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Torrefaction: Process Review

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Abstract

There is an urgent need for replacement of fossil fuels worldwide. Raw biomass has a low energy density, contains too much moisture, can rot, and it is hygroscopic. This paper presents a very prominent thermal technology that could overcome mentioned deficiencies of raw biomass. This technology is known as torrefaction. Torrefaction is mainly used to convert lignocellulosic materials into 'fuels' that can be used in power plants, combustion units, or gasifiers.

Keywords

torrefaction, biomass, biofuels, biochar

1 Introduction

Energy crisis is a consequence of great amount of burden on world fossil fuel supply and reserve. The growth of fossil fuels cost in the past, clearly designated that biomass-based fuels could be more competitive during peak demand times. Also, growing concern over climate change is another issue that has emphasized the environmental advantages of biomass application [1, 2].

Biomass can offer a wide range of suitable feedstock for energy, metallurgical, and chemical industries. Carbonization of biomass as a method for production of solid fuels has been present for many thousands of years. It delivered charcoal, the first appropriate solid fuel and a feedstock for iron extraction later. The process of torrefaction has been used for tea and coffee making. However, in recent years this process attracted the attention of power industries for the production of a coal substitute from biomass. Torrefaction is very often used as a pretreatment step, because it prepares biomass for further application. Torrefied biomass can be used on following ways: cofiring biomass with coal in large coal-fired power plant boilers, as a fuel in decentralized or residential heating system, as a convenient fuel for gasification, as a feedstock for chemical industries, and as a substitute for coke in blast furnace for reduction of carbon foot print [3].

1.1 Biomass explained

Any organic material, living or dead for a short period of time, derived from plants or animals is classified as biomass. In plants, biomass is formed by conversion of carbon dioxide in the atmosphere into carbohydrates in the presence of sun's energy. Biological species will grow by consuming these botanical or other biological species adding to the biomass chain. In the presence of light from visible spectrum (blue and red range), green plants breakdown water to obtain electrons and protons, and use them to turn carbon dioxide into glucose and release oxygen as a waste product – process of photosynthesis [4]. Biomass definition that is most relevant is given by the United Nations Framework Convention on Climate Change [5]: "A non-fossilized and biodegradable organic material originating from plants, animals and microorganisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes".

Biomass is often used for energy production [6]. Most common sources of biomass are: *agricultural* (food grain, bagasse, corn stalks, straw, seed hulls, nutshells, and manure from cattle, poultry, and hogs), *forest* (trees, wood waste, wood and bark, sawdust, timber slash, and mill scrap), *municipal* (sewage sludge, refused-derived fuel, food waste, waste paper, and yard clippings), *energy crops* (poplars, willows, switchgrass, alfalfa, prairie bluestem, corn, and soybean, canola, and other plant oils), and *biological* (animal waste, aquatic species, and biological waste) [3].

Biomass composition is very diverse. So, wood and plant residues are composed of cellulose, hemicellulose,

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and lignin with different percentages (Fig. 1). On the other side, cattle manure is rich in proteins and cereals contain starch. Diverse chemical structures result in different chemical properties. However, we can say biomass consists of carbohydrates, lignin, proteins, lipids, and other substances like vitamins, pigments, aromas, etc. Separation of these substances is the first and most important step for their further processing [7].

Biomass is a complex mixture of organic materials: carbohydrates (hemicellulose, cellulose, and starch), lignin, fats, and proteins, together with slight amounts of minerals like sodium, phosphorus, calcium, and iron. The physiochemical characteristics of biomass differ with their source [1, 3].

The main constituents of plant biomass are extractives, fiber or cell wall components, and ash [3]:

- Extractives include substances of vegetable or animal tissue, which can be separated by treatment with solvents and recovered by evaporation of solution. They comprise protein, oil, starch, and sugar.
- Cell wall provides structural strength to the plant and it allows the plant to stand above the ground. It is made of carbohydrates and lignin. Carbohydrates are cellulose and hemicellulose fibers that give strength to the plant, and the lignin grasps the fiber together. The constituents differ with the plant type. Some plants like corn or potatoes store starch and fats as energy sources in seeds or roots.
- Ash is the inorganic part of the biomass.

The polymeric composition of biomass constituents varies, but they are made of three main polymers: cellulose, hemicellulose, and lignin. Unlike, carbohydrates or starch, lignocellulose is not degradable by humans. As the lignocellulosic biomass is not a part of the human food chain, its application for biogas or bio-oils, does not put a treat the world's food supply [3]. The rigid crystallinity of the structure makes it rigid and tough to process.

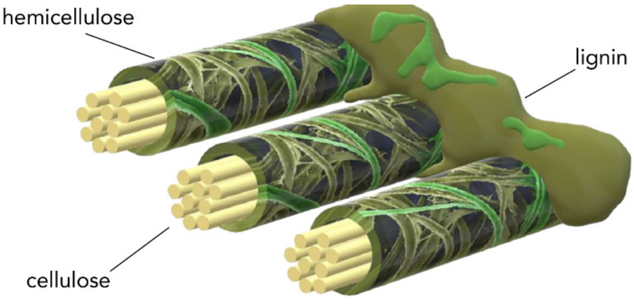

Fig. 1 Composition of lignocellulosic biomass [7]

Cellulose $(C_6H_{10}O_5)_n$ is a polar compound, a long chain polysaccharide, with high molecular weight, and has a high degree of polymerization. Glucose monomers are firmly bonded holding the formation of strong intramolecular and intermolecular interactions amongst hydrogen bonds that create the glucose monomers [8, 9]. Cellulose is a main component in wood, making up 40–44% by dry weight. Cellulose is a key contributor of tar during gasification of biomass. Hemicellulose has a random, amorphous structure with little strength. It is a carbohydrate with a branched chain structure and a lower degree of polymerization, $(C_5H_8O_4)_n$. There is a significant difference in the composition and structure of hemicellulose between different biomass types. Mostly, hemicellulose comprises some simple sugar residues like D-xylose, D-glucose, D-galactose, L-ababinose, D-glucuronic acid, and D-mannose. Hemicellulose normally tends to yield more gases and less tar than cellulose. Hemicellulose makes up between 20 and 30% of the dry weight of most wood [3]. Mostly hemicellulose decomposes during torrefaction, leaving cellulose and lignin intact (considering mass loss) [10]. Lignin is a natural polymer, or an aromatic compound in which phenyl-propane with hydroxyl and ethoxy groups are linked by ether bonds. Lignin has similar morphological characteristic of amorphous form as hemicellulose. It is less soluble similar to cellulose and it is hydrophobic. The important feature of lignin is the higher energy content in comparison to the other two compounds. This leads to higher heating value of the product [8]. As it is already said, lignin is the cementing agent for cellulose fibers. The leading monomeric units in the lignin polymers are benzene rings. Wood contains between 18 and 35% lignin by dry weight (depending on the wood type) [3].

1.1.1 Biofuels

Fuels produced directly or indirectly from biomass are called biofuels [6]. Biofuels can be categorized in two categories: primary and secondary biofuels. Primary biofuels imply unprocessed biomass, i.e., biomass used only in mechanical technologies, like for example (firewood, wood chips, briquettes, pellets), while secondary biofuels are processed biomass (bioethanol, biodiesel, dimethyl-ether, etc.) [11].

Biofuels can be classified in three categories: solid, liquid, and gaseous. Solid biofuels are the oldest type of fuels in human history. Solid fuels derived from biomass have similar properties like coal. They are produced through carbonization or torrefaction, and they are burned directly for the generation of heat and power [4, 12]. Mostly used solid biofuels are: *refuse-derived fuel (RDF)* – the fraction produced from municipal solid waste after mechanical and thermal treatment, plastic and paper residues, *briquettes* – produced from virgin biomass by thermo-mechanical process, *pellets* – produced by densification of finely chopped biomass (forestry and agricultural residues), pellets and briquettes have the same application purpose, however pellets are smaller in size. Energy content of briquettes and pellets is higher related to the biomass from which they originate, *wood* – not only the wood from the forests, but also the agricultural and forestry residues, *sewage* – originates from municipal or industrial sewage cleaning process, and *industrial wastes* – byproducts from different industrial processes (residues of wood industry, cotton industry residues, etc.) [12]. Biomass can be transformed into liquid products, like bio-oil, biodiesel or bioethanol through various technologies (pyrolysis, transesterification, fermentation, anaerobic digestion, and/or saccharification processes) [4]. Gasification is a process by which biomass is converted into gaseous products, mainly syngas (mixture of H_2 and CO, CO_2 and CH_4 gases) [4, 12].

Biofuels are also classified into three generations based on types and biomass origins. The first-generation biofuels are produced from agricultural raw materials (soybeans, sugar cane, corn, etc.). The second and third generation biofuels are also known as advanced biofuels. The second-generation biofuels are obtained from non-food biomass (energy crops, wheat straw, etc.). The third-generation biofuels include biofuels produced from micro- or macroalgae [11, 13]. Today there is also an idea of biofuels of forth generation, where genetic modified algae are used for biofuels production [14–16].

2 Torrefaction, and differences from carbonization and pyrolysis

Torrefaction process was firstly used in wood pretreatment in the 1930s in France, where the production of torrefied wood was investigated for its application in gasifiers. In the 1980s rose the interest in substituting charcoal with torrefied wood in metallurgic processing plant [16]. Torrefaction is used as a first stage followed by pyrolysis and gasification [4]. Torrefaction is a process, which is mainly used for the upgrading the properties of wood and algal biomass. The process is carried out at temperatures between 200 and 300 °C, with no oxygen present. The main product of torrefaction is biochar [17]. It is an endothermic process, which means that it needs energy input to start the process and to sustain it [4]. Torrefaction process is sometimes mixed up with related processes like carbonization, mild pyrolysis, roasting, and wood cooking, but the process conditions, and the difference is that carbonization does not hold maximum amount of energy of the biomass and therefore it gives lower energy yield. The main motivation of pyrolysis is producing of liquids and minimizing the char yield. On the other side, the main goal of carbonization is production of solid stuff, i.e., maximization of fixed carbon and minimization of hydrogen hydrocarbon content of solid product, while that of torrefaction is to make the most energy and mass yields with reduction in oxygen to carbon and hydrogen to carbon ratios. Other differences are that during carbonization most of the volatiles are driven away, but torrefaction keeps most of it, driving away only the early volatized low energy dense compounds and chemically bound moistures. Carbonization and torrefaction need slow heating rates, but pyrolysis relies on fast heating rates in order to increase the liquid yield. During carbonization, there is a certain level of oxygen present and it allows necessary combustion to source heat for the process. On the other hand, torrefaction tries to avoid oxygen and combustion [3].

In the process of torrefaction, the chemical structure of biomass is changed, which leads to formation of a different volatile products, from which some are liquid at room temperature (condensable). On the mass basis, other important reaction products than the char or torrefied biomass are: carbon dioxide, carbon monoxide, water, acetic acid, and methanol. After condensation, liquid products appear as a yellow/black liquid. Non-solid reaction products have more oxygen than the untreated biomass. The oxygen to carbon ratio of torrefied biomass is lower than untreated biomass resulting in ensuring a rise of the calorific value of the solid product [10]. Biomass is totally dried during torrefaction and its hygroscopic nature alters to hydrophobic. Moisture uptake after torrefaction is restricted. Torrefaction increases the grindability biomass properties of biomass, which contribute when in co-firing with coal in existing coal-fired power stations. Because of the increased higher calorific value, hydrophobic nature, and improved better biomass grindability, the characteristics of torrefied biomass approach resemble those of coal [18].

When the torrefaction is completed, the reactor cools down below 80 °C under the inert atmosphere, so that self-ignition and combustion of solid products are avoided. After that, products are collected and post-treated, e.g., densified by pelletization (see Section 3.3). Another major benefit of torrefaction is improving biomass properties by reducing its biological degradation. Raw biomass shows poor resistance to fungi. After torrefaction, biomass gains a higher durability to microbial degradation. Torrefaction degrades hemicellulose in biomass, which is the central nutritive source for the development of wood rotting fungi. Therefore, by biomass torrefaction, biomass gets a higher resistance to microbial decomposition [19].

2.1 Reaction mechanism and reaction stages

During initial stages of torrefaction include (basic drying), where only the surface moisture is removed. Further drying leads to removal of moisture and other volatiles through chemical reactions thermo-condensation process, which occurs at temperatures above 160 °C. At this temperature, beside moisture, volatiles, CO_2 is also released [20]. At the temperatures lower than 270 °C, the torrefaction is mildly endothermic, but the process gets mildly exothermic as the temperature approaches 280 °C, because of the sugar decomposition [3]. From this point on, the biomass gets dark and gives off further moisture, carbon dioxide, and large amounts of acetic acid, with some phenols. It comes to production of CO_2, phenols, acetic acid, and other higher hydrocarbons. The major reactions of decomposition affect mostly hemicellulose, and lignin and cellulose to a lesser degree. The biomass keeps most of its energy and loses its hygroscopic characteristics. Temperatures above 300 °C are not advised, as these conditions initiate pyrolysis [20]. So, generally, the torrefaction process is mildly exothermic, and beside for the heat loss, torrefaction needs only little energy. However, in reality, it could need heat for making up for the inevitable heat loss from the torrefier [3].

The overall torrefaction process has several steps (Fig. 2): heating, drying, torrefaction, and cooling [21]. Initial heating implies that biomass is initially heated until stage of drying is reached and biomass' humidity starts to evaporate [22]. In this stage it comes to increase in temperature, and at the end, moisture starts to evaporate. In pre-drying step (at 100 °C), comes to the evaporation of the free water from the biomass, at the constant temperature. In post-drying and intermediate heating stage, the temperature of the biomass is increased to 200 °C. Physically bound water is released. Some mass loss can take place, due to the evaporation of light fractions can evaporate. Torrefaction stage is stage where the process happens. It starts at 200 °C, and it finishes, when the process is again cooled down from the specific temperature back to 200 °C. The most of the mass loss of the biomass is occurring in this stage. Solids cooling means that the torrefied product is cooled below 200 °C to the desired temperature (room temperature) [21]. Pre-drying step requires a relatively small fraction of the heat, while drying is the most energy-intensive step of torrefaction. Because the moisture from biomass evaporates during this stage, it is the most energy-intensive step of the torrefaction process There is only slight change in biomass temperature, since evaporation occurs at constant temperature, until surface moisture or free water is driven away completely [3].

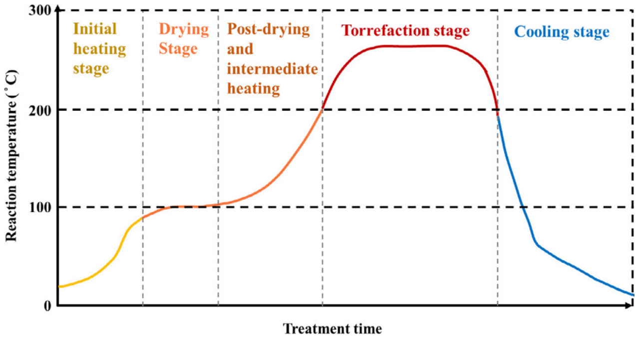

Fig. 2 Schematic representation of torrefaction stages [19]

During torrefaction there are different thermochemical changes in biomass, and they can be divided into five regimes [3]:

- Regime A: non-reactive drying regime, at temperatures between 50 and 120 °C, there is a loss in physical moisture in biomass, without changes in its chemical composition; the structure can be regained by rewetting.
- Regime B: this regime is separated out only in case of lignin, which experiences softening that makes it serve as a binder (temperature from 120 to 150 °C).
- Regime C: or "reactive drying", it comes to biomass structural deformity and it cannot be recovered by wetting. Here it comes to cracking of hydrogen and carbon bonds and depolymerization of hemicellulose (temperatures from 150 to 200 °C).
- Regime D: together with regime E comprise torrefaction zone for hemicellulose by limited devolatilization and carbonization of solids structure created in previous regime. It comes to breakage of most inter- and intramolecular hydrogen, C-C, and C-O bonds, creating condensable liquids and non-condensable gases (temperature from 200 to 250 °C).
- Regime E: decomposition of hemicellulose into volatiles and solid products. Lignin and cellulose experience only a limited extent of devolatilization and carbonization (temperatures between 250 and 300 °C).

Major devolatilization and carbonization of the biomass polymers occur in a different temperature range. For example, temperature range for hemicellulose is 225–300 °C, for cellulose 305–375 °C, and for lignin 250–500 °C [3]. In Table 1 [23–33], degradation of lignocellulosic components during torrefaction is summarized based on each component and the temperature range [4]. Due to the differences in reactivity of hemicellulose, cellulose and lignin, it can be distinguished between two different torrefaction regimes. A light torrefaction is characterized by hemicellulose decomposition at temperature below 240 °C. A severe torrefaction takes place at temperatures above 270 °C, where both, lignin and cellulose are affected. Main biomass constituents (hemicellulose, lignin, and cellulose) react during torrefaction individually, without synergetic effects [21].

Biomass can be torrefied either under dry or wet conditions. In dry torrefaction, biomass can be torrefied in dry and non-oxidative (inert) or oxidative atmospheres, where the temperature is between 200 and 300 °C. Nitrogen and carbon dioxide can be used as carrier gases in non-oxidative torrefaction. For oxidative torrefaction, air, flue gas, and other gases with different oxygen concentrations can be used as carrier gases for biomass pretreatment. Oxidative torrefaction has a higher reaction rate than that of the non-oxidative torrefaction, due to the presence of oxygen and exothermic reactions from thermal degradation, and so torrefaction duration shortens. Using air or flue gas to torrefy biomass leads to reduction of operating costs, as nitrogen separation from the air is not required. Oxidative torrefaction achieves lower solid yield than non-oxidative torrefaction. Also, higher heating value of torrefied biomass drops with increasing oxygen concentration when torrefaction temperature is lower than 300 °C. In wet torrefaction, biomass is upgraded by water and dilutes acid solutions at temperatures between 180 and 260 °C. When biomass is treated in wet mediums, such as water or dilute acid, the produced solid is called 'hydrochar' [19]. Wet torrefaction is also known as hydrothermal carbonization [16]. Comparison between non-oxidative and oxidative torrefaction is given in Table 2 [19].

When biomass is torrefied in hot compressed water or hydrothermal media, there is no significant reaction of biomass in liquid water when temperature is under 180 °C. The reaction time is between 5 and 240 min, and the reaction temperature is between 180 and 260 °C. When water temperature increases, its properties are also changing (dielectric constant, ion products, density, viscosity, and diffusivity). When torrefaction is operated under conditions close to subcritical [19]. In wet torrefaction, the hemicellulose in biomass is depolymerized through hydrolysis and converted into monomers and oligomers. During this process, hydrolysis of hemicellulose in monomers

Table 1 Degradation of lignocellulosic components during torrefaction adapted from [4]

Temperature	Hemicellulose	Cellulose	Lignin	Ref.
Degradation temperature	180–300	275–355	250–500	[23, 24]
25–105	No effect	No effect	No effect	[25]
105–150	No effect	No effect	No effect	[26]
160–180	Degradation starts due to devolatilization reactions that release H_2O and CO_2	No effect	No effect	[27]
180–200	Endothermic reaction	N/A	N/A	
200 Light torrefaction				
200–250	Degradation continues, color of biomass changes; formation of acetic acid, methanol, CO, and CO_2	Color change of biomass is noticeable	Color change of biomass is noticeable	[26, 28]
250 Mild torrefaction				
200–270	Partly endothermic reactions	Partly endothermic reactions	Partly endothermic reactions	[26, 29–31]
250–300	Complete degradation, formation of char and release of CO, CO_2, and H_2O	Degradation starts at 275 °C releasing water and forming anhydrous cellulose and levoglucosan	Degradation starts 250 °C. At 280 °C degradation gives phenols due to cleavage of ether bonds	
290 Severe torrefaction				
250–300	Depolymerization of remaining hemicellulose	Depolymerization of cellulose	Decomposition of lignin	[26, 29–31]
270–300	Exothermic reactions	Exothermic reactions	Exothermic reactions	
330–370		Total degradation, forming char	Total degradation, forming char	[32, 33]

Table 2 Comparison between non-oxidative and oxidative torrefaction adapted from [19]

Non-oxidative torrefaction	Oxidative torrefaction
Advantages: higher solid and energy yields and easier temperature control	Advantages: lower operating costs (no separation of nitrogen), lower heat supply and faster reaction rates
Disadvantages: requires higher heat, lower reaction rate and nitrogen should be separated from air	Disadvantages: lower solid and energy yields, difficult temperature control

and oligomers takes place with minimum impact on lignin, which produces solid biochar with a reduced moisture content related to raw biomass [34].

2.2 Products of torrefaction process

The yield of torrefaction product depends on torrefaction conditions, mostly on temperature, time, and properties of the biomass. The torrefaction product is made of solid biochar and volatile products, which can be further divided into liquid or condensable gases, and permanent gases [4]. Table 3 gives an overview of torrefaction products [35].

Torrefied biomass or biochar is dry, partly carbonized solid left after volatile products have been driven away together with bio-ash and unreacted carbon. The torrefied biomass comprises unreacted lignin and cellulose polymeric structures, while hemicellulose mostly contributes to volatile products. As the torrefied biomass retains about 70% of the mass, and 30% escapes as volatile products [4]. Solid products consist of a structure of the original sugar structures and reaction products. Solid reaction products are large modified sugar structures, newly formed polymeric structures, with a certain degree of aromatic rings, typical carbon-rich char structures and ash fractions [35]. The solid fraction keeps about 90% of the original energy content, and the heating value of torrefied biomass is between 15 and 20% higher compared to the original untreated biomass [4]. The gas phase is considered as permanent gases. These are compounds with a boiling point below −33 °C, but also beside the permanent gases, there are light aromatic components like benzene and toluene [35]. Permanent gases mainly consist of CO, CO_2, small amounts of CH_4, and low molecular weight hydrocarbons together with unreacted hydrogen, oxygen, and nitrogen. Decarboxylation leads to formation of CO_2, while CO comes from the reaction between CO_2 and steam with porous char surface of the biomass, which means that CO starts to be produced after CO_2 is produced. CO is the key source of the heating value for permanent gases during torrefaction [4]. The condensables or liquids are distributed into three groups. One group is comprised of reaction water that is a product of thermal decomposition. Organics produced during devolatilization and carbonization represent the organics group. Lipids are present in the original biomass. They can be understood as inert compounds that might evaporate under torrefaction conditions [35].

Table 3 Biomass torrefaction products adapted from [35]

Phase	Components
Solid	Original sugar structures Modified sugar structures Newly formed polymeric structures Char Ash
Liquid	Water Organics (sugars, polysugars, acids, alcohols, furans and ketones) + lipids
Gas	H_2, CO, CO_2, CH_4 Light aromatic compounds

3 Applications of torrefied biomass

The fuel yielded from torrefied biomass has very high quality. The high quality makes it very attractive for combustion and gasification application. Some other applications are: biomass solid fuel for thermal power plants for generation of heat and electricity, cofiring in pulverized boilers, co-gasification in entrained-flow gasifier, fuels for domestic and commercial use, pellets or briquettes as fuels, small-scale pellet boilers or stoves, and high-quality fuel for advanced bioenergy application [16].

3.1 Co-firing and combustion

During co-firing it comes to the simultaneous use of two or more fuels in the same furnace. The combustion of raw biomass materials needs special infrastructures for application in coal- fired power plants due to the industrial challenges of biomass agglomeration, slag creation, ash clinker, and low energy content destabilized by biomass moisture. On the contrary, torrefied biomass (or torrefied pellets) can be used straight or together with coal in coal-fired power plants. The co-firing of torrefied biomass with coal can be a great option for power plants for reduction of fossil fuels usage [36]. The potential application of torrefied biomass is firing and co-firing with coal in existing large-scale facilities, like pulverized coal boilers [19, 37]. In this process, biomass is fed to the reactor as a powder [16]. The common combustion technology for electricity generation is pulverized coal combustion, where mixture of fine coal particles and the air is blown into the burner from the bottom of boilers [18]. Because of great combustibility and grindability, torrefied biomass is the best option for co-firing with coal. Higher surface area, high porosity, and smaller granular size of torrefied biomass ease its application for efficient co-firing and combustion. Torrefied biomass can be used directly with coal and indirectly by combustion of syngas products in the boilers from gasification of torrefied biomass [36]. It is found out that combining of coal (50%) with torrefied biomass (beech wood) (50%) gives the most stable reaction and minimizes the NO_x emissions almost for 30% and SO_x emissions for about 50% compared to coal combustion. The ash melting reactions displayed that initial deformation temperature of combustion of torrefied fuels with coal was higher compared to raw biomass and coal. Also, the fly ash contents analysis showed that K_2O content is much lower during co-firing of coal and torrefied biomass [38].

Co-firing of biomass with coal can be directly and or indirectly. Direct co-firing encompasses direct feeding of biomass into the coal firing systems, while in indirect co-firing it comes to gasification of the biomass and combustion of the product fuel gas in the boiler are involved. The simplest method for co-firing is mixing of the biomass fuel with coal before the fuel enters the coal feeders. This process has been used when co-firing biomass has one of the following forms: granular, pelletized, or dust form. Another option is to handle biomass fuel distinctly from the coal and inject it into the pulverized fuel pipework upstream or at the burners. This method involves some modifications of the system and it increases the costs of existing coal power stations. Separate handling of the biomass and combustion through a number of dedicated burners are the most costly options for direct biomass co-firing [18]. An interesting study was done by Lasek et al. [39], in which combustion properties of torrefied willow were investigated and compared with the properties of Polish lignite and hard coal. This study showed that the combustion process of torrefied willow resulted in low SO_2 emissions, but high NO_x emissions. When this limitation is solved, torrefied willow could be used in stationary combustion chambers.

This technology is a costly and achievable only at low capacities in typical coal mills. Because of this restraint, wood pellets are at the moment, the state-of-the-art for co-firing. Nearly complete combustion of torrefied biomass is possible for heat generation that further leads to electricity generation, and centralized heating systems [16]. Also, co-firing systems based on torrefied biomass should be further investigated in terms of common issues, like fouling, corrosion of the boiler, fly ash utilization, influences on performance of the flue gas cleaning, etc. [40].

3.2 Gasification

Very important application of torrefied biomass is in gasification. Compared to unprocessed biomass, torrefied biomass has a lower moisture content and smaller particle size. So, dried biomass with small particle size can be quickly gasified, in only several seconds [41]. For gasification of torrefied biomass, there are different systems used: air-blown circulating fluidized bed gasification of wood, wood torrefaction and circulating fluidized bed gasification of torrefied wood and wood torrefaction combined with entrained flow gasification of torrefied wood. Gasification turns biomass into carbon monoxide, hydrogen and carbon dioxide. This is accomplished at high temperatures (above 700 °C), without combustion, with controlled amount of oxygen and/or steam. The resulting gas is known as syngas, and can be used as a fuel. Syngas can be burned directly in gas engines, or it can be used for methanol and hydrogen production, or it can be transformed into synthetic fuel by Fischer-Tropsch process [16]. Wood is a clean and renewable fuel, but it is not an ideal fuel for gasification. Due to the high O/C ratio and high moisture content, its optimal temperature for gasification is below 700 °C. Consequently, wood is over-oxidized in gasifiers, which lead to thermodynamic losses [42]. Prins et al. [42] have showed that it is possible to reduce these thermodynamic losses by wood torrefaction [42]. Another work that studied gasification of torrefied biomass was conducted by Tapasvi et al. [43]. They showed that torrefied biomass has higher hydrogen and carbon monoxide contents in the produced gas and higher energy and exergy efficiencies compared to untreated biomass [43].

The quite low moisture content, good grindability and promising C/H/O ratios of torrefied wood/biomass make torrefaction an important pretreatment technology for gasification. Particle size and moisture contents are decisive aspects for operation of biomass gasifiers operation. The gasification of torrefied biomass advances flow properties of the feedstock, increases levels of hydrogen and carbon monoxide in the resulting syngas, and improves overall process efficiencies [44].

3.3 Densification (Pelletization)

Densification of biomass is a method where the biomass properties are improved by employing mechanical force to compress the material into an uniform shape of pellet, briquettes, and logs. The most important purpose of densification is to increase the bulk density of biomass, reduce the storage space and costs associated with transportation and handling. Fuel pellets produced from torrefied biomass have higher heating value, high-energy content, and hydrophobic nature. The densification of torrefied material is more challenging than that of the raw biomass. Torrefied pellets demand high die temperature and higher compression pressures. This is because torrefaction removes the moisture and volatiles together with decomposition of the lignin, which normally acts as a binder during pelletization. High-quality pellets can be produced when the torrefied biomass has around 10% moisture [36, 45]. Lately, a biomass treatment process that combines the densification and torrefaction has been studied. This process increases the bulk density and the calorific value of biomass. This process is also energy-efficient and cost-effective compared to conventional processes [16, 36].

In the study of Peng et al. [46] the quality of torrefied pellets was determined mainly by the density and the hardness by using torrefied samples prepared at different conditions in a press machine. Also, hygroscopicity of torrefied pellets was evaluated in a humidity chamber by measuring the moisture uptake rate. The study showed that the density and the hardness of torrefied pellets mostly depended on the densification die temperature and the weight loss of torrefied samples. In order to make strong torrefied pellets of high density and low moisture uptake from 30 wt% weight loss torrefied samples, a die temperature of 230 °C is needed.

3.4 Pyrolysis

Torrefaction is also used as a pretreatment step for pyrolysis. This is a promising way to improve physicochemical properties of bio-oil for its application as a fuel. The quality and quantity of pyrolysis products can be improved after torrefaction [36]. Bio-oils gained after pyrolysis of torrefied biomass have lower water content and higher carbon content than the raw biomass used for the process [19]. Chen et al. [47] have studied pyrolysis of torrefied biomass, and concluded that the torrefaction process improves pyrolysis products in terms of the ratio and chemical composition of the products. Also, torrefaction improves product quality and conversion process and increases conversion efficiency. Additionally, catalytic pyrolysis of torrefied biomass is a promising way to convert biomass into useful chemicals. However, the work of Louwes et al. [48] studied fast pyrolysis of torrefied wood, compared to pyrolysis with the untreated wood. The study concluded that torrefaction as a pretreatment can be useful from an energy perspective, but it lowers the oil yield. Additionally, the work of Ru et al. [49] have highlighted the hemicellulose degradation of biomass during torrefaction, which has led to the lower yields of acids and furfural in the pyrolytic product distribution.

3.5 Application in non-power generation industries

The iron and steel industries are the largest industrial CO_2 emitters. This sector needs high-quality fuels, and many biofuels cannot meet these criteria for energy density, ash production and ease of handling. One possibility could be to substitute coal with torrefied wood. The application of torrefied biomass in replacing fossil fuels would decrease CO_2 emissions compared to fossil fuel emissions [50, 51].

Steelmaking process is divided into four main paths: blast furnace/basic oxygen furnace, direct reduction/electric arc furnace, smelting reduction/basic oxygen furnace and melting of scrap in electric arc furnace [52]. The blast furnace is the most employed facility to produce hot metal in the iron industry [19, 52]. In the work of Chen et al. [53] torrefaction and burning properties of different wood types were examined and compared with a high-volatile bituminous coal. The potential of biomass consumption in blast furnace was evaluated. The results showed that torrefaction at 300 °C is a possible operating condition to convert biomass into a solid fuel approaching a high-volatile bituminous coal used in blast furnaces.

Biomass application plays a significant role in energy production in the pulp and paper industry. Torrefaction process has drawn attention of large pulp and paper producers. Some examples are Andritz in Austria in their two facilities, and Japanese paper manufacturing company Nippon Paper [50]. Although mathematical modelling shows good results on the moderation of CO_2 emissions by adding of torrefied biomass in blast furnaces, the application of torrefied biomass in modern and large blast furnaces is still lacking [52].

4 Torrefaction efficiency

Torrefaction efficiency can be described through different attributes.

Firstly, solid or mass yield is a measure of the solid yield of the torrefaction process. It measures the fraction of the original mass of biomass which remains in the torrefied product. Because the torrefaction is related to the change in the hydrocarbon content of biomass, a simple definition of a ratio of product mass and the original mass is not enough for getting the whole picture of the process. So, the mass or solid yield can be described as the fraction of the original component of biomass that is transformed into solid char, and it is defined on dry ash free basis (Eq. (1)) [3].

$$MY_{daf} = \frac{\text{mass of torrefied biomass on } daf \text{ basis}}{\text{mass of original biomass on } daf \text{ basis}} \quad (1)$$

Equation (1) is the most precise, but its effectiveness in design calculations is constrained. It does not provide the actual solid mass in the torrefied product; it only gives the rest of the organic component. When the sensible heat or the mass of solid is calculated, the entire solid amount with ash included, is necessary. This is important for organic feedstock like, rice husk and sewage sludge, where inorganic content is high. The other definition of mass yield is based on dry basis (MY_{db}) see in Eq. (2) [3].

$$MY_{db} = \frac{\text{mass of torrefied biomass on dry basis}}{\text{mass of original biomass on dry basis}} \quad (2)$$

Mass yield can be also roughly calculated, when the mass yield is expressed "as-received" (*ar*) basis (Eq. (3)) [3].

$$MY_{ar} = \frac{\text{total mass of torrefied biomass}}{\text{mass of wet biomass as} - \text{recieved}} \quad (3)$$

The relationship between these three previous equations of mass yield can be described on following way (Eqs. (4) to (6)) [3]:

$$MY_{ar} = (1 - M) MY_{db}, \quad (4)$$

$$MY_{daf} = \frac{MY_{db} - ASH_{db}}{1 - ASH_{db}}, \quad (5)$$

or:

$$MY_{db} = MY_{daf} (1 - ASH_{db}) + ASH_{db}. \quad (6)$$

M and ASH are fractions of moisture and ash on as-received basis.

The ash fraction on dry basis is related to that on as-received basis (Eq. (7)) [3].

$$ASH_{db} = \frac{ASH}{1 - M} \quad (7)$$

Energy yield (EY) is the fraction of the original energy in the biomass that is preserved after the process (Eq. (8)) [3].

$$EY = \frac{\text{energy in torrefied product}}{\text{energy in raw biomass}} \quad (8)$$

Energy yield can also be described by using heating values of the raw and processed biomass (Eq. (9)) [4].

$$EY = \frac{\text{mass}_{\text{product}} \times \text{heating value}_{\text{product}}}{\text{mass}_{\text{feed}} \times \text{heating value}_{\text{feed}}} \quad (9)$$

When the higher heating value is described on dry ash free basis (HHV_{daf}), the energy yield can be expressed on following way (Eq. (10)) adapted from [3, 54].

$$EY_{daf} = \frac{\text{product mass}_{daf}}{\text{feed mass}_{daf}} \times \frac{HHV_{\text{product } daf}}{HHV_{\text{feed } daf}} = \\ = MY_{daf} \times \frac{HHV_{\text{product } daf}}{HHV_{\text{feed } daf}} \quad (10)$$

The relation between higher heating value of product and higher heating value of feed (Eq. (11)) is called energy densification ratio (R_{HHV}) adapted from [55].

$$R_{HHV} = \frac{HHV_{\text{product}}}{HHV_{\text{feed}}} \quad (11)$$

4.1 Grindability and hydrophobicity

Torrefaction can significantly improve grindability and hydrophobicity of processed biomass. These properties are important for products to be used for gasification and combustion [2].

Grindability is assessed by the amount of energy employed in the griding process. The lower the energy applied, the higher the grindability. Another way to define the grindability is particle size distribution, the smaller the particle, the higher is the grindability. Also, the fiber content in unprocessed biomass is high. These fibers are connected to each other and it makes the biomass hard to grind. So, the grindability of the torrefied biomass is better, because the changed properties of biomass fibers lead to the decreased fiber tenacity and bigger brittleness. The reduced fiber tenacity is due to degradation of hemicellulose during the process of torrefaction [56]. As it is presented in the work of Phanphanich and Mani [57], the specific energy consumption for grinding was reduced with increase of torrefaction temperature for torrefied pine chips and logging residues. And the relation between specific grinding energy consumption of torrefied biomass was linearly correlated with the torrefaction temperature. Also, when the grinding energy consumption between untreated biomass and torrefied biomass is compared, torrefaction reduced grinding energy consumption by 10 times for pine chips and 6 times for logging residues [57]. Simplicity of grinding is advantageous for entrained flow gasifier [44]. The enhanced grindability of biomass results in the increase in weight percentages of fine particles under the same grinding conditions. Also, it comes to reduction of the specific energy consumption for grinding, torrefied wood chips by up to 90% compared to raw wood chips [45].

The raw biomass has hygroscopic nature due to its inherent hydrogen bonding to the hydroxyl groups of the cell wall components that easily absorb water [19]. Hemicellulose has the greatest ability for water sorption, and lignin has the lowest. Degradation of hemicellulose, decrease of H/C and O/C ratios in torrefied biomass impact the capacity of hydroxyl groups to attach water through hydrogen bonds. Torrefied biomass can be stored long in the open without any problems and worries about the hydrophilic behavior and biological deterioration or rotting to raw biomass. When the biomass is torrefied at higher temperatures, it absorbs less moisture, i.e., it has higher hydrophobicity. The hydrophobicity mechanism can be described through following steps [41, 58]:

1. hemicellulose breaks down and it comes to unbinding of cellulose and lignin, which further affects the release of water molecules stored at the cell level;
2. when hemicellulose is destructed, it comes to greater brittleness for cellulose and lignin;
3. removal of OH groups decrease the creation of hydrogen bonds with water;
4. the breakdown of hemicellulose leads to formation of more nonpolar molecule.

So, destroying of OH groups leads to production of hydrophobic products and the biomass loses its capacity to form hydrogen bonds. Because of the chemical rearrangement reactions, nonpolar unsaturated structures are created that preserve the biomass for a long time without biological decomposition, similar to coal [27].

4.2 Advantages and drawbacks of torrefaction process

Torrefaction is a process that takes place at temperatures between 200 and 300 °C, with no oxygen present. It comes to removal of volatiles, and upgrading of biomass quality. Torrefaction products could find application in broad spectrum of industries (coal substitutes) [59]. However, torrefaction industry is not commercial yet [60]. Some other advantages are: increased bulk densities combined with densification, increased heating value, reduced oxygen content, dry and hydrophobic nature, better quality and homogeneity. Some drawbacks and limitations are high investment and operating costs, storage problems (dust or smell, leakage) [61]. An idea how to speed up the commercialization of torrefaction process is to combine torrefaction with already existing bioenergy value chain (e.g., wood pellet industry) [60].

5 Conclusion

This review has presented detailed torrefaction process, an emerging technology for biomass pretreatment and its application as a coal substitute. Torrefied biomass can be used for electricity generation, or in co-firing with coal, or in gasification, or in metallurgical processes. When torrefied biomass is applied together with coal, it comes to reduction of greenhouse gas emissions, because lower amount of coal is used. Gained solid products after torrefaction are hydrophobic, which makes them ideal for long storage, without any biological decomposition. Torrefied biomass also needs less energy for grinding, which eases its application in gasification reactors.

This work should serve as a basic research of torrefaction process technology. Further topics of interest would be types of reactors for torrefaction process, different feedstocks for the process, and effects of catalysts, temperature, particle size and heating rate, as well as experimental procedures under torrefaction conditions.

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