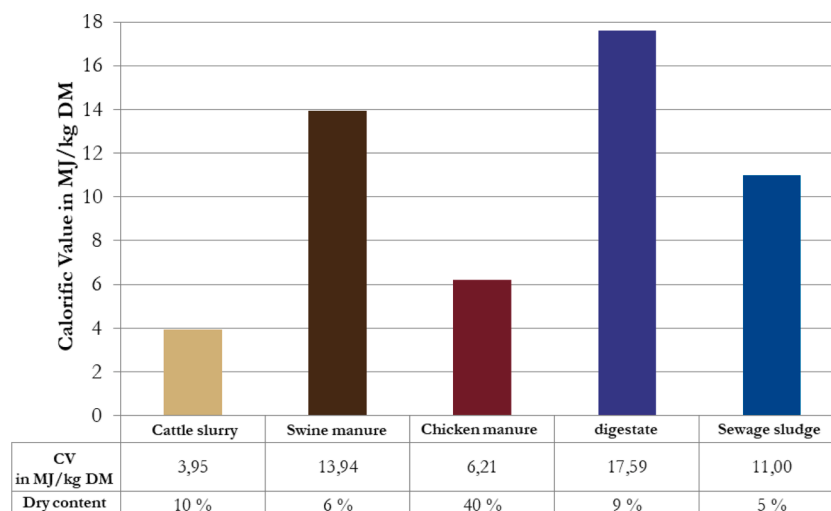


Fig. 12. Calorific values of the considered residues (manure [67, 68], sewage sludge [65], digestate [66]).

Table 5

Net efficiency of the respective technologies in the utilization of the residues [65].

| Residues | Technology | Thermal efficiency (η_{th} , net) | Electrical efficiency (η_{el} , net) |
|---------------|--------------|-----------------------------------------|--------------------------------------------|
| Sewage Sludge | Incineration | 10% | 9% |
| Digestate | Incineration | 21% | 11% |
| Manure | Digestion | 20% | 32% |

If the resulting quantities of residues were used in traditional systems for thermal incineration, there would be an energetic technical potential for use in the heating sector. Table 5 shows the efficiencies used for the respective usage path used to determine the technical energy potential.

The theoretical and technical energetic potential of the excess quantities of digestate, sewage sludge and liquid manure resulting from the procedure described above, as well as their regional distribution, is shown in Fig. 13. As expected, the highest technical energetic potential is found in the municipalities with a high number of cattle (Alpine foothills) and in large cities (e.g. Munich, Nuremberg). Furthermore, a sensitivity analysis with regard to the central input variables shows that, as expected, the limit of total nitrogen per hectare and year (initial value 170 kg/(ha.a)) followed by the amount of livestock has the greatest influence on the theoretical coverage ratio in the heating sector.

Fig. 14 shows the effects of the corresponding input variables on the fictitious coverage ratio. An alternative way to use the excess quantities outside of the above-mentioned thermal incineration is to utilize the residual materials with TCR systems so that in addition to heat and

electricity, the added value can be increased using the products oil and coal. Based on the excess quantities of residues occurring throughout Bavaria, around 61,000 t of TCR coal and around 23,000 t of TCR oil could be provided if excess liquid manure, digestate and municipal sewage sludge are utilized with TCR systems.

Fig. 15 shows the mass flows and energy requirements of the individual process steps in Sankey diagrams. The basis is the energy balances of a TCR pilot plant as well as state of the art with regard to the remaining components such as biogas plants, dewatering, drying and sewage sludge incineration. Since industrial sewage sludge is very heterogeneous, it was assumed that it would be utilized in a sewage sludge incineration plant.

4. Conclusion

Sustainable and renewable energy sources have received consideration because of the growth in demand for fossil fuels and concerns with regard to climate change. Thermo-Catalytic Reforming (TCR) is a novel technology combining intermediate pyrolysis with post catalytic treatment (catalytic reforming) in a single step upgrading system to convert waste into valuable fuels. As a result, TCR bio-oil has superior physicochemical fuel characteristics compared with other technologies. In addition, TCR delivers high-quality syngas and biochar.

Long-term storage of carbon or CO₂, which was naturally captured by wood during its growth phase, is possible by converting wood into biochar. However, to make the biochar production more sustainable, the range of feedstock has to be extended to biogenic residues like agricultural residues, sewage sludge, digestate from biogas production, and

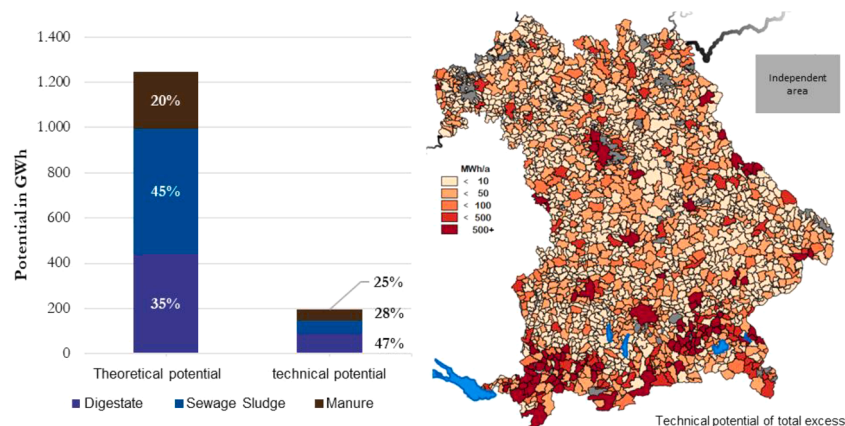


Fig. 13. The theoretical and technical energetic potential of the respective excess quantities in Bavaria (left) as well as Bavaria map of the technical energetic potentials of the total excess quantities (right).

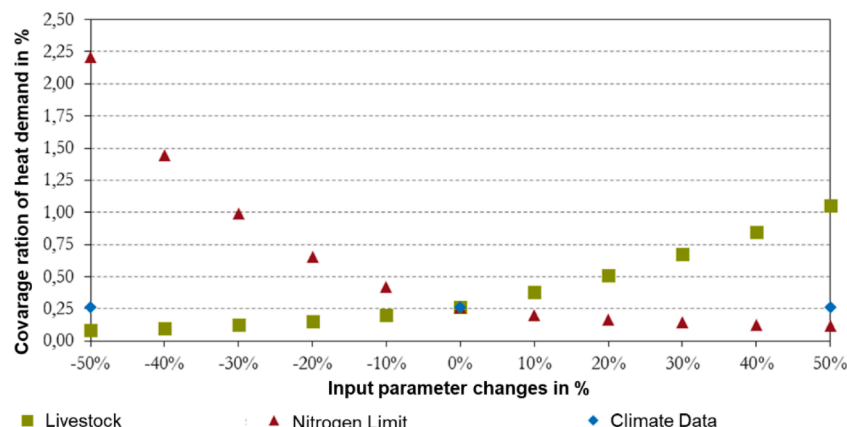


Fig. 14. Theoretical coverage ratio of the Bavarian heat demand according to the input parameters changes.

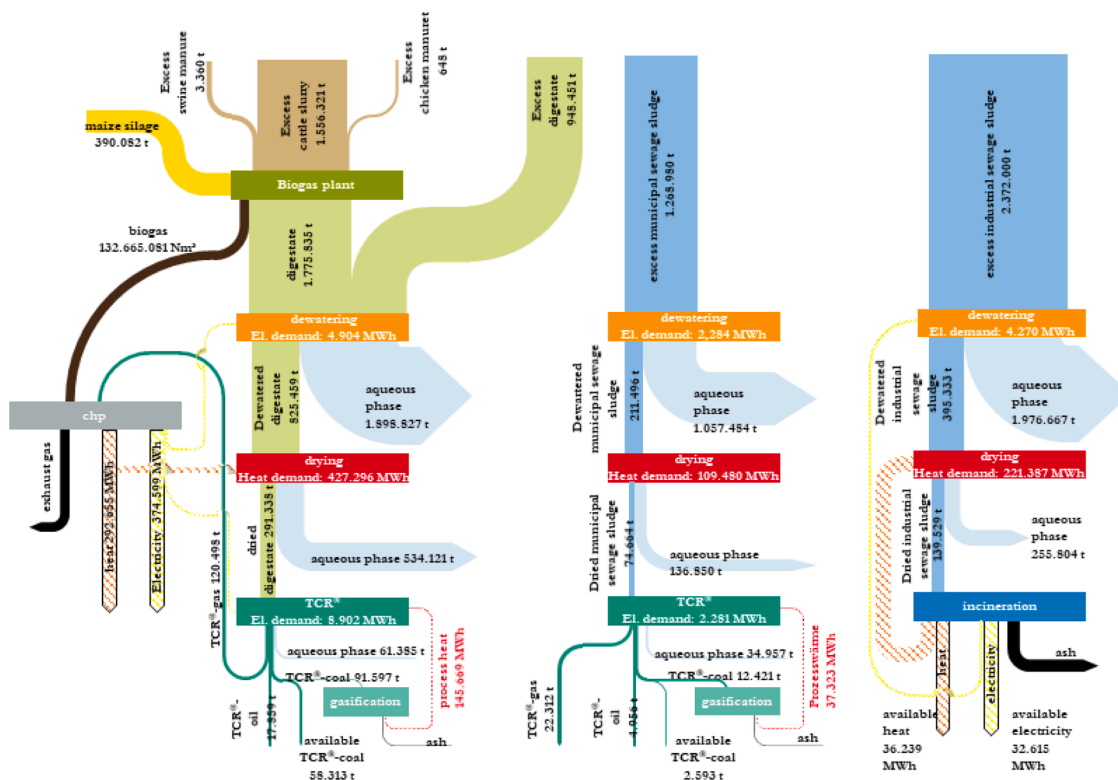


Fig. 15. Sankey diagram of an exemplary utilization path for excess quantities of residues from agriculture and wastewater management for Bavaria.

residues from the food industry (e.g. brewer spent grain) or residues from modern processes like ethanol production from straw and macroalgae.

To sum up, even if the biochar applications market is growing and obtainable prices are high, business cases are more robust if side products like the liquids from pyrolysis can be turned into valuable products. For TCR, with its stable thermal oil, EN 228 and EN 590 standard fuels for gasoline and diesel can be obtained (via TCR hydrogen-rich syngas), generating further income. In addition, the fuels become CO₂-negative because of the carbon stored in the char.

5. Outlook

Having demonstrated the successful run of a 500 Kg/h TCR technology on sewage sludge refineries in Germany and Canada have shown the applicability of such technology in their refineries to reduce the CO₂ footprint of their products. Also, biochar as a substitute for fossil coal in industrial processes similar to steelmaking is getting interested. The hydrogenated products will be the basis for consolidating the interest of the chemical industry. All in all, the demonstration of the TCR technology at a commercial scale and the production of several 10,000 litres of green crude and related char are required to convince existing market players.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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