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THERMOREFINERY: PROSPECTS FOR THE SECOND GENERATION OF THERMO-CHEMICAL BIOMASS CONVERSION SYSTEMS

Abstract: The *ThermoRefinery* is a new concept and an associated practice representing the 2nd generation of thermochemical processes for the conversion of renewable feedstocks (biomass and wastes) to fuels, chemicals and other biobased products, while solving the most significant problems limiting the potential of this type of technologies to contribute to global and regional targets. This paper aims at demonstrating the *ThermoRefinery* approach and its applications, aiming at several objectives: optimising pretreatment processes for each feedstock, including leaching and torrefaction; designing optimal production systems; and, putting together optimal product vectors. The major optimization challenges are taking into account ash chemistry, which affects the ash melting point. These include minimising other ash-related problems, controlling tar content in the producer gas, minimizing emissions, and reducing feedstock handling problems.

Rafineria termiczna: perspektywy dla drugiej generacji termochemicznych systemów do przekształcania biomasy

Słowa kluczowe: biozasoby, wstępna obróbka biomasy, technologie przekształcania termochemicznego, postępowanie z popiołami, wymywanie, toryfikacja.

Streszczenie: Rafineria termiczna to nowa koncepcja i związana z nią praktyka reprezentująca drugą generację procesów termochemicznych w zakresie przekształcania surowców odnawialnych (biomasy i odpadów) na paliwa, chemikalia i inne produkty biologiczne, przy rozwiązywaniu najważniejszych problemów ograniczających potencjał tego typu technologii w zakresie przyczynienia się do realizacji celów globalnych i regionalnych. Niniejszy artykuł ma na celu ukazanie podejścia do rafinerii termicznej i jej zastosowań, mając na uwadze kilka celów: optymalizację procesów obróbki wstępnej dla każdego surowca, w tym wymywanie i toryfikację; projektowanie optymalnych systemów produkcyjnych; łączenie optymalnych wektorów produktów. Głównym wyzwaniem optymalizacyjnym jest uwzględnienie składu chemicznego popiołu, który ma wpływ na temperaturę topnienia popiołu. Obejmuje on minimalizację innych problemów związanych z popiołem, kontrolę zawartości substancji smolistych w gazie produkcyjnym, minimalizację emisji i zmniejszenie problemów z obsługą surowca.

Introduction

The *ThermoRefinery* concept and its associated practice represent a knowledge-based response to a number of critical *challenges* that process, product, and production system design and engineering are facing today. These include the following: (1) to shift away from the presently dominant use of fossil *carbon*, and move towards renewable C sources, such as biological and waste-derived/recycled carbon-containing feedstocks; (2) to unlock the huge potential of still untapped renewable *resources*, including wastes and residues, especially for local, regional and inter-regional *development* purposes; (3) to empower the full potential of *thermochemical conversion* processes to contribute to the other challenges, which is presently blocked by several problems related to the thermal behaviour of most available feedstocks and their components (e.g., ash), as well as other characteristics of feedstocks, intermediate and final products and by-products [1–6]; (4) to open the way for the synthesis of *new product vectors*, consisting of a set of high value-

added products, either acting as substitutes of fossil-based ones or having novel functions and properties, in critical market sectors, e.g., in health, energy, quality of life, and materials; and finally, (5) to make full use of the already accumulated valuable knowledge *in chemistry and chemical engineering* of petrochemical and coal-based systems by its efficient transfer, e.g., from the Petroleum Refinery to the *ThermoRefinery* level.

An alternative definition of the *ThermoRefinery* will be to call it the *2nd generation* of thermochemical conversion processes, with the 1st generation consisting of pyrolysis, gasification, carbonisation, combustion, and their process families. This 2nd generation is oriented towards designing production systems rather than individual processes.

1. State of the art

One of the greatest challenges of our time is that of the shift away from the use of fossil carbon. In search for renewable feedstocks that can be used as alternatives to fossil resources, biomass and wastes represent attractive options. Their utilisation as feedstocks for the production of fuels, power, chemicals, and materials offers the advantages of renewable, cleaner, and almost CO_2-neutral sources of carbon. To unlock this potential, appropriate conversion processes transforming the renewable organic feedstocks to specific, high-value added market outlets are necessary. The broad field of thermochemical conversion processes, including combustion, pyrolysis, gasification, liquefaction, carbonization, and other technologies, represent a promising reservoir of responses to such critical socio-technical demand.

As far as biomass and waste conversion processes are concerned, the need to meet the Kyoto protocol directives and to decrease the environmental footprint of energy and fuels produced from fossil energy sources has recently led to the development of several advanced thermochemical conversion technologies, including supercritical combustion, pressurized fluidized bed combustion and gasification, as well as entrained flow gasification. These new thermochemical conversion processes operate at high temperatures (>1500°C) and pressures (>50 bar) and can achieve very high conversion efficiencies (>50%). Thermal gasification processes can be combined with Fischer-Tropsch modules or other catalytic processes to produce liquid fuels and chemicals, e.g., synthetic diesel, aviation fuel, higher alcohols, etc. [1].

As a rule, the use of such high-temperature and pressure environments puts additional requirements on the feedstock quality, as significant, feedstock-derived problems could be created that would limit the conversion potential of the specific biomass and waste raw materials to generate energy and product vectors

in an economical and sustainable way. Based on the available literature and research by our team, the most significant of such problems, which limit the potential of thermochemical processes to contribute to the above stated socio-economic challenges, are summed-up as follows [1, 6–9, also: 10–17]: the negative roles of inorganics (K, Cl, P, S, N, heavy metals, ash) in the chemistry and physics of the conversions; technical problems due to the use of solid feedstocks (feeding, milling, mixing, etc.); co-production of tars that have to be removed from gas streams, thus raising costs and risks; and, complexities in the further refining and upgrading of outputs (water content, chemistry etc.). Moreover, due to the above, the technical solutions developed tend to be strongly feedstock-specific, thus characterised by local applicability and high development costs, and this results in the research field becoming fragmented, limiting learning, and deployment. Research strategy is mainly oriented towards fuels and power, missing more competitive opportunities linked with the pathways to high-value organic chemicals and materials. Thus, the potential from the employment of the "refinery" concept is not fully utilised; consequently, less emphasis is given to the co-products and the circular economy aspects. Overall, the potential of efficient utilisation of available resources in a region is blocked.

In the next few paragraphs, we will examine in more detail the state of the art regarding some major problems from the above list.

Inorganics: The thermal and chemical behaviour of the inorganic components (ash) of most types of renewable feedstocks, especially agro-residues, energy crops, and most bio-wastes, during their thermochemical conversion is one of the most important subjects to be addressed. With the term "ash," we refer to all inorganic components of biomass and waste materials present in a variety of forms, including organically-bound cations, inorganic salts, and other minerals. Agro-residues and energy crops contain mainly alkali metals, such as K present in the form of inorganic salts, e.g., KCl dissolved in the inherent moisture, or connected to carboxylic or other functional groups, or as complex ions and chemisorbed material, and silicon in the form of hydrated silica or as deposits on the cell walls, as their principal ash forming inorganic constituents. They are also relatively richer in chlorine and sulphur compared to wood fuels, and they also contain small amounts of alkali earth elements, i.e., calcium present either on the cell walls or as crystalline calcium oxalate in the cytoplasm, and magnesium, and also phosphorous, with the latter two present mainly in biological forms [18, 19].

Ash chemistry: The presence of large amounts of these inorganic constituents in some biomass feedstocks is associated with serious technical problems, such are deposition, sintering, agglomeration, fouling, corrosion, and erosion, all caused during the operation of high-temperature combustion and gasification plants. In

particular, alkali metals, and especially potassium, which has high mobility, tend to react either with silica, even at temperatures far below 900°C by breaking the Si-O-Si bonds, and forming low melting point silicates, or with sulphur to produce alkali sulphates. Chlorine acts as a facilitator of these reactions by increasing the mobility of potassium, since most of it is present as KCl. Potassium chloride is among the most stable, high-temperature, gas-phase, alkali-containing species, while the amount of chlorine in the fuel often dictates the amount of the alkali possible to be vaporized during combustion or gasification. Calcium also appears to react with sulphur to form sulphates, but the lower mobility of calcium in combination with its limited quantity in these bio-feedstocks does not result in significant problems [6–9, 18]. The produced alkali silicates and/or sulphates have very low melting points that may reach as low as 700°C and tend to deposit on reactor walls or heat exchange surfaces in the case of the conventional grate fired systems; whereas, in the case of the fluidized bed reactors, they contribute significantly in bed sintering and the de-fluidization of the bed inert material through the development of a sticky deposit on the surface of the bed particles [10, 11, 19–21].

Solid biomass feedstocks: The optimal use of solid agricultural biomass and energy crops as feedstocks in high temperature and pressure conversion systems, either alone or in combination with coal, requires particular mixing, feeding, and sizing properties of the solid biomass particles. Biomass materials, as a rule, are difficult to be milled, mixed, and fed, both alone as well as in combination with other biomasses and solid fossil fuels. In particular, feeding in high temperature and pressure environments requires the use of very small particle sizes (<70microns), as well as of storage, mixing and feeding systems that have been developed for use with coal feedstock. However, biomass cannot be milled efficiently at the specific particle size or handled efficiently through any of the specified infrastructure

that has been developed for use with the various coal materials [9, 10].

Solid waste risks: Ash-related problems in the forms of fouling, slagging, corrosion, and erosion constitute one of the biggest obstacles towards a safe, economical, and environmentally friendly utilization of a large variety of wastes, including Municipal Solid Waste (MSW), sewage sludge, and various industrial bio-wastes, via thermochemical conversion routes. In the case of the MSW incineration plants, the deposition and the corrosion processes can be affected by the presence of heavy metals, such as zinc and lead, in the form of chlorides and sulphates. These compounds have very low melting points, e.g., 290°C for $ZnCl_2$, 501°C for $PbCl_2$ and 680°C for $ZnSO_4$, and also interact with compounds such as KCl and alkali metal sulphates present in large amounts in the ashes generated during MSW incineration. This leads to the formation of molten phases with even lower melting points compared to pure salts, i.e. 250°C for a $ZnCl_2$/KCl, 48/52% wt. mixture, thus accelerating significantly the deposition and the corrosion processes [22–25]. The presence of large amounts of heavy metals (Zn, Pb, Cu, etc.) and also alkali chlorides and sulphates in the ash formed during the MSW incineration, apart from their contribution to the ash-related problems, also constitute a significant problem regarding the safe treatment and disposal of the generated ash material in economical and environmentally friendly ways [26–28].

2. ThermoRefinery approach

A simplified view of the comparison between the two generations is presented in Figure 1, and Figure 2 shows a real model.

Based on a detailed survey of the literature (see the previous section) and long years of original research [9–12, also: 13–17], a number of critical factors
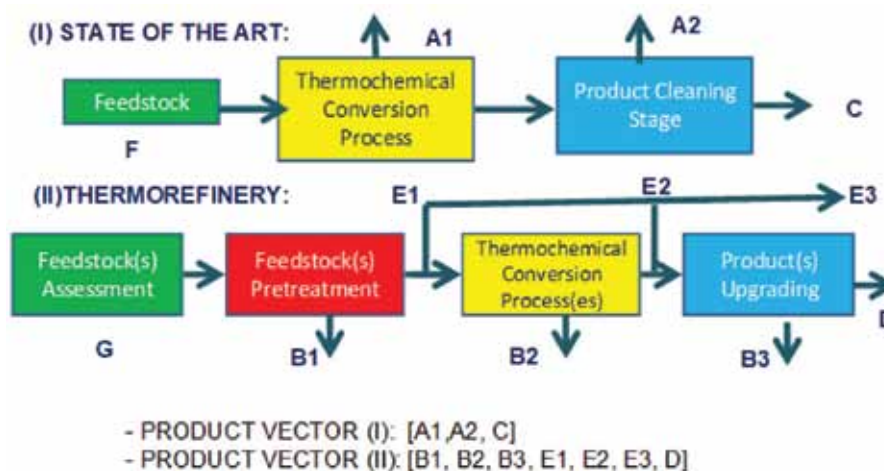

(I) STATE OF THE ART:

Feedstock — F → Thermochemical Conversion Process → A1 ↑ → Product Cleaning Stage → A2 ↑ → C

(II) THERMOREFINERY:

Feedstock(s) Assessment — G → Feedstock(s) Pretreatment → B1 ↓ → Thermochemical Conversion Process(es) → B2 ↓ → Product(s) Upgrading → B3 ↓ → D

E1 — E2 — E3

- PRODUCT VECTOR (I): [A1,A2, C]
- PRODUCT VECTOR (II): [B1, B2, B3, E1, E2, E3, D]

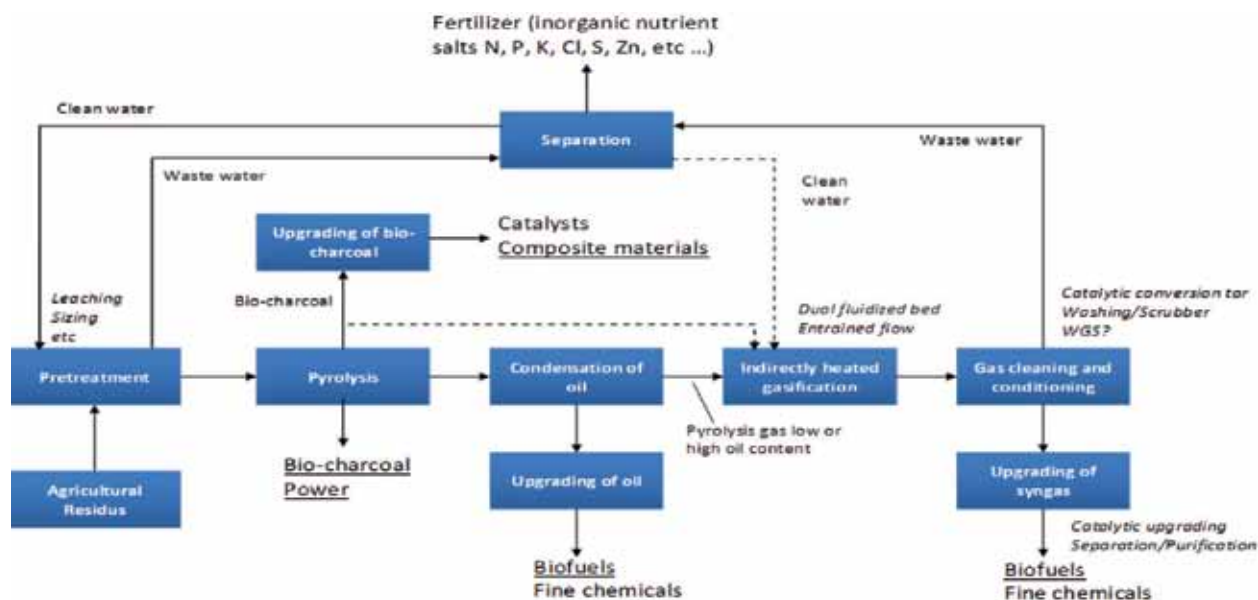**Fig. 1. Thermorefinery vs. State-of the Art**

Fig. 2. Example of an integrated ThermoRefinery, combining agro-residues, leaching, pyrolysis and gasification, and a 9-product vector

affecting the successful conversion of renewable feedstocks, i.e. biomass and wastes to high value-added energy and product vectors by thermochemical methods have been identified. The transition from the 1st generation thermochemical conversion processes to the ThermoRefinery approach can take place through addressing the research goals corresponding to the critical points.

3. Assessing thermochemical conversion technologies [10]

Low quality biomass and waste materials may be used today in a variety of applications for the production of energy and fuels using thermochemical conversion processes. These processes include biomass and waste combustion and gasification in fluidized bed boilers and gasifiers, in stokers and fixed bed systems, such as updraft and downdraft gasifiers, pressurized fluidized bed boilers and gasifiers, as well as entrained flow reactors.

There is also a growing interest for co-combustion and co-gasification applications where biomass and waste could be utilized together with fossil fuels in conventional pulverized fuel (pf)-boilers for the production of energy, as well as in more advanced systems such as integrated gasification combined cycle (IGCC), supercritical combustion boilers, and entrained flow reactors, where the percentages of the biomass and waste materials could be as high as 40% of the fuel mixture in energy basis. There is also a strong interest for fast and slow pyrolysis applications for the production of bio-oils as well as solid char that could be used as an advanced energy carrier.

To illustrate the importance of process heuristics, in Table 1 we present the operating characteristics regarding the temperature and pressure of the main thermochemical reactors that can be used today for the conversion of renewable resources:

Table 1. Operating Characteristics of Main Thermochemical Reactos [10]

Thermochemical Conversion Processes	Operating Pressure (bar)	Operating Temperature (°C)
Atmospheric Combustion/Gasification	1	900
Atmospheric Combustion/Gasification	1	1300
Super Critical Combustion/ OxyFuel Combustion	1	1600+
Pressurized Combustion/Gasification	2–50	1000
High Temperature Pressurized Gasification	2–50	1600
Pyrolysis Production of Biooil/Char	1	600

Table 1 indicates the following:

– Pyrolytic applications have the lowest temperature and pressure requirements, but the produced bio-oil/char have to be almost free from alkali metals, chlorine, and sulphur, in order to ensure their stability and thermal behaviour during their later utilization in combustion and gasification applications.

– Atmospheric combustion and gasification can be divided in 3 main categories depending on the operating temperature. The first one, where the operating temperature is limited below 900°C, is mainly used for small scale energy and fuels production. The second category, where the temperature is limited below 1300°C, is mainly used today for large scale energy production; and, the third category, where the operating temperature is limited below 1600+°C, constitutes the future option for large-scale, high conversion efficiency energy production.

– Pressurized combustion and gasification can be divided into two main categories, where the first category, where the operating temperature is limited below 900°C, is commercial today regarding combustion and in the demonstration phase regarding gasification, and it is used mainly for energy and in a smaller degree for fuels production, while the second category, where the operating temperature is limited below 1600°C, is in the demonstration phase today with a few commercial plants in the case of combustion and some large demos in the case of gasification and is considered to be the technology of tomorrow for energy and fuels production.

– All of these technologies, regardless of their commercial status, are currently using very low amounts of low quality biomass and waste materials, either as firing or co-firing feedstock, due to the substantial ash-related problems associated with the use of these low quality materials in high volumes [7, 9, 20, 29].

4. Optimising feedstock pretreatment [10, 30]

Biomass pretreatment technologies constitute a key way to overcome the problems associated with the use of large amounts of agricultural residues, energy crops, and other types of biomass and waste. These pre-treatments comprise both physicochemical, as well as thermal process stages, and are expected to offer a number of advantages, including the following: (a) To be relatively simple and easy to apply; (b) To require not sophisticated equipment; (c) To be cost and energy effective; and, (d) To transform the pretreated material into a clean and easy to handle, mix and feed feedstock, which can be then used in modern thermochemical conversion systems with high efficiency and without ash-related problems.

The most promising pretreatment technologies for thermochemical conversion systems are leaching, pre-pyrolysis/low temperature gasification, as well as their combination [9].

Leaching biomass via solid–liquid extraction with water as the extraction means has been shown to improve the feedstock properties for high temperature processes and it may be a promising pretreatment of food processing residues. Water-leaching effectively removes water-soluble alkali metals, Cl as well as P and S from biomass, and upgrades crude biomass to better quality feedstock for biofuel and bioenergy production [31–32]. Leaching biomass with water has also demonstrated improvements for reducing deposit formation during thermal conversion [32–34]. Leaching generally improves the properties of biomass by lowering the ash concentration, increasing the heating value, and altering slag-forming ash compositions [35]. Removing chlorine from feedstock reduces acid gas formation, corrosion, and toxic species production, such as dioxins and furans, during thermal processing [36–38].

In general, large fractions of K, Na, Cl, S, and P in biomass fuels can be removed by leaching with water. Several biomass leaching techniques have been studied, such as repeated soaking and draining [15, 39]. Another method is to rinse biomass with water, drain, and mechanically dewater the wet biomass [34]. Biomass leaching can also be done naturally by rain-washing in the field [13–15, 32–34, 39–43]. As it has been shown, leaching can be performed using any kind of water [15]. In combustion and gasification tests with the water-leached biomass, the operation of the reactors increased by >10 times compared to the original untreated feedstock.

Depending on the leaching method and the structure of biomass, significant amounts of alkali metals, chlorine, sulphur, and phosphorous can be removed within a few minutes although the fraction removed varies depending on ion type [31]. Water-leaching also removes organic compounds such as organic acids, water soluble carbohydrates, and ethanol from biomass [13]. On the other hand, the industrial potential of leaching has been affected by the limited success of the water-only leaching application in combustion and gasification, where higher temperatures and pressures are utilized, which, in combination with the higher cost of the leached biomass and the low prices of electricity, prevented the commercial application of such solutions until today [13, 33, 34, 41]. Obviously, there is a clear need for optimization.

Table 2 presents the best estimate ranges of the main properties of the chemically leached biomass. These properties may vary depending on the type of feedstock, the solvents, and additives used in the pretreatment and any the special properties and characteristics we would like to maximize and/or minimize by the pretreatment.

Table 2. Main Properties of Leached Biomass

Thermochemical Process Parameter	% Change after Biomass Leaching
Ash Content	-80 /+10
Higher Heating Value	+5 -+ 20
Chlorine Content	-99
Reactive Alkali Metals Content	-99
Reactive Sulphur Content	-50
Reactive Phosphorus Content	-50

The main goal for the optimization of chemical leaching as a pretreatment is the optimal removal of harmful feedstock components in order to secure a smooth operation of the thermochemical conversion stage. These data are based on our research group's systematic research, including extensive lab-, and pilot-scale testing performed during the last 15 years with various combustors and gasifiers operating at temperatures and pressures as high as 1300°C and 40 bar, respectively, and after a thorough study and understanding of the composition and properties of a large number of low cost biomass and waste material.

As seen from these studies [10], the first and most important condition to target is the almost complete removal of Cl to substantially reduce/eliminate the ash-related problems from the use of biomass and waste materials. The role of Cl in the inorganic transformations during thermo-chemical conversion was already explained above in the State-of-the-Art Section of this paper.

The second condition is the removal of the reactive forms of alkali metals, such as those being present in water-soluble and ion-exchangeable forms, in percentages higher than 99% for combustion and gasification applications and at least higher than 90% for bio-oil production. Finally, the reactive forms of phosphorus and sulphur in low quality biomass and waste materials should also be removed to below 50% of the respective amount present in the raw feedstock. Although heavy metals are not included in the above targets, our recommendation is that, for metals such as Zn and Pb, the removal rates have to be similar to those proposed for alkali metals, while for metals such as Cu, Cd, Ni, etc. similar to those proposed for P and S.

5. Managing ash chemistry

Biomass ash chemistry plays a very significant role regarding the ash-related problems appearing during thermochemical conversion of biomass at high T and P conversion environments. In specific, the alkali metals, Na and K, as well as Cl have long been associated with the fouling tendencies of biomass ash. Volatile forms of these elements are vaporized in the furnace/gasifier at combustion/ gasification temperatures, and they react with S in the flue gas and other elements in the ash, thus forming compounds that deposit on convection surfaces.

The base-to-acid ratio of ash also affects the slagging potential. The basic constituents are Fe, the alkaline earth metals Ca and Mg, and the alkali metals Na and K. Acidic constituents are Si, Al, and Ti. Ash that has either high or low base-to-acid ratio generally has high ash fusion and melting temperatures. However, ash with moderate values of base-to-acid ratio tends to have low fusion and melting temperatures. Agricultural residues and energy crops appear to be rich in alkali metals especially K, as well as Cl, and also contain low-to-average amounts of S and – in most cases – high amounts of Si and Ca. As a result, significant ash-related problems are caused during the thermochemical conversion of these materials that substantially inhibit the use of these biomass materials in high efficiency thermochemical conversion systems for the production of energy and fuels [13, 29, 31–32].

6. Value of ash melting point

Apart from ash chemistry, another parameter that plays a significant role in the mechanism of ash-related problems, caused when agricultural and energy crop biomass as well as various wastes are used in thermochemical conversion systems, is the ash melting point. Ash melting temperatures provide an indication of the temperature range over which portions of the ash will be a molten fluid or semi-molten, plastic state. High melting temperatures indicate that ash released in the furnace will cool quickly to a non-sticky state, resulting in minimal potential for ash-related problems. Conversely, low melting temperatures indicate that ash will remain in a plastic or molten state longer, exposing the furnace to potential deposition, agglomeration, and corrosion.

In the case of using agricultural residues and energy crop biomass, the ash melting point might not be a very accurate method to predict the ash-related problems in all cases. This is due to the ash chemistry of the specific materials. A combination of both the ash melting point and the ash chemistry is required, in most cases, to be able to make a better estimation regarding the ash melting behaviour and the ash-related problems during the combustion/ gasification of these materials [14, 15, 29].

7. Minimizing ash-related problems

Ash-related problems constitute a major factor affecting the use of low-quality biomass, such as agricultural residues and energy crops in thermochemical conversion systems. The ash content of these biomass materials is rich in alkali metals, Cl, and also contains

significant amounts of P and S in reactive forms. High temperature conversion of these biomass materials results in severe ash-related problems, especially when temperature exceeds 800°C, which make impossible the use of these raw materials in high temperature/pressure thermochemical process environments.

7.1. Corrosion

In the case of combustion/gasification processes, corrosion is defined as the reaction of the metal surface of a tube, wall, etc. with chemical compounds, such as alkali metals, chlorides, sulphur, and oxygen to form a layer of oxides that gradually grows until it results in the wastage and mechanical failure of the specific surface. In the case of biomass, firing/co-firing corrosion is caused due to the reaction of alkali, sulphur, and chlorine with the metal surfaces of the reactors as well as the tubes used downstream for heat exchange and gas transfer. Corrosion can be accelerated when the deposition of biomass ash is a serious problem during combustion and gasification processes [15, 29].

7.2. Deposition

Deposition is a process that includes two different processes that are defined as slagging and fouling. Slagging is the formation of molten or partially fused ash solid phases that are called deposits on the reactor walls or convection surfaces exposed to radiant heat during combustion and gasification. Fouling is defined as the formation of ash deposits on convection heat surfaces such as super-heaters and re-heaters.

Slag is formed when melted or softened ash particles are not cooled down to a solid state when they reach the heat surface. In the case of biomass, such as agricultural residues and energy crops with high alkali, P and Cl content, the deformation temperatures could be as low as 800°C. Most ash tends to be re-solidified due to the relatively lower T at the tube surface and the particles factures on impact and partially bounce back into the gas stream. However, if the reactor is too small, the exit gas T is too high, or the melting point of ash is relatively low, molten ash may not have enough time to be re-solidified when they hit the heat surface; therefore, they are easy to stick to the surface and cause the accumulation of deposits leading to slagging.

Fouling is generally caused by the vaporization of volatile inorganic elements in the feedstock (biomass, coal) during combustion/gasification. When heat is absorbed and temperatures decrease in the convection area of the boiler, compounds formed by these elements condense on ash particles and the heating surface, forming a gluelike material, which initiates deposition. Power plant deposits occur on the grate, in the bed, or on the refractory as hard fused glassy deposits,

an agglomeration of grate ash or bed media, and as accumulations of fly ash in hot gas ducts. Fouling of the boiler convection passes includes buildup on screen tubes or superheater tubes, bridging between tubes, and hard deposits on tubes. Deposits on convection surfaces develop quickly when furnace exit temperatures exceed 750°C.

Corrosion is found under many deposits. Deposits collected from similar temperature zones in different boilers have similar compositions. Grate and wall deposits are seen to be similar in composition to the fuel ash. Potassium and calcium silicates and sulphates deposit on screen tubes and upstream super-heaters. Chlorides and carbonates appear in the cooler convection passes. There are three principal undesirable effects of deposits: (1) deposits retard the heat transfer and lead to an eventual decline in boiler efficiency and capacity if they cannot be removed according to the design assumptions for the boiler; (2) deposits can grow to the extent that flow through the boiler is restricted, often bridging across tubes and tube bundles, and causing mechanical damage; and, (3) deposits are associated with corrosion.

Alkali and alkaline earth metals as well as S, P, and Cl in the biomass fuel ash are important to the formation of fireside deposits. Furthermore, the presence of Si in large amounts in the case of many agricultural residues and energy crop biomass in combination with high amounts of alkali metals and Cl leads to increased deposition problems when these biomass materials are used in combustion and gasification environments. Especially, Cl can be an important facilitator in fouling, leading to the condensation of alkali chlorides on heat transfer surfaces in the boiler, and promoting the development of alkali sulphates. Cl may be an important element in the vaporization of alkali species, leading to the formation of more severe deposits [15, 29, 33, 41–43].

7.3. Agglomeration-sintering

Agglomeration occurs in fluidized bed combustion and gasification reactors and is caused by the reaction of the bed material, such as silica, with the reactive elements of the biomass ash, such as alkali metals, phosphorus, chlorine, and sulphur. In a second stage, alkali earth metals, such as calcium and magnesium, are also added into the agglomerate. In case the biomass material contains large amounts of silicon in its ash, then agglomeration occurs regardless of the type of the bed material. In most fluidized bed combustion/gasification systems, the tendencies of the bed particles to sinter and form agglomerates are a key process, the avoidance of which is an important reactor design and operational issue.

Sintering is defined as the process through which the ash particles of the feedstock (biomass, coal, other)

tend to coalesce, when heated at high temperatures and form an initially solid phase that, with time and temperature, and, depending on the ash composition, could be transformed to a viscous liquid that could attract and capture more ash particles while being used as a bridge to connect bed particles together. The presence of large amounts of alkali metals, phosphorus, sulphur, and chlorine in the ash of the biomass materials as well as of silicon, favours the ash sintering and the formation of a viscous semi-liquid phase that could be used to bond the bed particles together and cause severe agglomeration problems during high temperature and pressure thermochemical conversion processes (>800°C). In bubbling fluidized bed systems, in particular, excessive agglomeration of the bed particles can lead to poor air distribution and eventually defluidization of the bed. In extreme cases, it may be necessary for the operators to reduce the bed temperatures or to bring the reactor off-line to remove and replace the bed material. In operating fluidized bed combustion/gasification plants, the key issue is the control over the bed temperatures and the fuel distribution [14, 15, 29].

8. Tar content in the producer gas

The product gas formed from biomass gasification contains as major components CO, H_2, CO_2, CH_4, H_2O, and N_2, in addition to organic (tars) and inorganic (H_2S, HCl, NH_3, alkali metals, etc.) impurities and particulates. The organic impurities range from low molecular weight hydrocarbons to high molecular weight poly-nuclear aromatics. The lower molecular weight hydrocarbons can be used as fuel in gas turbines or various engine applications, but they are undesirable products in fuel cell applications and methanol synthesis, due to their negative effects on downstream applications. The higher molecular weight hydrocarbons are known as "tar." A definition is that "tars" are considered as the condensable fraction of the organic gasification products and are predominantly aromatic hydrocarbons, including benzene. The diversity in the operational definitions of "tars" usually comes from the variable product gas compositions required for a particular end-use application and how the "tars" are collected and analysed.

Tars are problematic in integrated biomass gasification systems for a number of reasons. Tars can condense in exit pipes and on particulate filters leading to blockages and clogged filters. Tars also have varied impacts on other downstream processes. Tars can clog fuel lines and injectors in internal combustion engines. Luminous combustion and erosion from soot formation can occur in pressurized combined-cycle systems where the product gases are burned in a gas turbine. The product gas from an atmospheric pressure gasification process needs to be compressed before it is burned in

a gas turbine, and tars can condense in the compressor or in the transfer lines as the product gas cools.

The removal of problematic tars from the producer gas using catalysts, as well as physical processes has been seen to be problematic itself and cause large drops in efficiency, while its increase in capital cost could reach 50% of the total gasification system capital cost. Thermal cracking could be a more efficient and less costly tar elimination process, but it requires high temperatures (>1000°C) that, in the case of agricultural residues and energy crop biomass, could cause significant ash-related problems. As a result, a pretreatment technology eliminating these problems could also enhance significantly the removal efficiency of tars from producer gas [4–6, 44].

9. Minimising handling problems

Biomass has been proved to be a difficult-to-handle material. Pulverization (<200microns) of 1 metric ton of biomass, such as wheat straw or olive residue, to be used in a pulverized coal combustion boiler requires more than 11 times the time for pulverization of 1 metric ton of coal. In addition, the pulverization of biomass using existing coal pulverization mills causes significant problems to them due to the high temperatures developed during the milling process, and, the resulting high wear and tear leading to substantially higher milling costs, when co-combustion and or co-gasification are considered. Furthermore, the pulverized biomass still contain large % of particles above the particle size required by the pf-boiler feeding system for an optimum feeding and efficient combustion.

The use of screw-type feeders has shown to have the lowest problems when biomass is fed into boilers as well as gasifiers. However, problems are caused mainly in the case pneumatic type feeders are used for feeding the biomass as well as when valves or other kinds of intermediate mechanisms are used during the moving of the biomass from the storage bins to the reactor. Biomass tends to bridge, and, the smaller the particle size, the higher the bridging problems observed. Bridging is a very significant problem when agricultural energy crop biomass is used regardless of the biomass particle size.

Biomass is very difficult to be milled to the small particle size (<200 microns) required normally for feeding into pulverized fuel boilers or entrained flow gasifiers, where the optimum particle size is even lower (<60 microns). However, even milling at particle sizes below 6 mm requires a significant amount of energy and could result in high costs. The energy requirements to reduce the particle size of biomass to below 2 cm is estimated to be around 10–20 kWh/metric ton. As a result, the milling energy requirements for a pretreatment unit that will process 120 kt/year will be around 1200–2400 MWh. As a result, and depending

on the cost of electricity per MWh, which could range between \$60 and 120, the energy cost of milling will be \$ 0.6–2.4 per dry metric ton. Actually, a value closer to \$ 0.6–1.8/metric ton is considered to be most likely today in the US, as well as in most other parts of the world, taking into consideration the current prices of electricity for industrial use. By analysing experimental data from various sources regarding the energy required for milling various biomass materials in different particle sizes [45], we have found that the specific energy requirement for milling various feedstocks vary between 1 and 60 kWh/t, and Milling below 3 mm is very costly and significantly decreases the viability of the milling stage and of the whole conversion relative process.

Biomass and bio-waste materials are difficult to mix with either other types of biomass and/or coal. This is mainly due to the different bulk density, particle size, and flowing characteristics that are very different in each biomass and waste material. In general, fruit pits and woody biomass are found to have the best mixing characteristics and flowing properties compared to the other biomass materials, and they also have average to high bulk density. Straws and grasses are found to be amongst the worst cases regarding mixing and flow properties. They also have very low bulk densities, which makes very difficult their mixing with other biomass and/or coal materials in rather large ratios. As a result, the application of a technology/process stage to improve the mixing as well as flowing properties and bulk density is required in order for these biomass raw materials to be able to be used as feedstocks to thermochemical conversion systems in rather high ratios, together with other biomasses and/or coal materials.

10. Pre-pyrolysis/low-temperature gasification, combined pretreatment

Pre-pyrolysis, also known as torrefaction, includes the thermal treatment of the biomass materials in the temperature range 200–300°C under inert atmosphere aiming at the partial decomposition of the biomass and change of its chemical and physical structure. Pre-pyrolysis causes a decrease of the volume of biomass, thus increasing its energy density, it reduces the amount of volatiles, and it increases fixed carbon and the ash content of the pre-pyrolyzed biomass. It also considerably increases the grindability of the biomass and retains most of its energy value. Pre-pyrolysis achieves equilibrium moisture content of 3%, a reduction of mass by 20 to 70% (primarily by release of water, carbon oxides, and volatiles) while retaining 50% to 90% of the biomass's original energy content in the solid phase. The highest mass loss as well as energy loss is observed in the case of the agricultural residues and waste biomass due to its higher reactivity and the lower lignin content compared

to the woody biomass. Pre-pyrolysis provides fuels that are rich in energy, low in moisture content, resistant to moisture, and easily applied via direct co-firing with coal at conventional pf-fired power plants. The pre-pyrolyzed biomass can be easily ground, mixed, and fed into commercial boilers and gasifiers using grinding, mixing, and feeding systems having developed for coal materials. As a result, substantial savings are realized when pre-pyrolyzed biomass is used as feedstock in direct firing as well as co-firing applications [16, 46].

In the case that the thermal treatment of the biomass material is performed in a low oxygen (<30% of the stoichiometric) environment, the process is called low temperature gasification, and it results in similar carbonized material as in the case of pre-pyrolysis. It has to be mentioned that, in both cases, apart from the energy that remains bound in the solid phase after the end of the pretreatment process [17], a substantial part of the initial biomass energy content that could vary from 10–40% is available as a low BTU gas stream that could be used for the production of energy simultaneously with the solid pre-pyrolyzed/carbonized material. This substantially improves the economics of the process and increases its efficiency. A major challenge for both pre-pyrolyzed and carbonized biomass plant developers is the availability of commercial equipment that will reduce the processing time, energy inputs, and production costs for manufacturing bulk pre-pyrolyzed/carbonized materials to acceptable levels.

The combination of both pretreatment technologies, pre-pyrolysis/low temperature gasification and leaching, leads to the production of a very clean coal substitute material that contains trace amounts of alkali metals and chlorine and very low amounts of sulphur and phosphorus and has grinding, mixing, and feeding characteristics similar to coal. As a result, the derived material could be used for energy and fuels production in high temperature and pressure thermochemical conversion systems without ash-related problems and catalyst deactivation problems, and with high efficiencies and improved economics.

Concluding remarks

Through the establishment of an inventory and mapping of regional feedstocks, complete with potential, geographical distribution, physicochemical, energy, and other properties, biomass and wastes obtain the status of a *resource*, while keeping their features.

Solving long overdue, complex problems limiting the utilisation of resources and technologies, such as the ash-related ones, by an original compilation of knowledge from the chemistry, physics, metallurgy, engineering and bioresource fields, will improve the prospects of this technological pathway.

The shift away from production of only fuels opens the way to new chemistry and engineering, involving knowledge-based synthesis of novel molecules with innovative functions, which can be the corner-stone of regional smart specialization, and a major stepping stone for sustainable biobased development.

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