Pyrolysis and Gasification of Lignocellulosic Biomass

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1 Introduction

Thermochemical conversion processes (combustion, gasification, and pyrolysis) are widely used to recover energy from biomass. In a biorefinery context, pyrolysis and gasification are especially interesting as both platforms offer high feed and product flexibility, providing the possibility to convert many different biogenic feedstocks into a wide variety of products such as heat, electricity, chemicals, transport fuels, and high-value ash and char products.

Pyrolysis is a thermal decomposition process of carbonaceous materials in the absence of air/oxygen. The cracking of chemical bonds leads to the formation of molecules with a lower molecular weight. Different product fractions are obtained: a solid (char), a liquid/condensed (tars), and a non-condensable gaseous fraction. Depending on the heating rate and solid residence time, biomass pyrolysis can be divided into three main types: slow pyrolysis, fast pyrolysis, and flash pyrolysis. Slow pyrolysis (typically <20 °C/min and retention times >15 min) has been conventionally used for the production of charcoal and to maximize the solid yields. Fast pyrolysis and flash pyrolysis processes are often applied in systems with focus

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on bio-oil production and typically involve much higher heating rates and shorter residence times. In fast pyrolysis the heating rate is typically around 10–200 °C/s and the residence times around 0.5–10 s but typically <2 s (Demirbas and Arin 2002). Bio-oil yield from optimized fast pyrolysis processes can be as high as 50–70 wt% on dry biomass basis. The flash pyrolysis process is characterized by extremely high heating rates of >1000 °C/s and even shorter residence times (<0.5 s), resulting in very high bio-oil yields which can achieve up to 75–80 wt% (Jahirul et al. 2012; Bridgwater et al. 1999). Bio-oils from pyrolysis have a great potential to be used in refineries to synthesize chemicals and fuels. However, more research is needed to overcome the problems they present like strong corrosiveness (pH = 2–4), high viscosity, immiscibility with conventional fuels, and poor chemical stability with polymerization of components on storage (Milina et al. 2014).

The gasification platform adds to the pyrolysis a char conversion process where carbon in the char reacts with a gasification agent such as steam or carbon dioxide at elevated temperatures. The gasification reactions are endothermic, and the heat is either supplied externally (allothermal gasification) or by supplying air/oxygen to the gasifier. The main product from the gasification process is a non-condensable gas product (CO_2, CO, H_2, H_2O, and other gaseous hydrocarbons), and by-products can include smaller quantities of char, ash, and several condensable compounds (tars and oils). Biomass gasification involves a sequence of several stages occurring at different temperatures: drying (100–200 °C), pyrolysis (200–700 °C), partial combustion (>800 °C), and reduction or gasification (700–900 °C). These stages often overlap depending on the specific gasifier design. The quality of the gas produced varies according to the gasifying agent used, feedstock, bed material, operational conditions (temperature, pressure, air to fuel ratio), and gasification technology. The gas obtained covers a wide range of calorific values from 4 to 7 MJ/m^3 when using air to 12–28 MJ/m^3 when pure oxygen is used. Thermal gasification can play an important role in the future energy system because it offers a flexible and efficient platform that can meet a variety of needs. However, despite the many advantages that biomass gasification presents, it has not yet been able to consolidate its role and become a mature technology in other areas than small-scale CHP from wood with mediocre thermal efficiencies. Around 1000 units of this type exist in Germany and surrounding countries. However, in other areas, great expectations have led to great disappointment because insufficient resources have been allocated for immediate and future operational issues related to:

- Handling and feeding the biomass feedstock
- Optimizing the energy efficiency to high moisture content feedstocks
- Addressing variations in biomass fuel properties
- Unrealistic fuel flexibility expectations
- Upscaling
- Ash-related problems including sintering, agglomeration, deposition, erosion, and corrosion
- Tar-related issues, e.g., condensation at lower temperatures, which can lead to fouling and plugging of the plant pipelines, filters, catalyst units, or engines
- Problems with gas cleaning trains and impurities such as sulfur compounds (e.g., H_2S, COS), hydrogen chloride, alkali, and ammonia

Despite past experiences with these challenges in several projects and plants, there is a firm belief in academia, industry, and among energy political consultants and advisors that thermal gasification of biomass will play a crucial role in future energy systems. Thus, in order to increase the utilization of biomass pyrolysis and gasification and make it commercially interesting in future energy systems, new integrated biorefinery designs with optimized thermal concepts and combinations of different technologies are required to maximize product yield and value, increase the overall process efficiency, and improve the economic viability.

The present chapter provides an insight on the versatility and potential of biomass pyrolysis and gasification processes and their products. It also describes some new concepts and solutions like process integration schemes, polygeneration strategies, biochar uses, and tar abatement strategies that can help to overcome the operational challenges that the technology is facing.

2 Thermal Pyrolysis and Gasification of Secondary Resources and Fuel Mixes

Pyrolysis and gasification platforms are often designed for conversion of one or several conventional biomass types such as wood, straw, macroalgae, and *Miscanthus* grass (Trinh et al. 2013; Saleh et al. 2014; Ahrenfeldt et al. 2013). However, in a biorefinery context, it may be valuable to extend the potential range of organic material fractions converted in thermal processes to cover more of the biogenic materials in the category *organic secondary resources*, not only the classic biomass fractions. Secondary resources refer, in this chapter, to a category of organic residues and degraded organic materials, which often have a low or negative price due to undesirable circumstances and characteristics, e.g.:

- Difficulties in collection, transport, storage, or handling
- Low energy density per unit of mass or volume due to a high moisture content or ash content
- Very inhomogeneous, requiring flexible and resource consuming handling
- Highly polluted, polluting, and/or harmful
- Very volatile, difficult to contain and generates local odor or dust problems

If a resource is sufficiently problematic, management of the resource will be costly, and, in many cases, the price of the resource will be low. A low price does not necessarily entail a low value of a given resource. The category of secondary organic resources includes many different subgroups. Some of the most important groups include:

- Agricultural by-products and residues, e.g., crop residues (stalk, leaf, cob, etc.), manure fibers, muck and bedding, and fibers from biogas slurry
- Municipal by-products and residues, e.g., source-segregated organic waste, used textiles, grass and cuttings from road and park maintenance, beach cleaning waste, and sewage sludge

- Industrial by-products and residues, e.g., residues from breweries, food packaging, food retail, and food preparation or residues from production of nonfood products based on the partial conversion of animal and vegetable raw materials

Optimized treatment of secondary resources has great potentials from an economic, environmental, and resource political point of view. The positive effects of thermal pyrolysis or gasification of organic secondary resources can include (1) increased non-fossil energy production, (2) reduced emissions of greenhouse gases from storage and direct application of unstable fractions, (3) carbon sequestration and soil enhancement, (4) nutrient recovery and recycling, (5) increased security of supply, and (6) reduced risks of terrestrial toxicity in soil management (Thomsen et al. 2016). For these reasons, it may prove beneficial to develop biorefineries and waste refineries to convert or co-convert secondary resources. Finally, application of thermal processes developed for low-quality fuels will also increase the technical potential for waste and by-product valorization within the biorefinery concept and add to the energy and mass integration of the system.

Recent research in thermal valorization of secondary resources in systems with pyrolysis- or gasification-based processes have indicated a huge potential for optimizing the present management systems. However, the thermal conversion of secondary resources has often proven problematic due to undesirable fuel characteristics (e.g., high moisture contents, low energy density, low melting points, and particle bridging). To reduce the impact of varying and problematic fuel characteristics, it may become useful—or necessary—to mix two or more different fuels in optimized ratios to match the criteria of the conversion technology as well as the potential end use of the produced products. In this way, the practical impact of problematic fuel characteristics can be reduced, and potential synergies obtained. Potential benefits that could be obtained from proper fuel mixing include:

- Reduced requirements for drying by mixing wet and dry fuels
- Standardized fuel characteristics such as energy density, proximate composition, and char reactivity
- Thermal purification of valuable elements in problematic resources like waste, manure, and sludge
- Optimized ash composition for fertilizer use by mixing fuels with, e.g., high P content with fuels with, e.g., high K content
- Potentially increased P fertilizer quality and decreased heavy metal content in ashes by co-gasification of P-rich secondary resources with fuels with high K, Na, Cl, or Mg content (Herzel et al. 2016; Nanzer et al. 2014; Nowak et al. 2012; Stemann et al. 2015; Vogel et al. 2013; Adam et al. 2009)

A small study published in 2016 (Thomsen et al. 2016) illustrates the potential benefits and drawbacks of mixing different fuels in different thermal processes (Fig. 1) by investigating, in laboratory conditions, which fuel mix characteristics were linear combinations of the characteristics of the individual fuels and which deviated substantially from such linearity.

The screening included proximate composition; higher heating value of fuels and chars; bulk density of fuels, ashes, and chars; char reactivity; char deposition

Fig. 1 (Left) Mix 1—palm kernel shells and rice husks, 50/50 w/w. (Center) Mix 2—palm kernel shells and animal meat and bone meal C1, 50/50 w/w. (Right) Mix 3—rice husks and animal meat and bone meal C1, 50/50 w/w. All weights on as-received basis

and formation of char agglomerates during pyrolysis; ash deposit sticking and vaporization; and P extractability of incubated ash and char samples. Results showed (1) good agreement between measured and calculated values of proximate composition, higher heating values (fuel and char), and fuel bulk densities; (2) inconsistent, but substantial, deviations from the linear predictions within char reactivity; (3) generally lower char and ash bulk densities of the mixes than predicted by linear sums of the char and ash bulk densities of the involved fuels; (4) substantial improvement of char deposition and char agglomeration during pyrolysis, especially for the animal meat and bone meal samples; (5) huge improvements also in ash deposit sticking as well as ash sintering in incineration or gasification processes, especially in samples with palm kernel shells and animal meat and bone meal; and (6) tremendous increase in the Mix 1 ash sample and Mix 3 char sample P fertilizer quality compared to the predicted values (Thomsen et al. 2016). In this context, mixing biomass into animal meat and bone meal before pyrolysis was previously found to increase extractability of bone meal char P (Zwetsloot et al. 2015). Similarly, positive experiences were obtained in studies with thermochemical treatment of waste and sludge with Na- and Cl-rich additives, and it is therefore expected that the high Na and Cl content of the palm kernel shell sample could have a positive influence on the P extractability of the mixed chars and ashes (Herzel et al. 2016; Nanzer et al. 2014). Based on these results and other studies recently published in the open literature, e.g., (Zwetsloot et al. 2015; Jiang et al. 2016; Pettersson et al. 2008; Lin and Ma 2012; Ding and Jiang 2013; Ong et al. 2015; Rong et al. 2015; Seggiani et al. 2012a, b; Skoglund et al. 2013; Ren and Li 2015; Li et al. 2013; Kern et al. 2012; Manara and Zabaniotou 2012), it is anticipated that further investigations into fuel mixing and thermal co-conversion of problematic residual resources could contribute greatly to increase the economy and the level of sustainability in the agricultural and waste handling sectors.

3 Fuels and Chemicals

The use of renewable resources such as biomass to produce synthetic fuels, chemicals, and other high-value products has attracted a lot of interest worldwide. One of the possible routes is synthesis of fuels and chemicals from syngas, produced via biomass gasification. Hydrogen and carbon monoxide, the major components of clean and conditioned syngas, are the basic building blocks of a number of products, including fuels and chemicals. Figure 2 shows the huge potential of biomass gasification to produce bio-products. In addition, a gasification plant can be designed to produce more than one product at a time (polygeneration), such as electricity and chemicals.

The production efficiency of synthetic fuels and biofuels depends on the type of fuel and the production pathway. Theoretically, LHV efficiencies of 84, 82, and 78% can be obtained for production of methanol, DME, and Fischer-Tropsch diesel using natural gas as feedstock (Van der Drift and Boerrigter 2005). However, for biofuels produced via biomass gasification, the total biomass to fuel efficiency is lower. In principle, biofuel production from biomass-derived syngas is not different from processes where fossil syngas is used. There are, however, a few biomass-related challenges that influence the conversion efficiency. One of those is the scale of operation. A large-scale plant will suffer less heat loss per unit of product, whereas fossil-based syngas plants are typically huge; it is believed that biomass plants may not be larger than a few hundred MW_{th} due to the limited availability of biomass feedstock at a negotiated price. Another difference between biofuel synthesis and the fossil fuel-based processes relates to the additional conversion steps required in the biomass conversion pathway and the related need for additional process integration. All stages in the biomass conversion pathway lead to potential losses as heat or by-product losses. Therefore, biomass-based plants require a biorefinery approach and have to be integrated with other technologies to increase the process efficiency and the internal use or external valorization of by-products.

Several pilot-scale plants for synthesis of biofuels can be found in research institutions and universities, but full-scale plants are scarcer. Bioenergy2020+ GmbH maintains a database of facilities for the production of advanced liquid and gaseous biofuels for transport (http://demoplants.bioenergy2020.eu). In the present chapter, three remarkable facilities are presented:

- GoBiGas: BioSNG production in Sweden
- Fortum Otso® bio-oil plant in Joensuu, Finland
- Enerkem Alberta Biofuels plant producing methanol and ethanol in Canada

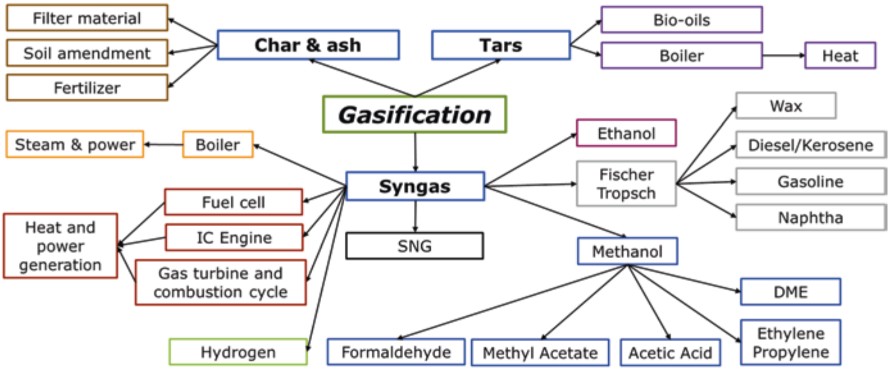

Fig. 2 Potential bio-products that can be obtained from biomass gasification

In addition to these three, it is also worth mentioning the Piteå BioDME pilot plant in Sweden producing around 4 tons of BioDME from black liquor from an adjacent pulp mill. The plant is based on oxygen-blown high-pressure gasification of the black liquor followed by gas conditioning, methanol synthesis, and dehydration to DME.

GoBiGas (Gothenburg Biomass Gasification Project) in Sweden is the world's largest plant, producing high-quality bio-methane from gasification of wood pellets and forest residues. It produces 20 MW of BioSNG, 5 MW of district heating, and 6 MW of heat to heat pumps. The plant was originally designed as a two-phased project. Phase I of the project, which involved the construction of the 20 MW gas demonstration plant, was inaugurated in March 2014 and became fully operational in December 2014 when it started injecting BioSNG to the grid. The capacity of the demonstration plant is big enough to supply BioSNG to approximately 15,000 cars or 400 buses a year. Phase II of the project consisted of a 80–100 MW gas commercial plant, scheduled for 2016, but that was cancelled due to the large amount of biomass needed and because the plant lacks the economy of scale achieved in coal-based plants. The 20 MW demonstration plant is currently looking for new owners/investors. The process (Fig. 3) involves indirect gasification of forest residues. The feedstock is fed into the circulating fluidized bed gasifier and gasified at approximately 850 °C by steam injection from a separate combustion chamber, producing nitrogen-free and low-tar syngas. The synthesis gas is purified by removing tar, sulfur, and carbon dioxide and upgraded in a methanation plant, where bio-methane (BioSNG) with a methane content of more than 95% is produced. The TREMP methanation technology including catalyst for the process reactors and engineering for the gas cleaning facilities was provided by Haldor Topsøe, whereas the gasification technology for the project was provided by Repotec in collaboration with Metso Power.

Other BioSNG projects and plants include the "Go Green Gas" 1 $\mathrm{MW_{BioSGN}}$ pilot plant connected to an industrial waste gasification unit in the UK, the AMBIGO 4 $\mathrm{MW_{th}}$/2.8 $\mathrm{MW_{BioSGN}}$ demonstration project in Alkmaar in the Netherlands, and the 600 $\mathrm{kW_{th}}$ Gaya project in France.

Fortum Otso® bio-oil plant in Joensuu, Finland, is the first CHP-integrated pyrolysis plant in commercial size. It produces bio-oil from forest residues, wood chips, and saw dust. The bio-oil plant is integrated with Fortum's Joensuu combined heat and power (CHP) plant. Joensuu's bio-oil plant is based on fast pyrolysis technology (Fig. 4) and was commissioned in autumn 2013. The annual production capacity of the Joensuu bio-oil plant is 50,000 tons, which is equivalent to the heating needs of more than 10,000 single-family homes. Fortum Otso bio-oil can be used as a replacement for heavy and light fuel oil in heat production plants or in the production of industrial steam. In the future, bio-oil could also be used as a raw material for various biochemicals or transport fuels. Fortum uses the bio-oil at the heat plants in Espoo and Joensuu (Finland). Savon Voima, a Finnish energy company, has also started to use bio-oil at their plant in Iisalmi. According to Fortum, the bioliquid is acidic (pH 2–3) and sulfur free (<0.05%) and has a LHV of 15 MJ/kg, a density of 1.2 $\mathrm{t/m^3}$, and a viscosity "between heavy and light fuel oil." The development and

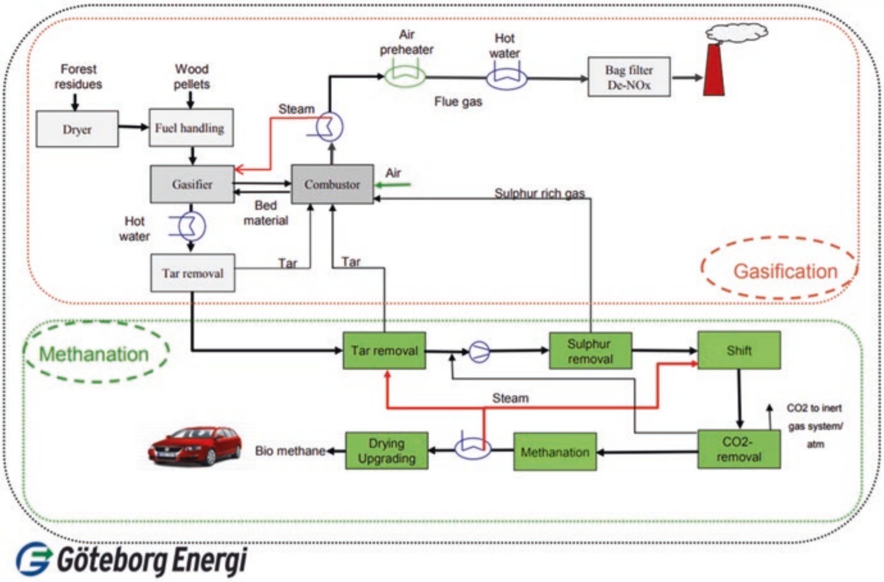

Fig. 3 Schematic of the GoBiGas BioSNG production plant. Copyright Göteborg Energi

conceptualization of the new technology were done collaboratively between Fortum, Metso, UPM, and VTT Technical Research Centre of Finland. The research was part of Tekes – the Finnish Funding Agency for Technology and Innovation's Biorefine program.

Enerkem Alberta Biofuels in Canada is the first of its kind to convert non-recyclable, non-compostable municipal solid waste into liquid biofuels. It was commissioned in 2014 and built adjacent to the Edmonton Waste Management Centre. The facility produces methanol and ethanol and contributes to the City of Edmonton's goal to divert up to 90% of household waste from the landfill. This commercial-scale facility has the capacity to process 100,000 metric tons of solid waste annually, which includes items like textiles, non-recyclable plastics, or soiled food containers, to produce over 40 million liters of biofuels. The Enerkem Alberta Biofuels plant initiated the commercial production of biomethanol in the summer of 2015.

Enerkem's gasification technology (Fig. 5) is based on a bubbling fluidized bed reactor with a front-end feeding system that is capable of handling fluffy material with no need to pelletize it. The fuel is continuously fed into a reactor where an inert heat carrier (i.e., sand) is fluidized under relatively low temperatures (700–750 °C) and moderate pressures of ~2 atm. Slurries or liquids can also be fed into the gasifier through appropriately designed injectors. Oxygen and steam are used as fluidizing gases and gasification agents. The produced gas is drawn from the top of the gasifier and goes through a cleaning and conditioning system. This process, including cyclones to remove particles and scrubbers and absorption to remove impurities, upgrades the gas to a chemical-grade syngas that can be synthesized into liquid

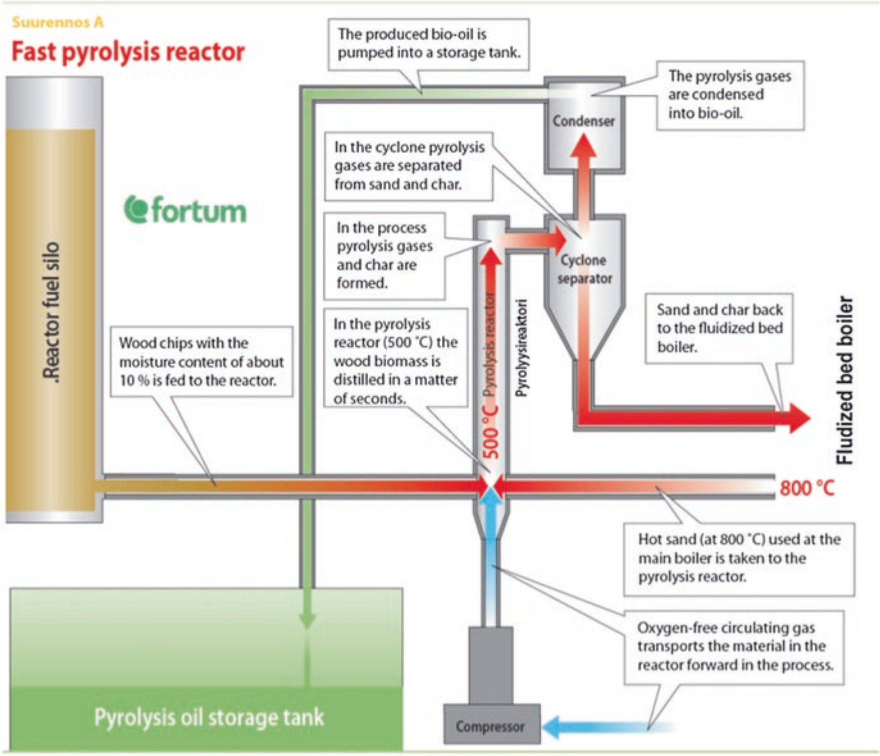

Fig. 4 Schematic of the Fortum Otso® bio-oil plant. Copyright Fortum

fuels and chemicals. A portion of the syngas reacts with a commercially available catalyst to produce methanol, which can either be sold as an end product or used as a chemical intermediate to form other products. To produce ethanol, methanol reacts with carbon monoxide from the syngas with a commercially available catalyst to produce methyl acetate. The final conversion step in the ethanol production process entails splitting the methyl acetate by inserting a hydrogen molecule that is also extracted from the produced syngas. The resulting ethanol is then distilled in a final refining step to improve product quality.

3.1 Bio-Oil Production, Separation, and Upgrading

Pyrolytic vapors upon their condensation in condensers form bio-oil. Bio-oils have a dark brown color and a complex structure and may contain a wide range of organic compounds including aromatic hydrocarbons, phenol derivatives, ketones, esters, ethers, sugars, amines, alcohols, furans, and water. The bio-oil has a H/C molar ratio higher than 1.5 (Guedes et al. 2018; Isahak et al. 2012). This composition results in

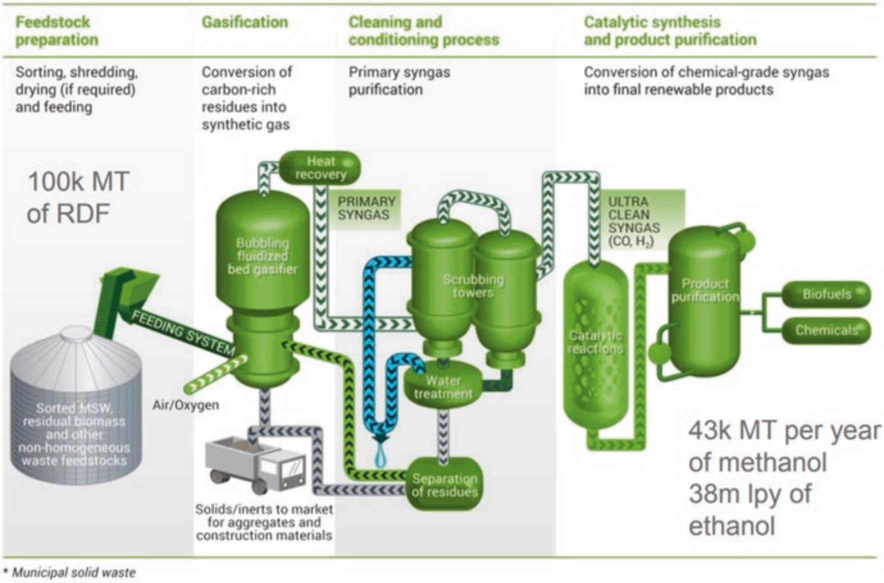

Fig. 5 Schematic Enerkem Alberta Biofuels plant for methanol and ethanol production from municipal solid waste. Copyright Enerkem Inc.

a significant oxygen content in bio-oils, which needs to be reduced in order to use the oil product for most applications. Bio-oils can have many application areas including their direct use as fuels in boilers. After upgrading, the oil can be used to produce fuels and bulk chemicals (Guedes et al. 2018). Partly deoxygenated bio-oil may be used as a feed for gasoline and diesel production in a conventional oil refinery and thereby provide a renewable transportation fuel.

Several types of condenser units have been tested for bio-oil collection, including a simple condenser chamber filled with isopropanol (Trinh et al. 2013), ethanol, ethyl acetate (Asadieraghi and Wan Daud 2015), but also two condensers or even a condenser train (Zhang et al. 2012; Jae et al. 2014). More advanced condensing systems may include spray condensers, where cooled recirculated condensed bio-oil can be used to condense the pyrolysis oil. Droplets escaping from the different condensers can be captured and collected with an electrostatic precipitator (ESP) (Palla et al. 2015; Hossain et al. 2013; Mante and Agblevor 2011). Wet electrostatic precipitation has proved itself over many years at the gasification plant in Harboøre, Denmark (Ahrenfeldt et al. 2013), and so has oil scrubbers, which have been validated in the OLGA process by ECN (Boerrigter et al. 2005). It has also been demonstrated that the bio-oil composition can be controlled by the condensation temperature. Thus sequential condensation may result in a fractionation of the produced bio-oil and carry a positive effect in terms of energy efficiency (Chang et al. 2012; Westerhof et al. 2011).

The direct application of untreated bio-oil within existing infrastructure is impeded by its high oxygen content (17–50 wt%) and acidity (pH = 2.5–3). This composition results in undesirable properties such as low heating value, immiscibility with hydrocarbon fuels, thermal and chemical instability, high viscosity, and corrosiveness (Milina et al. 2014). Upgrading of bio-oils and reduction of the rather high oxygen content are hence required and can be done in a number of ways, such as hydrotreatment and catalytic deoxygenation, while other upgrading methods involve supercritical water processes or catalytic cracking and may be used to increase heating value or for the production of chemicals (Isahak et al. 2012).

Upgrading of hot pyrolysis vapors at atmospheric pressure using in situ catalytic measures is one of the most promising processes to produce enhanced bio-oils from biomass pyrolysis. Zeolite cracking is one of the attractive processes within this category due to process simplicity, no requirement for pressurized operation, and no need for add-in of hydrogen or other compounds (Mortensen et al. 2011). By coupling a pyrolysis unit directly to a hot catalytic reactor based on a zeolite, a relatively simple system can be provided, which can produce a high-quality low-oxygen hydrocarbon liquid product. Studies on atmospheric catalytic biomass pyrolysis combined with zeolite upgrading have been performed using different setups. Microscale fixed bed batchwise laboratory equipment using a mixture of catalyst and biomass (Mochizuki et al. 2013; Yu et al. 2012; Ma et al. 2014), fluidized bed with a feed mixed with catalyst (Jae et al. 2014), and continuous pyrolysis reactors directly coupled with a separate reactor for catalytic gas-phase deoxygenation (Zhou et al. 2016; Carlson et al. 2009; Patwardhan et al. 2011). The latter system type will probably be the most efficient for commercial systems. Recently there has also been development into zeolite-based upgrading of gasification producer gas, but this development has not progressed as far as pyrolysis gas upgrading.

Several other methods for deoxygenation of pyrolysis oil are also under development. However, most of these methods are based on processes operating at high pressure such as the hydrodeoxygenation (HDO) process (more than 20 bars). They often consume large amounts of hydrogen (Mortensen et al. 2011) which in return results in higher bio-oil yields. Jointly, HDO and zeolite cracking are referred to as catalytic bio-oil upgrading, and these could become routes for production of second-generation biofuels in the future (Zwetsloot et al. 2015).

4 Char and Ash

Pyrolysis and gasification generate gaseous, liquid, and solid products, namely, chars and ashes. In general, char is considered as the main product of pyrolysis, whereas gas is the main product of gasification, but in both cases all fractions are present in variable amounts. In the optic of a circular economy, all the process products and by-products should find use in order to minimize the waste streams and increase product and process value. Particularly, chars and ashes offer several options for being recycled in an efficient and sustainable way thanks to their chemical and structural properties. For example, they maintain most of the inorganics contained in the feedstock, including valuable elements such as phosphorus. Depending on the process conditions, char can have interesting surface properties such as developed porosity and large specific surface area, suggesting various technical applications. It is important to mention that residual char from pyrolysis and gasification could as well be used as biochar for soil amendment, remediation, and carbon sequestration, if the required quality and toxicity standards are satisfied, as specified by the European biochar guidelines or the International Biochar Initiative (European Biochar Foundation (EBC) and Arbaz 2016; International Biochar Initiative 2015).

The difference between pyrolysis char and gasification char or ash is the reduction in carbon content induced by the additional gasification reactions taking place during the last stage of the gasification process (Fig. 6).

During pyrolysis the feedstock is carbonized: volatiles are released, and a large part of the mass and energy potential is left as mineralized (fixed) carbon. During gasification, fixed carbon reacts with a gasification agent (e.g., H_2O or CO_2) at elevated temperatures. In most gasification processes, the carbon conversion is incomplete, and the solid residues appear black, attesting the presence of a significant carbon fraction.

The characteristics and possible applications of chars and ashes are very process-specific, as they are heavily influenced by the operating conditions of the feedstock conversion (e.g., temperature, pressure, residence time). With this in mind, repurposing of char and ash can be conceived in two ways: on-site, in the frame of a biorefinery, a system which integrates thermal conversion of feedstock with other processes, or as a commodity to be sold and used elsewhere. In the following, some of the possible solutions for the recycling of the solid residues of pyrolysis and gasification are described and discussed.

4.1 Direct (On-Site) Valorization of Char

A particularly convenient application of residual char within the system is the treatment of gasification producer gas for the removal of tar and other contaminants. The advantages would be manifold: char is continuously produced on-site and readily available and could offer a convenient alternative to costly metal-based catalysts. If

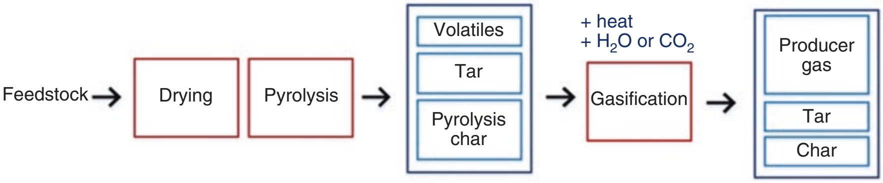

Fig. 6 Schematic of pyrolysis and gasification processes and products

the material gets deactivated as effect of poisoning or coking or adsorption saturation, it is possible to gasify it along with fresh feedstock.

Char-based tar removal can be carried out by physical adsorption from the gas phase (physisorption), or by using the char as a catalyst or tar reforming enhancer. In the case of physisorption, char is able to clean producer gas through filtering in the temperature range 150–250 °C. Higher temperatures would reduce the adsorption capacity of char, whereas lower temperatures could cause unwanted condensation of the tar species.

Mastral et al. (2001, 2003, 2004) investigated thoroughly the adsorption of PAHs from gas phase by using a variety of different activated carbons (ACs). They concluded that the porous structure of the adsorbent is determinant: the optimal AC should be rich in micropores (pores smaller than 2 nm), but the presence of larger pores, up to 50 nm (mesopores), is also important, especially for the adsorption of larger molecules (phenanthrene, pyrene). Similar conclusions were found also by Hu et al. (2007). Thus, if char is to be used as adsorbent, its porous structure should be somehow optimized for the tar mixture, which is to be removed.

The effectivity of biomass chars in the decomposition of tars has been observed in several studies (Boroson et al. 1989; Dabai et al. 2014; Matsuhara et al. 2010; Al-Rahbi et al. 2016; Zhang et al. 2015) within the temperature range 450–850 °C. If the contact between the char surface and the producer gas takes place at temperatures higher than 600 °C, cracking and reforming of tars into stable gases (H_2, CH_4) can be assisted. The most accredited mechanism for the decomposition of aromatics over the surface of char involves dehydrogenation and carbon deposition over the char surface (coking) (reaction 1).

$$\mathrm{C}_n\mathrm{H}_m = \mathrm{C}_n\mathrm{H}_x + m - x/2\mathrm{H}_2 \tag{1}$$

The reaction occurs mainly in the micropores, which can easily be blocked by coking in absence of a gasifying agent. However, in the presence of H_2O or CO_2, gasification reactions of solid carbon (2 and 3) are able to “clean up” or regenerate the micropores, maintaining the activity of char for a longer time.

$$\mathrm{C}_{(s)} + \mathrm{H}_2\mathrm{O} = \mathrm{CO} + \mathrm{H}_2 \tag{2}$$

$$\mathrm{C}_{(s)} + \mathrm{CO}_2 = 2\mathrm{CO} \tag{3}$$

Indeed, according to Hosokai et al. (2008), the activity of char for the decomposition of aromatics can be maintained if the gasification rate is higher than the rate of carbon deposition. With this in mind, it is possible to imagine an actual integration of a char-based cleaning system in gasification, where char is used as a substrate for gas cleaning and upgrading. However, it is important to design and dimension the gas cleaning step so to guarantee its sustainability: the char bed should not be quickly deactivated nor quickly gasified away.

As an example, the two-stage gasifier (known as "Viking") developed at DTU Risø is able to produce an almost tar-free gas, thanks to the passage of the producer gas through a bed of hot char (Brandt et al. 2000).

The use of char could also assist the removal of other undesired substances present in producer gas such as sulfur compounds. Hervy et al. (2018) studied the adsorption of H_2S on the surface of pyrolysis chars obtaining promising results, which were significantly improved after steam activation of the original chars.

In the frame of a biorefinery concept, the properties of biochar could also be exploited to adsorb ammonium (NH_4^+), ammonia (NH_3), and phosphates for manure/sewage sludge/biogas fiber treatment plants. Naturally occurring characteristics of biochar make it very suitable for the adsorption of organic molecules, but it might need to undergo functionalization to be used as an effective adsorbent for cationic and anionic pollutants, such as ammonium and phosphate.

Negatively charged oxygen groups on the surface of chars are responsible for ammonium retention. According to Wang et al. (2015a), oxidation of biochar (preferably through natural aging) is useful to improve the adsorption capacity of ammonium and cations in general. On the other hand, recent studies focused on impregnation of biochars with metals to improve the adsorption of anions (Wan et al. 2017; Wang et al. 2016). Biochar modification methods for optimized adsorption of various contaminants have been comprehensively reviewed by Sizmur et al. (2017).

Biochar has been found suitable for uptaking NH_3 (Asada et al. 2006; Taghizadeh-Toosi et al. 2012a), with reported uptakes ranging from <1 to over 60 mg/g biochar (Seredych and Bandosz 2007).

The application of biochar for adsorption of nutrients is, of course, useful to control eutrophication but could also help the recycling of nitrogen and phosphorus. Indeed, Taghizadeh-Toosi et al. (2012b) demonstrated that nitrogen taken up by biochar is plant available. Similar findings were reported for phosphorus (Zhang et al. 2016). As a consequence, biochar could be used to prevent nutrient leaching and then applied as a slow-release fertilizer (Vikrant et al. 2017), concurrently acting as a carbon sequester.

However, it is important to keep in mind that the physical and chemical properties of char—and biochar—are highly variable. Thus, to take advantage of these multiple benefits, it will be necessary to carefully "design" char production and if necessary post-treat it with impregnation or oxidation to guarantee the characteristics required by specific applications.

4.2 By-Products with Added Value: Repurposing Char and Ash to Active Carbon and Fertilizers

Chars and ashes from pyrolysis and gasification may also be sold as renewable substitutes for industrial products such as fertilizers for agriculture and active carbon for industry and remediation.

4.2.1 Fertilizer Value of Ashes and Chars from Thermal Biorefinery Processes

In an ideal biorefinery encompassing thermal processing of nutrient-rich feedstocks, the majority of the organic fractions of the converted biogenic material are utilized to produce, e.g., chemicals, fuels, or materials, while nutrients are preserved in a plant-available form in the ashes or chars. This will allow for recycling of the nutrients back into the system where the biogenic material originated from, closing nutrient loops, and increasing the level of long-term sustainability. In addition, the thermal process may allow for removal or reduction of heavy metals and destruction of organic xenobiotics. The most valuable nutrient to recover in this way is phosphorous (P). P is an essential macronutrient, and the main source for P fertilizer is mined phosphate rock, which is a critical nonrenewable globally demanded resource. There is an increasing concern about the commercial availability and cost of phosphate rock in the near future (Cordell and White 2014). With the proper match between thermal process design and operation, fuel characteristics and end use, it may be feasible to dispatch biorefinery and waste refinery technology to close, e.g., phosphorus loops in modern society while also produce high-quality products and reduce toxicity and risk issues as illustrated in Fig. 7 (Zwetsloot et al. 2015; Thomsen et al. 2017a, b; Klinglmair et al. 2015; Wang et al. 2015b).

The characteristics and potential fertilizer value of chars and ashes vary with the characteristics of the converted fuel, the thermal process design, the operational parameters, the post-process treatment (if any), the end use, and the overall match between these different aspects. An illustration of such solid P-rich residuals is provided in Fig. 8, showing variation in color, morphology, and particle size distribution of six potential fertilizer substrates originating from six different thermal treatments of the same sewage sludge sample (Thomsen et al. 2016, 2017b).

When considering application of chars or ashes as fertilizer and/or soil enhancer, it is essential to optimize key characteristics including nutrient content and composition, organic/inorganic toxicity, pH, nutrient fertilizer quality, carbon content, and other biochar-related characteristics (e.g., water retention).

The nutrient content and composition varies greatly with the fuel composition and temperature profile of the thermal process. In general, low temperatures, low heating rates, and short retention times will increase nutrient recovery in ash and char fractions.

Content of organic pollutants in pyrolysis char and gasification ashes in the form of PAHs have been investigated several times. Total PAH content in cyclone ashes from low-temperature gasification of straw, dry chicken manure fibers, dry pig manure fibers, digested pig manure fibers, and sewage sludge has previously been found to range from 0.2 to 6.2 mg/kg (Thomsen et al. 2016; Nielsen 2007; Stoholm et al. 2002). In a study on the influence of the thermal process design on PAH content in chars and ashes from sewage sludge conversion, it was found that no PAHs persisted in bottom ash from low-temperature gasification, while small amounts persisted in the cyclone ashes from the same process and in incineration ashes from a full-scale fluid bed sludge incineration facility. Significantly larger amounts were found in ashes from two-stage downdraft gasification and slow pyrolysis of the same material (Thomsen et al. 2016).

Heavy metal content also varies with the composition of the converted material, the design of the thermal process, the operation parameters, and the type of ash product. Filter ash will often contain more volatile heavy metals than cyclone ash, fly ash, and bottom ash, while bottom ash may contain more thermally stable heavy metals than the other ash fractions (Thomsen et al. 2017a). Heavy metal concentrations in a set of different ashes and chars from conversion of biomass and sewage sludge are provided in Table 1.

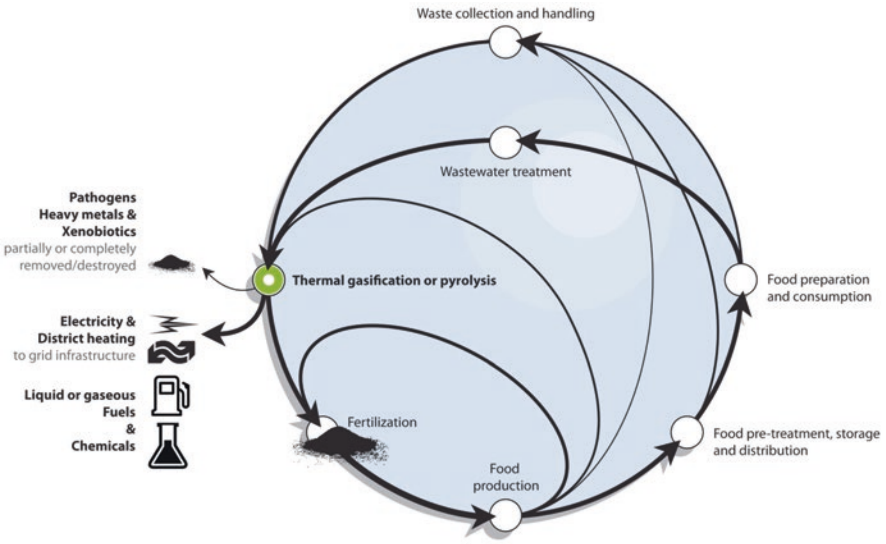

Fig. 7 Closing phosphorus loops in a modern society using biorefinery and waste refinery technology encompassing thermal processes (Thomsen et al. 2016)

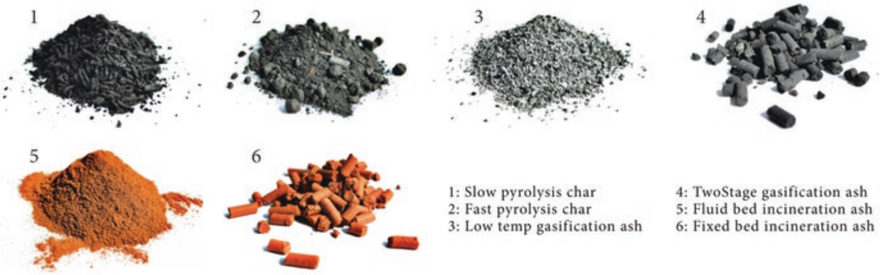

Fig. 8 Char and ash fertilizer substrates from thermal conversion of the same sewage sludge sample. Adapted from Thomsen et al. (2016)

Table 1 Content of selected heavy metals in ashes from thermal conversion of various fuels in a range of different conversion technologies

Fuel and reference	Ash/char product	Thermal plant	Cu	Zn	Cd	Ni	Cr	Pb
			mg kg^{-1}					
Wheat straw (Müller-Stöver et al. 2012)	Cyclone/fly ash	Low-temperature gasification	31	160	<1	48	100	<10
Citrus peel fiber residues (Müller-Stöver et al. 2012)	Cyclone/fly ash		12	60	<1	34	<100	20
Digested pig manure fibers (Nielsen 2007)	Cyclone/fly ash		350	1900	2	57	22	13
Danish sewage sludge (Thomsen et al. 2017b)	Cyclone/fly ash		380	1906	4.5	158	182	106
Danish sewage sludge (Thomsen et al. 2017b)	Bottom ash		591	1636	2	67	182	159
Danish sewage sludge (Thomsen et al. 2017b)	Grate ash	Two-stage downdraft gasifier	804	2226	1	124	165	47
Danish sewage sludge (Thomsen et al. 2017b)	Char	Slow pyrolysis	458	1617	4	47	135	109
Danish sewage sludge (Thomsen et al. 2017b)	Fly ash	Full-scale fluid bed incineration	769	2567	6	105	127	210

Db dry basis

In addition to toxicity, the fertilizer quality of the nutrients in the char or ashes is also very important. Fertilizer quality relates to the mobility and plant availability of the nutrients. This is usually determined by plant growth experiments in pots, small field plots, or large field plots. Approximations of the mobility of nutrients can also be attempted by incubation of soil and fertilizer substrate with subsequent nutrient extraction using a variety of procedures (Wüenscher et al. 2015; Wünscher 2013). Proper quantification of fertilizer quality is a very complex issue, and several factors influence the results of the assessment. These factors include (but are not limited to):

- The chemical composition and nutrient speciation in the substrate (Thomsen et al. 2017b)
- The liming effect of the substrate (Jakobsen and Willett 1986; Li et al. 2017)
- The structure, composition, and pH of the soil (Li et al. 2017)
- The particle size distribution of the substrate (Thomsen et al. 2016)
- The type of plant applied (plant growth experiments) (Pearse et al. 2007; Kalaji et al. 2014)
- The type of extraction method used to extract nutrients from soil or plant after the incubation or growth period (Wüenscher et al. 2015; Wünscher 2013)
- The temporal scope of the investigation (Thomsen et al. 2016)
- Nutrient dosage (Thomsen et al. 2017a; Müller-Stöver et al. 2012; Li et al. 2017; Six et al. 2012; Mackay et al. 2017)

- Limiting effects of deficient levels of macro- and micronutrients not examined in the study (Schmidt et al. 2016; Guo et al. 2016; Wang et al. 2015c)

Despite the complexity of plant-substrate-soil-climate interactions, it is possible to obtain useful indications about a substrate fertilizer quality with relatively simple measures. This may be done in a screening measure by incubating substrate/soil mixtures with high moisture levels and subsequently extract the investigated nutrients (e.g., P) from the incubated mixture using different methods (Wüenscher et al. 2015; Six et al. 2012; Nuernberg et al. 1998; Sibbesen 1983). An example of such screening of P fertilizer quality in a range of pyrolysis char and incineration ash substrates is provided in Fig. 9 (Thomsen et al. 2016).

The results (Fig. 9) show P fertilizer quality compared to a commercial P fertilizer with 100% mineral P. The variation in the results is substantial among different fuels as well as between char and ashes from the same fuels. In general, the different substrates show a substantially lower P fertilizer quality than the commercial P fertilizers with only two exceptions (beet seed ash and tomato residue ash). However, the results are from a 1-week incubation study and not representative for the full fertilizer potential obtained in full plant growth cycles. Short-term incubations are good for relative comparison between comparative samples, but the method often underestimates the fertilizer potential of char and ash substrates compared to mineral references. This is due to a double effect where the mineral fertilizer is fixed over time by soil particles in real plant growth systems while immediately inaccessible P substrates are solubilized over time in the same systems. In combination with other results from the published literature, it is emphasized that fuel characteristics and design and operation of the thermal process as well as the design of the

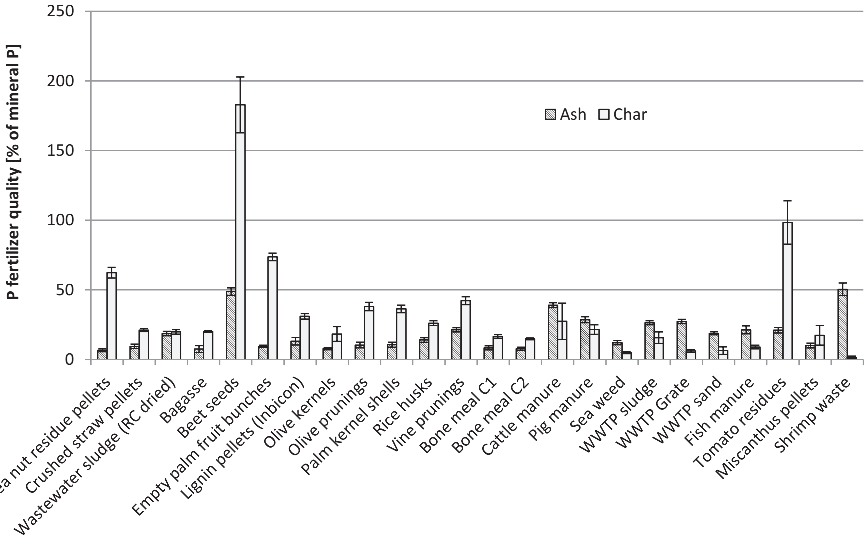

Fig. 9 Anion exchange resin extractability of phosphorus in incubated char and ash samples from the low-temperature gasification fuel screening

plant growth system severely influence the fertilizer quality measures of solid residuals from thermal biorefinery processes. For further results, see, e.g., Zwetsloot et al. (2015), Thomsen et al. (2017a, b), Müller-Stöver et al. (2012), Jakobsen and Willett (1986), Qian and Jiang (2014), Mellbye et al. (1982), Bierman and Rosen (1994), Kumpiene et al. (2016), Hossain et al. (2015), Song et al. (2014), Hansen et al. (2016), Kuligowski et al. (2012), and Kuligowski (2009).

Biochar contains a very large organic fraction, consisting primarily of highly recalcitrant carbon. Some of the most important physical characteristics of biochar are the total surface area, porosity (nano- and macro-), density, particle size, stability, mineral content, residual oils and tars, and surface chemistry and sorption properties. There have been substantial amounts of research done on biochar production, characteristics, and use in recent years, and much of it is available in the published literature, e.g., Bruun et al. (2014), Kizito et al. (2015), Van Wesenbeeck et al. (2014), Zielińska et al. (2015), Hossain et al. (2011), and Lehmann et al. (2011). In addition to potential nutrient release, chars or carbon-rich ashes also hold the potential to enhance soil structure and soil quality and sequester carbon for a very long time. In this way, these residual products may contribute to the mitigation of climate change while also enhancing the productivity and quality of the soil in which the char (biochar) is amended.

When amending biochar or gasification biochar, the recalcitrant carbon fraction remains unconverted in the soil for a very long time, and this positively affects the carbon balance. In a LCA study by Sigurjonsson et al. (2015), it was concluded that due to the fertilizing effect and content of recalcitrant carbon in cyclone ash from low-temperature gasification of cereal straw, a system with straw gasification and recycling of the ashes to soil could deliver carbon-neutral and even carbon-negative energy, depending on the carbon content in the ashes (Sigurjonsson et al. 2015). The stability of carbon in gasification biochar from straw gasification was investigated in a study by Hansen et al. (2015). It was found that after 110 days of incubation of ashes and dry straw in soil, about 3% of the ash carbon was respired as CO_2, while 80% of the carbon from a straw reference was respired. The structure of the ash was also investigated and was found to have a high porosity and specific surface area, which was proposed as key quality parameters in regard to improvements of soil structure and the soil ability to retain nutrients and water (Hansen et al. 2015).

4.2.2 Activated Carbon

Activated carbons (ACs) are industrially produced through carbonization followed by chemical and physical activation. The activation process is controlled and optimized to produce the desired pore structure and surface area for specific adsorption applications. The specific surface area of ACs ranges from 500 to 2000 m^2/g and the pore volume from 0.20 to 0.60 cm^3/g (Marsh and Rodríguez-Reinoso 2006). ACs are largely used for removing contaminants from liquids and gases: their global demand can be expected to reach 2.1 million metric tons in 2018 (Maneerung et al. 2016). As a consequence, cheaper precursors or substitutes for ACs such as residual biomass char could help decrease the costs and encourage the utilization of this material. Pyrolysis and gasification are not optimized for producing AC; however, under certain operating conditions, the properties of these chars can be comparable to AC in terms of surface area and pore volume.

Surface properties of pyrolysis char depend on the charring temperature, on the retention time, and on the feedstock. As an example, Keiluweit et al. (2010) observed that the surface area of wood char produced at either 100 or 700 °C changed from 1.6 to 347 m^2/g, with significantly higher values in comparison with straw char, which ranged from 1.8 to 139 m^2/g at the same charring temperatures. Liu et al. (2011) focused on the effect of retention time and found it to be a determining factor for the development of a large surface area and a consequently improved phenol adsorption capacity.

Pyrolysis chars do not undergo gasification reactions thus have generally a lower surface area and a less developed porosity in comparison with gasification chars. The fundamental steps of the gasification process (drying, pyrolysis, and gasification) are somehow comparable to the production phases of AC. However, the properties of gasification chars are variable and strongly dependent on the process conditions. Hérnandez et al. (2016) operated a lab-scale gasification reactor under different conditions and always obtained a solid residue with a specific surface area below 70 m^2/g. Klinghoffer et al. (2012) produced gasification char with a surface area ranging from 429 to 687 m^2/g, which increased with temperature and reaction time. The specific surface area of residual chars from four different small-scale gasifiers was found to range between 78 and 352 m^2/g (Benedetti et al. 2018). On the other hand, residual char from pilot-scale, two-stage gasification of wood was reported to be around 1027 m^2/g (Hansen et al. 2015). According to Benedetti et al. (2018), char with a larger specific surface area is produced in two-stage gasifiers, where pyrolysis and gasification are performed separately, and the burn-off of the pyrolyzed material is better controlled. If the conversion process is designed to produce a solid product of reasonable quality, it could be possible to use it directly as a substitute for active carbon, without further activation. Indeed, Runtti et al. (2014) tested gasification char with and without chemical activation for adsorption of metals (iron, copper, and nickel ions). In all cases, chars performed better than commercial ACs.

Nonetheless, oftentimes gasification char does not have a specific surface area as large as industrial AC, but it can be a good precursor for AC production. Promising results in this sense were reported by Kilpimaa et al. (2015) and Maneerung et al. (2016). They tested physically activated char from gasification for adsorption of nitrate and phosphate and dye (Rhodamine B), respectively, from aqueous solutions. Galhetas et al. (2014) focused on adsorption of caffeine and acetaminophen on K_2CO_3-activated gasification char, which performed comparably or even better than commercial AC.

ACs are often employed for wastewater treatment, thanks to their good adsorption capacity toward a number of contaminants. Again, pyrolysis and gasification chars could substitute AC produced for this purpose: Ahmad et al. (2014) and

Rosales et al. (2017) are authors of comprehensive reviews on the application of char as sorbent for contaminants in soil and water.

Water purification can also be performed by using biologically active carbon (BAC). Conventional and advanced water treatment systems use AC filtration: granular AC gradually becomes saturated with microorganisms and organic/inorganic matter, developing a rough and porous surface that can be favorable for bacterial colonization forming a biologically active film (biofilm). The biofilm is capable of biodegrading a significant fraction of waterborne nutrients, organic matter, minerals, and microorganisms (Simpson 2008). In a recent study by Dalahmeh et al. (2018), biochar filters with active biofilm were found to be more efficient than sand filters in removal of organic matter and nitrogen; in addition, biochar was able to efficiently remove pharmaceutically active compounds in sewage facilities.

Porous materials such as AC and similar materials can also be used for carbon capture and storage (CCS) to mitigate the risks and impacts of climate change. Indeed, large specific surface area and a microporous structure of char can be favorable for the adsorption of CO_2 emissions. For this application, Madzaki et al. (2016) tested residual char from sawdust gasification with positive results, measuring capture capacities of 0.47 kg CO_2/kg biochar and 0.30 kg CO_2/kg biochar at 30 and 70 °C, respectively. Gasification char was also tested by Benedetti et al. (2017) for CO_2 capture.

5 System Integration

Gasification and pyrolysis of biomass can be integrated with a number of processes in larger systems or biorefineries to improve the overall system performance. A biorefinery approach typically improves performance parameters related to energy efficiency and carbon efficiency but also system flexibility in terms of, e.g., feedstock flexibility or product flexibility (polygeneration).

The following two integration opportunities will be discussed in this section, as they could be very important in future energy systems based on renewable energy:

- Integration with water/steam electrolysis
- Integration with anaerobic digestion

The integration of pyrolysis and/or gasification with water/steam electrolysis in biorefineries or biofuel production plants enables storage of electricity from renewables as chemical energy bound in the produced fuel, feed, or chemical. Furthermore, the integration typically enables a doubling of the product output per biomass input, because a hydrogen deficit is usually limiting the production and the required hydrogen can be provided from the electrolysis cells (Clausen 2015).

The integration with anaerobic digestion has many benefits. In this section, focus is put on the system integration part, showing that even very wet digestate from anaerobic digestion can be converted in systems based on gasification or pyrolysis with high energy efficiency.

5.1 Integration with Water/Steam Electrolysis

By integrating water/steam electrolysis in a biorefinery based on gasification or pyrolysis, a highly flexible and energy-efficient system can be made. An overall diagram of such a system or biorefinery can be seen on Fig. 10. Such a biorefinery could be highly relevant in a future renewable energy system because it can (1) perform electricity grid balancing by storing electricity as chemical energy when the electricity demand is low and then produce electricity from input biomass when the electricity demand is high; (2) produce renewable fuels for the transportation system, providing also an indirect electrification of the transportation sectors where direct electrification is difficult, such as aviation, shipping, and heavy goods transport; and (3) produce bioash/biochar for agriculture in order to recycle nutrients and provide soil improvement and carbon sequestration.

Besides providing electricity storage, the integration with electrolysis can circumvent the need of an oxygen production plant, as by-product oxygen from electrolysis can be used for gasification (Fig. 11a). In biorefineries, steam electrolysis will typically be preferred over liquid water electrolysis from an energy perspective, because waste heat generated within the biorefinery can be used to raise steam for electrolysis (Fig. 11b). Furthermore, when also integrating biomass steam drying (Fig. 11c), the system will be able to handle biomasses with a very high water content such as mechanically dewatered sludge or manure without a decrease in energy efficiency (Clausen 2017).

Besides the advantages with steam electrolysis highlighted above, it is important to note that when using solid oxide electrolysis cells (SOEC) for steam electrolysis, the same cells can be used for reversed operation as solid oxide fuel cells (SOFC) (Jensen et al. 2015; Gadsbøll et al. 2017). The system displayed in Fig. 11b could in this way operate as shown on Fig. 12.

Combining biomass gasification with solid oxide cells (SOEC/SOFC) and biofuel synthesis is therefore one way of compiling a biorefinery that has the characteristics shown in Fig. 10. Another promising way of integrating electricity from fluctuating renewable energy sources in biorefineries is by high-temperature electric heating of, e.g., gasification or reforming processes (Spagnolo et al. 1992). If carefully integrated, high-temperature electric heating can be a cheaper and more

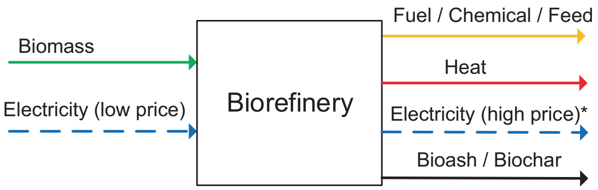

Fig. 10 Diagram of a biorefinery based on gasification or pyrolysis integrated with water/steam electrolysis. (Asterisk) The electricity output can be produced by a heat engine or by a reversible electrolysis system (e.g., solid oxide cells)

energy-efficient way of integrating electricity. The potential electric input that the biorefinery can absorb efficiently is however typically lower than by electrolysis because only energy is supplied by electric heating, whereas electrolysis supplies a mass flow of hydrogen.

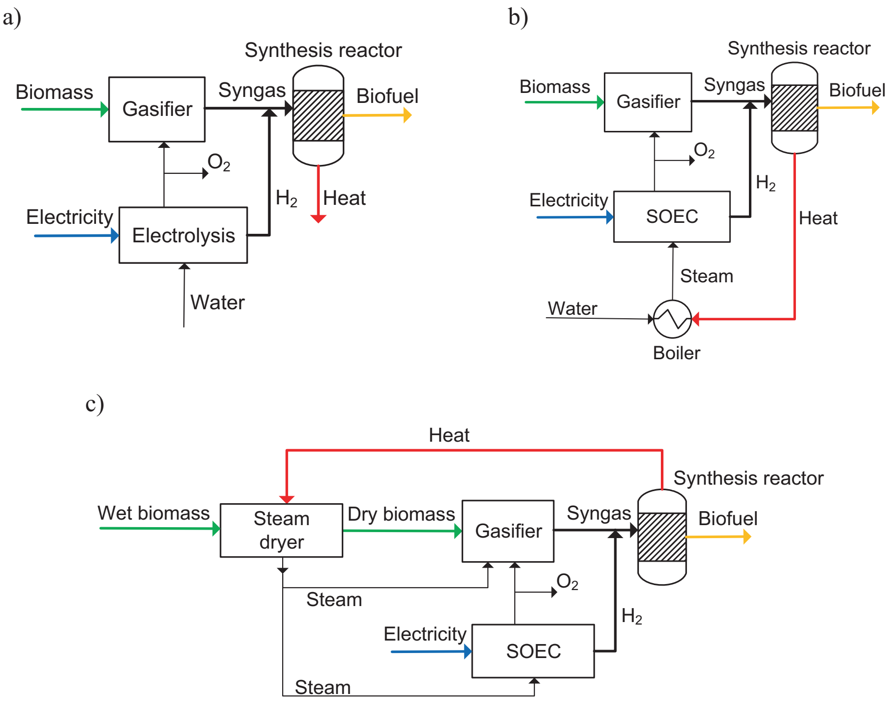

Fig. 11 Simplified biorefinery flowsheets based on biomass gasification and water/steam electrolysis. (**a**) Integration with liquid water electrolysis, (**b**) integration with steam electrolysis (SOEC = solid oxide electrolysis cells), (**c**) integration with steam electrolysis and steam drying of biomass to enable energy-efficient conversion of wet biomass. Note that the gasifier produces bioash/biochar although not shown on the figures

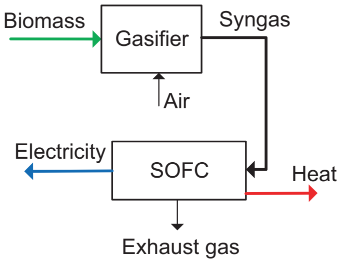

Fig. 12 Simplified flow sheet showing how the system from Fig. 11b could operate to produce electricity by operating the SOEC as an SOFC

5.2 Integration with Anaerobic Digestion

An energy-efficient integration of gasification and anaerobic digestion could turn out to be an important stepping-stone for biomass gasification because a cheap or perhaps free fuel in the form of digestate is available. If the gasification process can produce a high-quality bioash or biochar product for agriculture, this product could have a much higher value than the input digestate. The energy product from such a conversion would then only improve the economy of such a conversion plant. In contrast to this is wood-based gasification, which has a much greater potential in terms of worldwide feedstock availability and ability to supply large-scale conversion plants but suffers from higher feedstock cost and limited fertilizer value of the output bioash because of a low content of nutrients in wood.

Figure 13 shows a simplified flowsheet of an integrated system combining anaerobic digestion and gasification (Clausen 2017).

By combining gasification and anaerobic digestion, it will be possible to mineralize nitrogen in the anaerobic digester and thereby minimize the nitrogen loss in the gasifier. The main nitrogen flow will leave as ammonia with the liquid fraction after the mechanical dewatering (Fig. 13). However, recovering nitrogen as fertilizer is not as important as recovering phosphorous, as nitrogen is not a limited resource.

The integrated system from Fig. 13 would only be relevant for large-scale digesters due to complexity and size of the plant. Small-scale digesters could instead be integrated with an energy-efficient drying of the digestate and then send the dried digestate for further processing at a large-scale biorefinery. If combined with the system from Fig. 13, the dry digestate could be fed in as "dry biomass" to the gas-

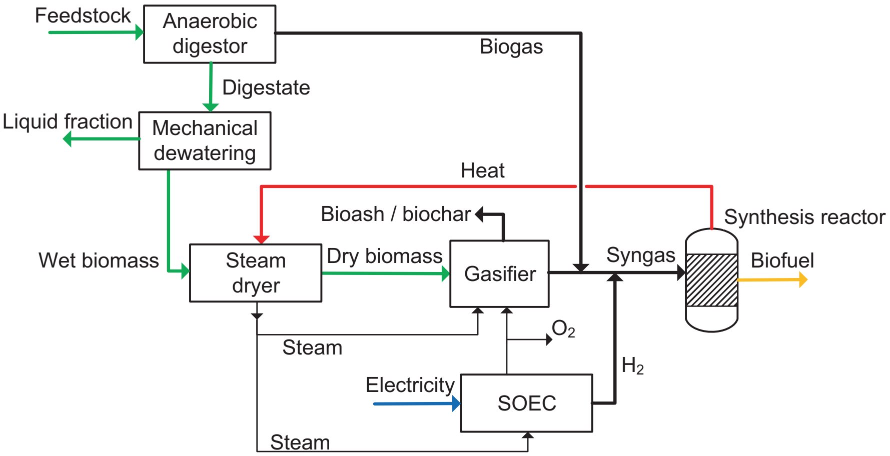

Fig. 13 Simplified flowsheet of an integrated system based on anaerobic digestion and gasification. The system is based on the system shown in Fig. 11c

ifier. An energy-efficient drying could be achieved by an integrated system combining steam drying and mechanical vapor recompression (MVR) (see Fig. 14).

6 Conclusions

Biomass pyrolysis and gasification processes are versatile processes which may provide substantial contributions to modern biorefinery concepts and energy systems. The purpose of this chapter has been to give an introduction to the current state-of-the-art, recent research and development efforts and classic challenges related to integration and operation of these technologies. The chapter focuses on key aspects and novel solutions which may become relevant in order to increase the utilization of biomass pyrolysis and gasification and make it commercially interesting in future energy systems.

The versatility of the thermochemical conversion platform is essential in a biorefinery context, especially when moving from high-quality biomass resources into low-quality organic secondary resources. Highly efficient utilization of these globally available resources is commercially and politically interesting because of its potential value from an economic, environmental, and resource political point of view. The combination of intelligent fuel design and specially designed thermochemical co-conversion systems for valorization of problematic residual resources could contribute greatly to increase the economy and the level of sustainability in the agricultural sector, waste handling sector, and transport sector.

Future development of thermochemical biorefinery processes will be fostered by the desire for a circular economy. All products and by-products from pyrolysis and thermal gasification should find use in order to minimize the waste streams and

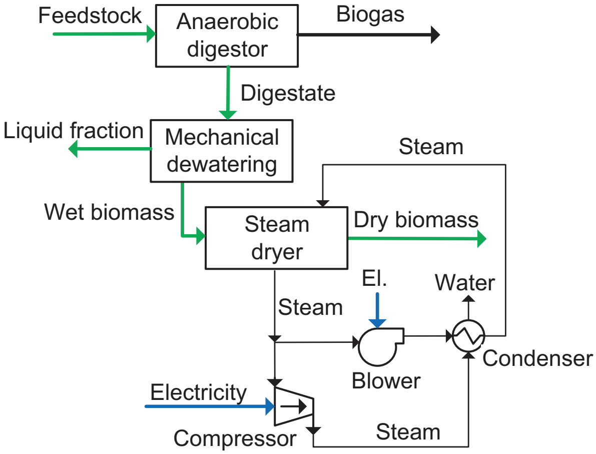

Fig. 14 Flowsheet of an integrated system for drying of digestate using steam drying and mechanical vapor recompression (MVR)

increase product and process value. Particularly, chars and ashes offer several options for being recycled in an efficient and sustainable way thanks to their chemical and structural properties. Some of the options mentioned in the chapter include the use of biochar as active carbon or for soil amendment, remediation, and carbon sequestration.

New biorefinery concepts with pyrolysis and gasification stages may benefit from further development in enhanced process integration schemes, combinations of different technologies and new polygeneration strategies. Such development is required to maximize total system product yield and value, increase the overall process efficiency, improve the economic viability, and overcome the operational challenges that the technology is facing in individual systems.

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