BIOMASS GASIFICATION

(LECTURE-6)

Views of Typical Biomass Gasification (Power) Plant (Source:BioEnergy Consult, July 2019)

Biomass Gasification

Lecture – 6

* Introduction

- it is a process of converting solid biomass fuel ~~into~~ into a gaseous combustible fuel (or gas) (called producer gas) through a sequence of themochemical reactions
- it produces a low heating value fuel with calorific values ranging from 1000 – 1200 kcal/m^3
- ~~it~~ the gas contains various percentage of CO, H_2, CH_4, CO_2 and N_2 depending upon the quality of fuel (biomass) used in gasification and the type of technology applied
- Overall reactions during biomass gasification

Biomass + Air + H_2O (Steam) →
- → Major gas components: CO, CO_2, H_2, N_2
- → Minor Carbonaceous species: LHC, Tars, Chars
- → Minor Nitrogeneous species: NH_3, HCN, NO_x
- → Minor Sulfurous species: H_2S, COS, SO_x
- → Others: Ash

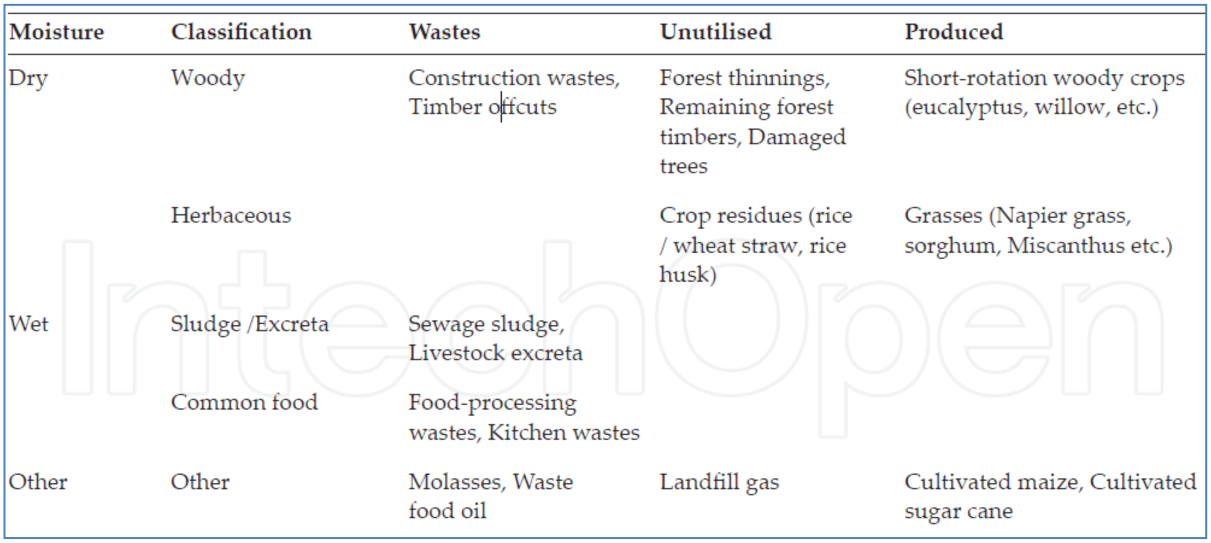
- factors effecting the biomass gasification
  - properties of biomass, such as size, shape, density, chemical composition, energy content, moisture content
  - gasification conditions, such as reactor type, temperature, pressure, type and flow of oxidising agent, biomass flow, and catalyst used, residence time
- biomass gasification is one of the most attractive technolog for producing hydrogen rich gas, like syngas
- gasification offers a viable solution to overcome ~~a~~ energy shortage
- feedstocks predominated by carbon, hydrogen, oxygen and nitrogen are oxidised at elevated ~~at~~ temperature to provide heat energy
- ~~carbon and hydrogen are oxidised to generate ca carbon monoxide, carbon dioxide and methane~~
- heat liberated during oxidation drives further chemical rxns. to generate carbon monoxide, carbon dioxide, hydrogen and methane
- different types of gasifiers are used depending on end use * and quality of producer gas needs *

BIOMASS GASIFICATION
(LECTURE-6)

Biomass Feedstock for Gasification

- biomass feedstocks are classified based on several factors, such as : moisture content, material, and form as shown in **Table-**1.
- biomass is broadly divided into three groups: dry, wet, and others
- dry biomass is classified as woody or herbaceous and wet biomass as sludge/excreta, common food, or other
- each classification has three sub-categories: waste, unutilized, and produced

Table-1: Classification of Biomass Feedstocks



Moisture	Classification	Wastes	Unutilised	Produced
Dry	Woody	Construction wastes, Timber offcuts	Forest thinnings, Remaining forest timbers, Damaged trees	Short-rotation woody crops (eucalyptus, willow, etc.)
	Herbaceous		Crop residues (rice / wheat straw, rice husk)	Grasses (Napier grass, sorghum, Miscanthus etc.)
Wet	Sludge /Excreta	Sewage sludge, Livestock excreta		
	Common food	Food-processing wastes, Kitchen wastes		
Other	Other	Molasses, Waste food oil	Landfill gas	Cultivated maize, Cultivated sugar cane

- among these, dry woody/herbaceous biomasses are used as feedstocks for BG plants in Japan
- woody biomasses contain waste woods (construction wastes and timber off cuts) and unutilized woods (forest thinning, remaining timbers, and damaged trees) composed of cedar, cypress, pine, etc.
- short-rotation woody crops (eucalyptus, willow, etc.) are categorized as produced woods
- energy crops such as willow may be cultivated in land fallow and used as biomass
- for unutilized herbaceous biomass, crop residues such as rice/wheat straw and rice husks
- while for produced herbaceous biomass, grasses such as Napier grass, sorghum, and Miscanthus are usable
- above all, rice husks contain abundant silica
- the ash byproduct from gasifiers has potential use in nanomaterials

Chemistry of Gasification

- the reactions taking place in the gasifier can be summarized as given below:

  Partial oxidation:

  $$C + O_2 \leftrightarrow CO \qquad \Delta H = -268\ \text{kJ/mol} \qquad (1)$$

  Complete oxidation:

  $$C + O_2 \leftrightarrow CO_2 \qquad \Delta H = -406\ \text{kJ/mol} \qquad (2)$$

  Water gas phase reaction:

$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H = 118 \text{ kJ/mol} \qquad (3)$$

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H = 170.7 \text{ kJ/mol} \qquad (4)$$

- the heat required for water gas phase and Boudouard reactions is provided by complete and partial oxidation reactions, and complete oxidation provides around 60% of the heat requirements during gasification
- in addition to the previous reactions that are common in combustion and gasification, hydrogen, steam, and carbon monoxide undergo further reactions as shown below:

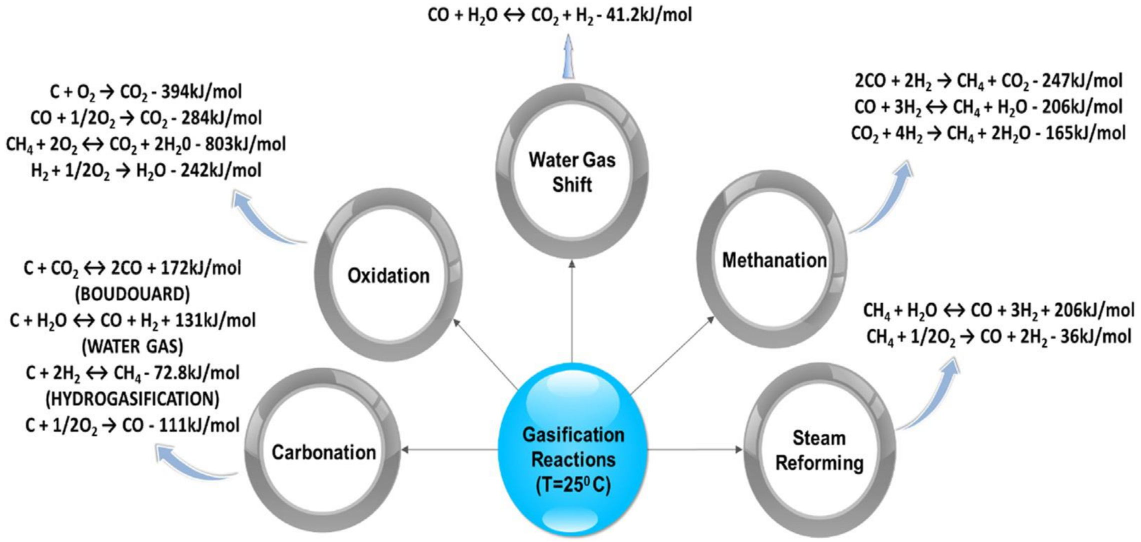
Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -\,42 \text{ kJ/mol} \qquad (5)$$

Methane formation:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -\,88 \text{ kJ/mol} \qquad (6)$$

- the water gas shift and methane formation reactions are in equilibrium and the governing parameters are: pressure, temperature, and concentration of reaction species
- the possible gasification reaction may also be summarized and shown by the following diagram



➢ Overall Steps Involved in Biomass Gasification

- the main steps involved can be categorized as upstream processing, the gasification process in the gasifier and the downstream processing as shown in **Figure-1**

Upstream Processing

- upstream processing includes processing of the biomass to make it suitable for gasification operations
- size reduction is needed to obtain appropriate particle sizes
- drying is needed to achieve appropriate moisture so that the process can work efficiently
- densification also may be necessary due to the low density of biomass

Gasification

- this is the second step where the gasification process is carried out under specified conditions in order to achieve optimum product yield, i.e. the producer gas
- different types of gasifiers are used for the purpose

Down Stream Processing

- this is the third step where the cleaning (purification) of the gaseuos products take place as per the desired sopecifications
- unit operations are applied foe the purpose

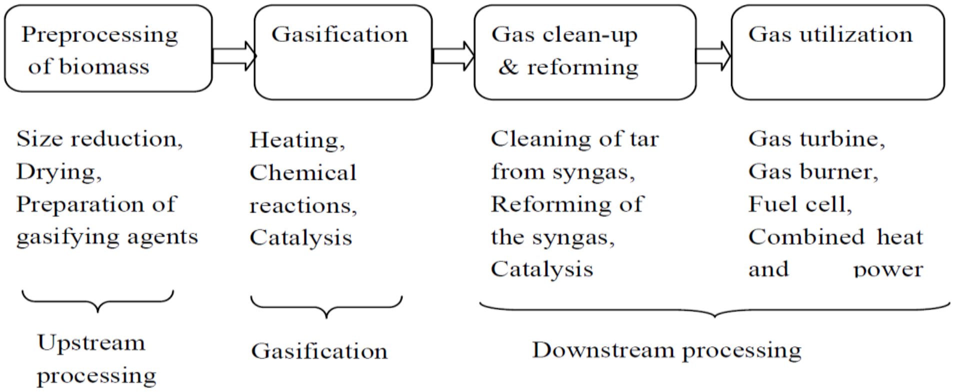


Figure-1: Processes involved in overall biomass gasification.

➢ The Biomass Gasification Process (Mechanisms of Gasification)

- the biomass gasification process consists in the conversion of a solid/liquid organic compound in a gas/vapor phase and a solid phase
- the principal reactions of gasification are endothermic and the necessary energy for their occurrence is, generally, granted by the oxidation of part of the biomass, through an allo-thermal or an autothermal phase
- in the auto-thermal process, the gasifier is internally heated through partial combustion, while in the allo-thermal process the energy required for the gasification is supplied externally
- considering the auto-thermal system, gasification can be seen as a sequence of several stages
- a simplified schematic representation of the gasification is demonstrated in **Figure-2**
- the main steps of the gasification process are:
    i. oxidation (exothermic stage)
    ii. drying (endothermic stage)
    iii. pyrolysis (endothermic stage)
    iv. reduction (endothermic stage)

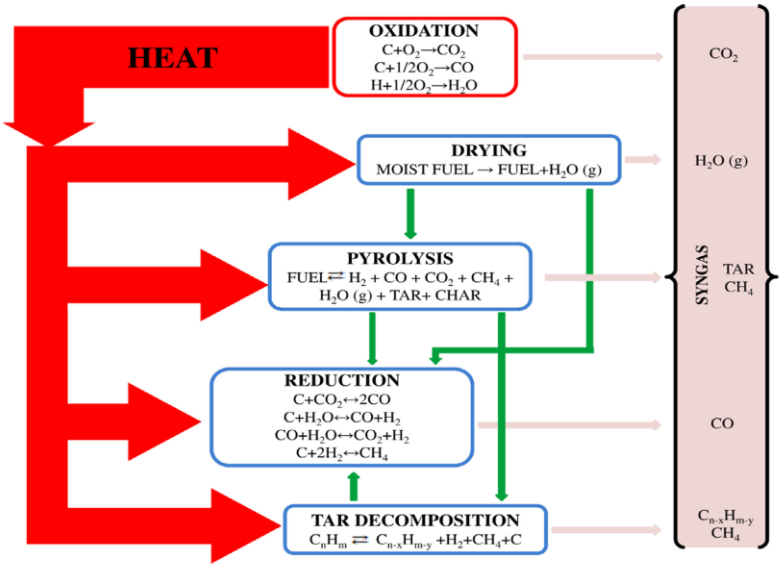


Figure-2: Main stages of the gasification process.

- **Oxidation**
  - ✓ in order to obtain the thermal energy required for the endothermic reaction and to maintain the operative temperature, the oxidation of part of the biomass is necessary
  - ✓ the oxidation is carried out in conditions of lack of oxygen with respect to the stoichiometric requirement
  - ✓ despite the partial oxidation involving all carbonaceous species (tars included), it is possible to simplify the system considering that only char and the hydrogen contained in the gas produced participate in the partial oxidation
  - ✓ the main reactions that take place during the oxidation phase are given in **Figure-2** and also discussed in the chemistry of biomass gasification
  - ✓ as evident, the main product of this step is the thermal energy necessary for the whole process, while the combustion product is a gas mixture of CO, CO_2 and water
  - ✓ in this mixture nitrogen can be present if the biomass oxidation is performed with air, otherwise nitrogen is practically absent if only oxygen is used
- **Drying**
  - ✓ drying consists in the evaporation of the moisture contained in the feedstock
  - ✓ the amount of heat required in this stage is proportional to the feedstock moisture content
  - ✓ generally, the heat required derives from the other stages of the process
  - ✓ drying can be considered complete when a biomass temperature of 150 °C is achieved
- **Pyrolysis**
  - ✓ pyrolysis leads to the thermochemical decomposition of the matrix carbonaceous materials
  - ✓ the cracking of chemical bonds takes place with the formation of molecules with a lower molecular weight
  - ✓ by pyrolysis, it is possible to obtain different fractions: a solid, a liquid/condensed gas and non-condensed gas
  - ✓ the solid fraction, which can range from 5–10 wt% for fluidized bed gasifiers to 20–25 wt% for fixed bed gasifiers, has a high carbon content and is characterized by a high heating value
  - ✓ the solid fraction includes the inert materials contained in the biomass in the form of ashes and a high carbon content fraction, called “char”
  - ✓ the liquid fraction, usually called "tars", varies according to the gasifier type, such as lower than 1 wt% for downdraft gasifiers, 1– 5 wt% for bubbling bed gasifiers, 10–20 wt% for updraft gasifiers and

    is constituted by complex organic substances, condensable at relatively low temperatures
  - ✓ the gaseous fraction is typically 70–90 wt% of the fed material and is a mixture of gases that are non-condensable at ambient temperature
  - ✓ the gaseous fraction is called "pyrolysis gas" and consists mainly of hydrogen, carbon monoxide, carbon dioxide and light hydrocarbons such as methane and other C2, C3 hydrocarbons; minor constituents are acid or inert gases
  - ✓ the pyrolysis reactions take place with a temperature in the range 250–700 °C
  - ✓ they are endothermic and, as in the drying step, the heat required comes from the oxidation stage of the process
  - ✓

- **Reduction**
  - ✓ the reduction step involves all the products of the preceding stages of pyrolysis and oxidation
  - ✓ the gas mixture and the char react with each other resulting in the formation of the final gaseous mixture
  - ✓ main reactions occurring in the reduction step have been shown in 'Chemistry of Biomass Gasification' and also demonstrated in **Figure-2**
- **Conceptual diagram with respect to the mechanism of gasification demonstrated in multiple steps fixed-bed (a) updraft and (b) downdraft gasifiers**

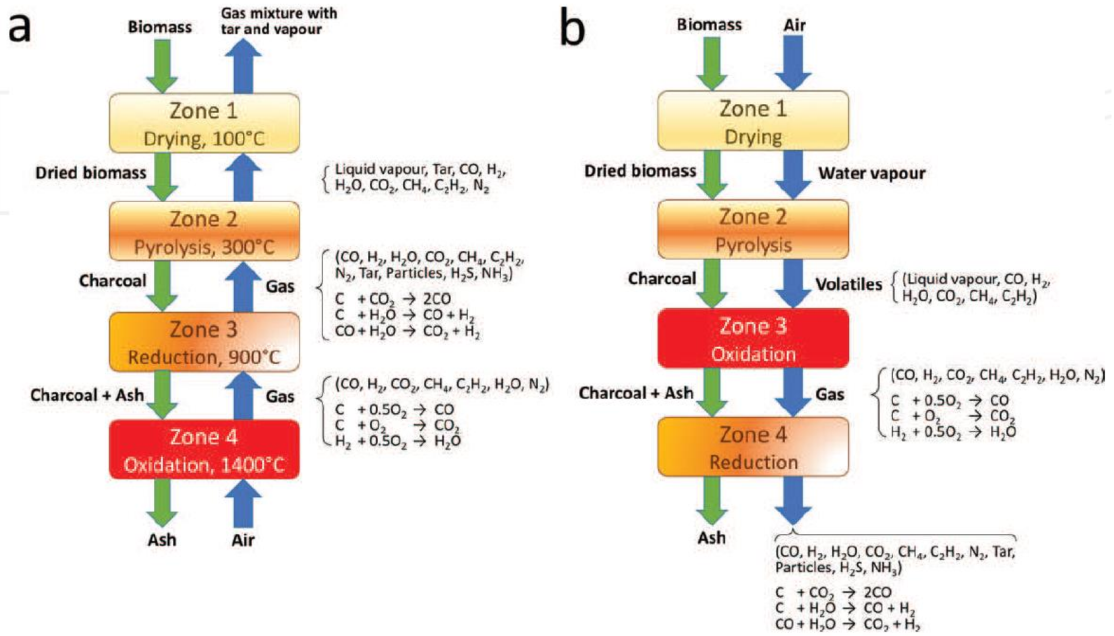


Figure-3: Conceptual diagram of multiple steps in fixed-bed (a) updraft and (b) downdraft gasifiers

➢ Factors Affecting the Gasification Process

- the biomass gasification units may be divided into small-, medium-, and large-scale biomass gasification and power generation units
- pretreatment of biomass is needed which includes size reduction, size screening, separation of magnetic materials, and storing as wet biomass
- then prior to gasification, drying and storing as dry material are accomplished to reduce the moisture content
- feedstock type and feedstock preparation are important factors affecting the yield and quality of produced gaseous mixture or the syngas
- shredding and drying are two processes conducted to prepare the biomass raw material for gasification process
- the main parameters affecting the gasification are: equivalence ratio (ER), biomass characteristics, moisture content, moisture content, Superficial velocity, Operating temperature, gasifying agent, residence time, pressure, catalyst, effect of biomass/steam ratio

- **Equivalence Ratio (ER)**
  - ✓ the equivalence ratio (ER), Φ is defined as the ratio of the actual air supplied to that of the stoichiometric/theoretical air used for gasification, i.e.

$$\Phi = \frac{\text{Actual Air supplied to the System for Combustion}}{\text{Theoretical/Stoichiometric requirement of Air for Combustion}}$$

  - ✓ the efficiency, η of a gasifier is defined as

$$\eta = \frac{\text{Chemical energy output in the dry Producer Gas at } 15\ {}^{0}\text{C}}{\text{Energy input from the Biomass}}$$

  - ✓ it may be seen from the following Figure-4 that total energy in the gaseous phase increases with the increase of equivalence ration, Φ .

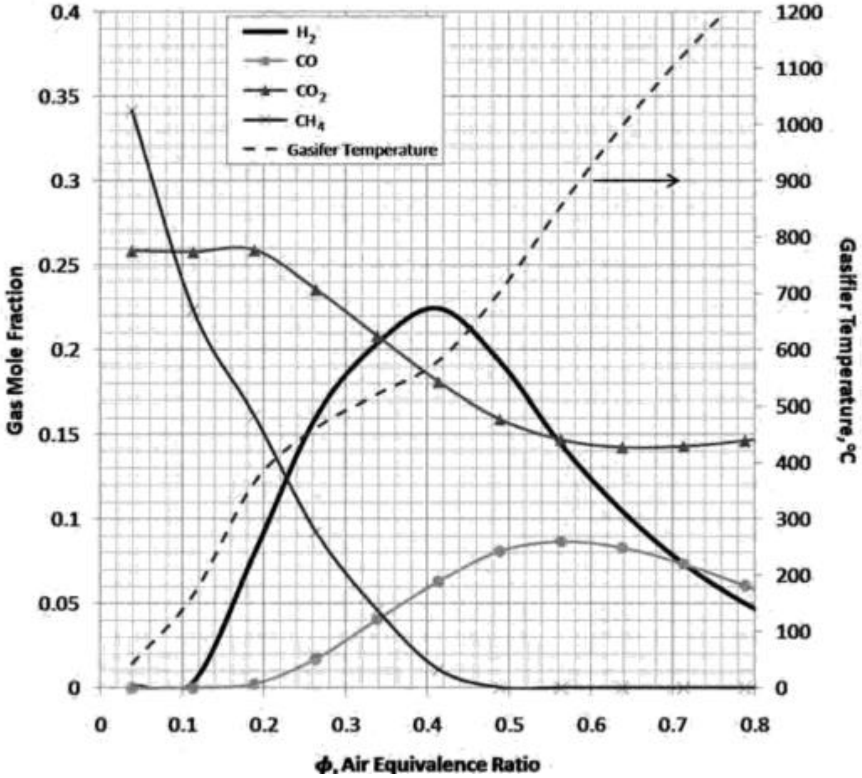


Figure-4: Producer gas composition with variable stoichiometric variation.

  - ✓ increasing ER decreases the heating value of the produced gas due to decreasing H_2 and CO concentration and increasing CO_2 concentration
  - ✓ higher ER helps in reducing tars and provides more O_2 to react with volatiles
  - ✓ typical values of ER ranges between 0.2 and 0.4.
  - ✓ it was reported that increasing ER decreases the concentration of combustible gases CO, CH_4, and CnHm, however H_2 increases till the value goes to 0.4 and then it decreases
  - ✓ increasing ER improves the reaction temperature and carbon conversion, and reduces the tar yield
  - ✓
- **Biomass Characteristic**
  - ✓ biomass characteristic is a major factor affecting produced gases during gasification
  - ✓ the physical properties that may have major effect are: absolute and bulk density, and particulate size

  - ✓ the chemical composition parameters that are of major importance to define the quality including volatile matter, moisture content, fixed carbon, ash content, and gross calorific
  - ✓ the ultimate analysis comprises the carbon, oxygen, nitrogen, and sulfur of the dry biomass on a weight% are also highly significant
- **Moisture Content**
  - ✓ the moisture content can be determined by complete drying of biomass sample
  - ✓ the moisture content is calculated by subtracting the sample weight after drying from fresh sample weight
  - ✓ maximum allowable moisture content in downdraft gasifier is 40% on dry weight basis
  - ✓ updraft gasifier can handle biomass with higher moisture content
  - ✓ the higher moisture content in biomass will increase the consumed energy for drying, and will reduce the pyrolysis of biomass
  - ✓ as a general rule, increasing moisture content decreases the conversion
- **Superficial Velocity**
  - ✓ it is the ratio of the biogas production rate at normal conditions and the narrowest cross-sectional area of gasifier
  - ✓ lower superficial velocity is linked with high yield of char, and large quantities of unburned tars, which may deactivate catalyst, plug lines, and destroy compressors
  - ✓ higher superficial velocity results in reduced amount of char and low overall process efficiency
- **Operating Temperature**
  - ✓ operating temperature affects conversion, tar content, gas composition, gas heating value, and char conversion
  - ✓ in order to select the optimum temperature, gasifier type, and biomass source is considered
  - ✓ generally, temperature higher than 800°C should be used to obtain high conversion and low tar content in the produced biogas
  - ✓ low temperature is associated with low tar content, low H_2 and CO content in the produced biogas
  - ✓ increasing temperature will increase gas yield, hydrogen, heating value, and ash agglomeration
  - ✓ the ash agglomeration problem can be overcome by keeping the temperature below 750°C
- **Gasifying Agent**
  - ✓ gasifying agents in use are air, steam, steam/oxygen mixture, and CO2
  - ✓ they affect the heating value of the produced gas
  - ✓ the heating value increases with increasing steam content of the gasifying agent, whereas heating value decreases as air increases in the gasifying agent
  - ✓ the steam/oxygen mixture represents a zero nitrogen-gasifying agent which increases the heating value and allows liquefying the produced gas after proper treatment
- **Residence Time**
  - ✓ it has a significant impact on the composition and produced tars in biomass gasification
  - ✓ oxygen-containing compounds may be decreased by increasing the residence time

  - ✓ increasing residence time decreases yield of one and two atomic ring compounds,
- **Pressure**
  - ✓ in gasification processes, either atmospheric or and higher pressures are commonly used
  - ✓ selection of the optimum pressure depends on the application of the produced gaseous product
  - ✓ if it is used for production of methanol or synthetic auto-fuels, higher pressures are preferred to improve the process yield and to reduce tar content
  - ✓ for generating burnable gases, atmospheric pressure should be used
  - ✓ high pressure applications are recommended for large scale gasification
  - ✓ however, atmospheric pressure is recommended for small-scale gasification
  - ✓ high pressure gasification is still not well developed and further research is needed to commercialize such processes
- **Catalyst**
  - ✓ The type of the catalyst is an important factor affecting gasification quality and the product
  - ✓ catalyst affects the composition of the syngas by manipulating the percentage volume of hydrogen, carbon dioxide, methane, and carbon monoxide
  - ✓ optimum quantity of catalyst plays a significant role in minimizing the gas content of carbon dioxide and maximizing the useful gases in the gaseous products such as hydrogen, carbon monoxide, and methane

➢ Technologies of Biomass Gasification

- **Introduction**
  - ✓ gasification process converts biomass, a low-energy density material, into a gaseous product mixture containing mainly CO, H_2, CH_4 and CO_2 .
  - ✓ gasification is a partial oxidation process and it is commonly operated at 800–900 ^{0}C.
  - ✓ in some cases, steam is also used as the gasification agents
  - ✓ the gaseous products from the gasifier can be utilized in gas engines or gas turbines for the generation of electricity
  - ✓ gasifier reactors are simple in construction, however the chemistry and physics involved in their operation is not well understood
  - ✓ gasifiers designs are generally categorized into three types: downdraft, updraft and fluidized bed
  - ✓ all of the gasification processes oxidize part of the biomass to generate energy and to carry out the process
  - ✓ the selection of the gasifier depends on the end use and quantity of the producer gas required
  - ✓ in fixed bed gasifier the biomass fuel is fixed or stable on the bed and does not move
  - ✓ fixed-bed biomass gasifiers are classified into two category: down draft and updraft
- **Downdraft Gasifier**
  - ✓ in downdraft gasifier, fuel is fed near the top of the reactor
  - ✓ the schematic diagram of the system is shown in **Figure-5**
  - ✓ air can be introduced alongwith the fuel or at some intermediate level below
  - ✓ hot producer gas alongwith char and ash exit the bottom of the reactor vessel
  - ✓ a slight vacuum is usually applied at the gasifier exit to withdraw producer gas

- the four different zones of drying, pyrolysis, combustion and reduction occur sequentially from the top to the bottom of the gasifier, respectively
- the top section of the gasifier acts as a surge vessel for fuel to br dried before entering the pyrolysis zone
- since the top of the downdraft gasifier is at ambient temperature and pressure, fuel feeding is quite simple

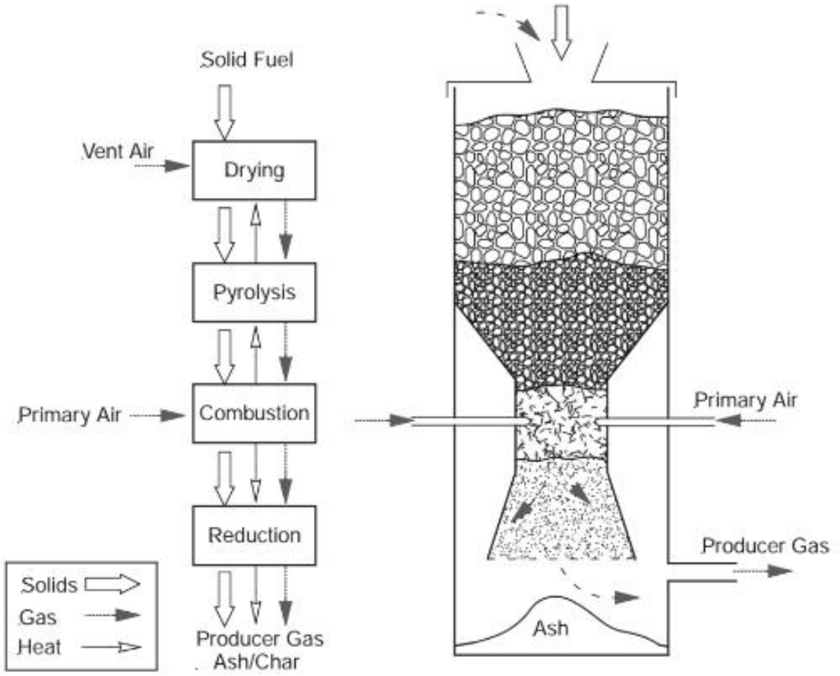


Figure-5: Downdraft gasifier.

- radiant and combustive heat transfer from the lower pyrolysis and the combustion sections provide the heat for drying
- water vapor from the drying zone flows downwards towards the pyrolysis and combustion section where a portion is reduced to hydrogen
- however, majoririty of water vapour remains in the final producer gas
- a small amount of air may be added in the drying section to facilitat the downward flow of gas, thereby sweeping out excess moisture
- the dried solid fuel moves downward by gravity into the pyrolysis zone and is heated such that volatile matter is evolved
- resulting gas flows through the reduction zone on an ash support grate before before exiting the reactor
- gaseous products of the pyrolysis reactions are drawn downwards alongwith the char into the combustion zone of the gasifier
- a portion of the pyrolysis products and char are burned in the combustion zone as free oxygen becomes available
- at this point, an oxidizer gas, such as air or oxygen is injected
- reactions with oxygen results in steep rise of temperature upto 1000 – 1200 ^{0}C , depending on the moisture content of the fuel
- some downdraf reactor reactor designs employ a restriction, commonly known as a throat section, to increase the velocity of gas to promote heat and mass transfer

- **Updraft Gasifier**
  - ✓ updraft gasification system has been shown by **Figure-6**
  - ✓ air is injected near the bottom of the reactor (in the combustion zone) with the resulting producer gas flowing upwards through the interstitial spaces in the solid fuel
  - ✓ the producer gas exit the top of the reactor where incoming biomass fuel is added
  - ✓ hence the updraft producer gas exits at lower temperatur (130 – 150 ^{0}C) than that of the downdraft reactor due to the drying of the solid fuel

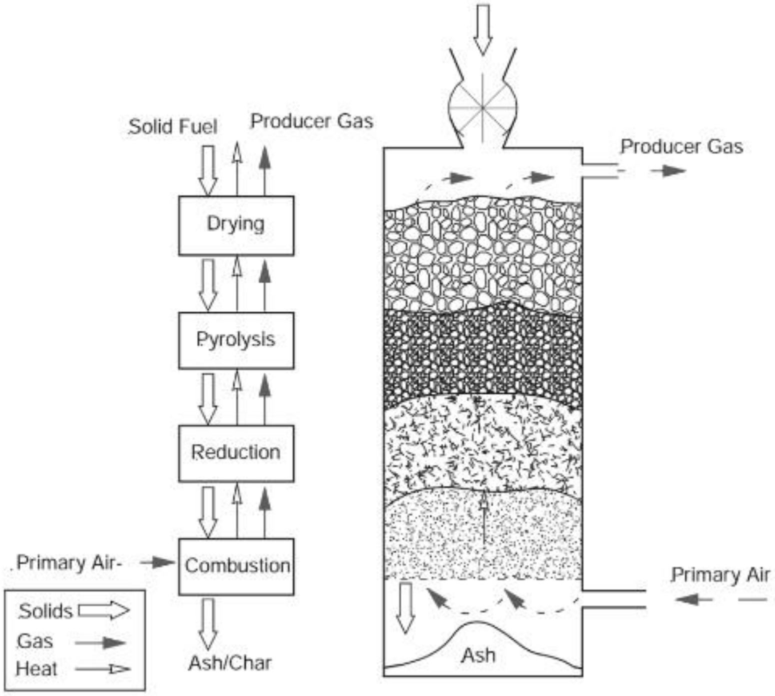


Figure-6: Updraft gasifier.

  - ✓ however, the gas is heavily contaminated by pyrolysis products (primarily tar, oils and partculate) from the incoming fuel
  - ✓ Since the producer gas exits at the top, special precautions are taken to avoid air in-leakage with the incoming biomass
  - ✓ the updraft gasification process is similar to that of the downdraft mode in that the major reaction stages are present: drying, pyrolysis, combustion and reduction
  - ✓ however, with respect to the solids, the order of these stages is changed
  - ✓ most of the miosture evaporated from the fuel solids and products of the pyrolysis reactions exit the top of the reactor with the producer gas
  - ✓ the charged solid migrates below to the reduction zone
  - ✓ heated combustion gases enter the reduction zone providing the required energy for the endothermic reactions
  - ✓ finally, the remaining char reacts with oxygen or airinjected into the bottom of the reactor vessel
  - ✓ ash is extracted from the bottom of the reactor
- **Fluidized-Bed Gasifier**
  - ✓ shcematically, the fluidized-bed gasifier is shown in Figure-7
  - ✓ it makes the use of an inert medium such as sand to mix the solid fuel with the

gas phase

- ✓ depending on the specific reactor design and average bed media particle size, the superficial gas velocity typically ranges from 0.5 – 1.0 m/s
- ✓ air is injected in the bottom of the reactor vessel through a distributor comprising of a perforated plate and series of nozzles such that the bed material is suspended in a fluid-like state as evident from the Figure – 7, below:

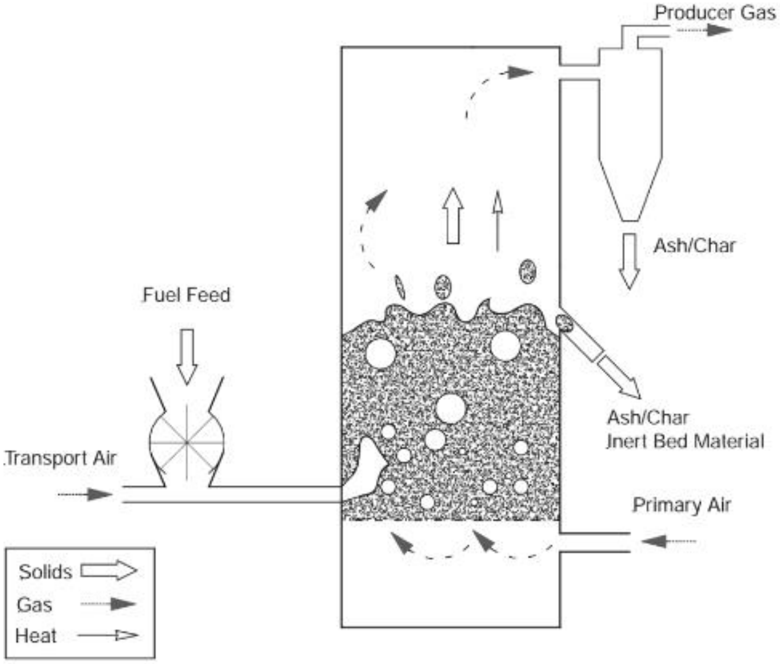


Figure-7: Fluidized-Bed Gasifier

- ✓ gas bubbles form at the distributor, increasing in size as they rise upward toward the bed surface due to the decreasing hydrostatic presuure
- ✓ air within the bubbles exchanges with combustion and pyrolysis gases formed in the dense phase as the fuel is converted to producer gas
- ✓ fly ash, char, and inert bed materials are ejected from the dense phase bed as gas bubbles erupt on the surface
- ✓ the turbulent fluidized medium promotes high heat-transfer rates, and as a result the bed-temperature is maintained in an essentially isothermal state
- ✓ the maximum temperature obtained during gasification is only 800 ^{0}C – 900 ^{0}C which is less than the temperature that of the fixed bed design (downdraft, updraft)
- ✓ this is combined with the low gas residence time which increases the yields of tars, oils, and light hydrocarbons
- ✓ the tar/oil concentration in the producer gas is higher than that derived from the downdraft gasifier
- ✓ fuel is pneumatically conveyed into the bottom of the dense-phase bed

- **Entrained Flow Gasifier**
  - ✓ entrained flow gasifier is a comparatively new design with high efficiency
  - ✓ it is normally employed for large-scale gasification of coal, biomass, and refinery residues
  - ✓ however, fuel particles should be highly pulverized for this kind of gasifier, and hence it is problematic when biomass is used as a feedstock

- ✓ on the other hand, gasification in these gasifiers takes place above 1000 ^{0}C which helps in cracking tar
- ✓ they are basically classified into two families, namely, top-fed gasifier and side-fed gasifier as shown in the **Figure-8**, below:

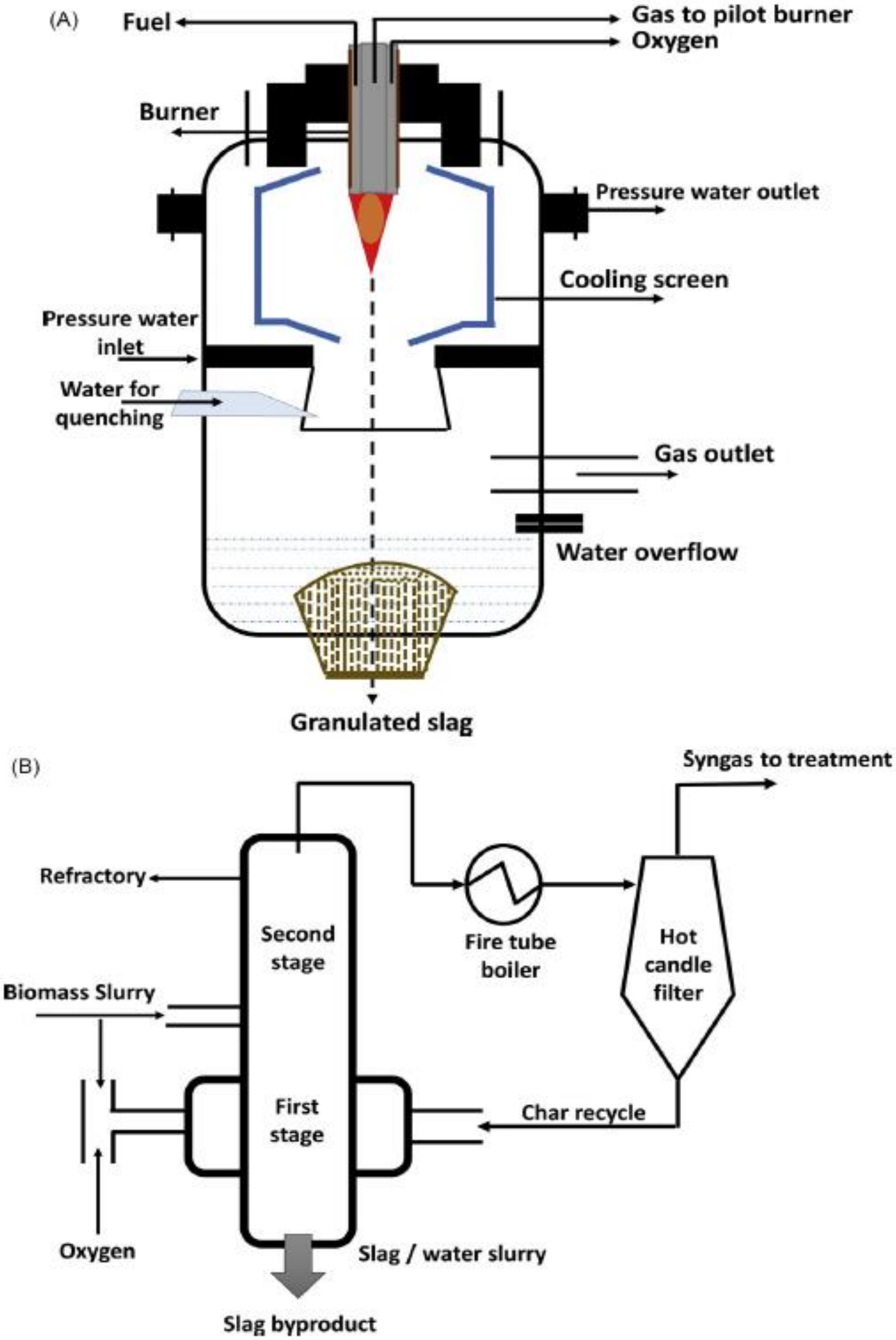


Figure-8: Top-fed entrained flow gasifier. (B) Side-fed entrained flow gasifier.

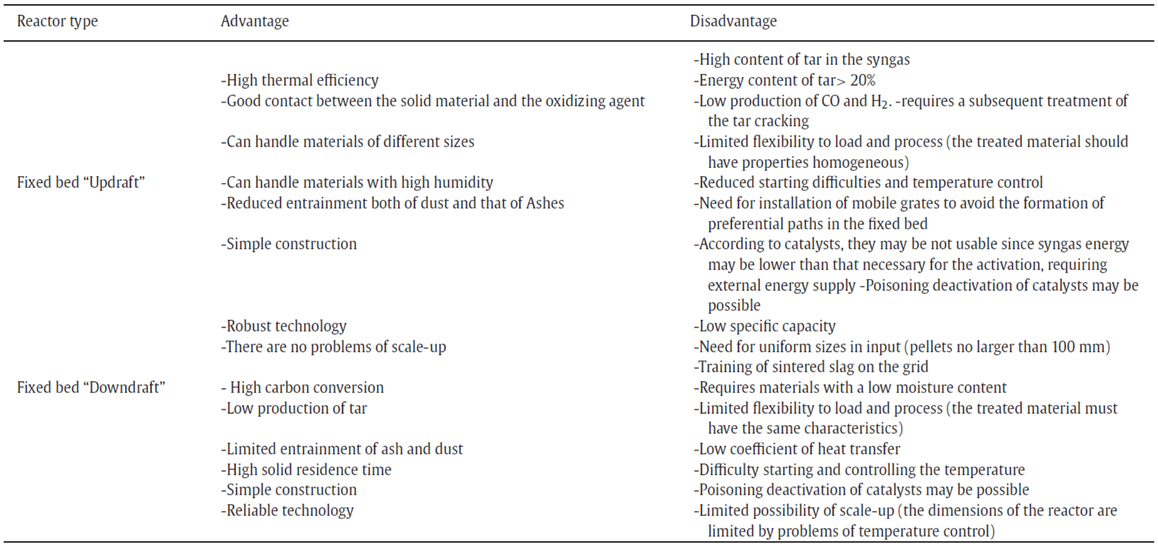
- ✓ top-fed entrained flow gasifiers are vertically aligned cylindrical shaped vessels
- ✓ finely refined fuel particles and gasifying media come in the form of a jet from the top end of the reactor (**Figure-8A**)
- ✓ an inverted burner results in their combustion followed by gasification

- ✓ product gas is taken out from the side of the lower section, whereas slag is deposited at the bottom of the reactor
- ✓ in side-fed gasifier, pulverized fuel and gasifying agent are fed through nozzles present in the lower part of the reactor (**Figure-8B**)
- ✓ this design results in appropriate mixing of fuel and oxygen
- ✓ the product gas is collected from the top and the slag from the bottom of the vessel
- ✓ other important issues that process designs need to deal with are slagging, fouling, and corrosion
- ✓ these issues arise out of the inorganic species present in the biomass and are, therefore, dependent to a large part on the biomass composition

➢ Advantages and Disadvantages of Various Biomass Gasification Technologies (Gasifiers) used

- **Fixed Bed**
  - ✓ Illutrated in the Table-2, below:

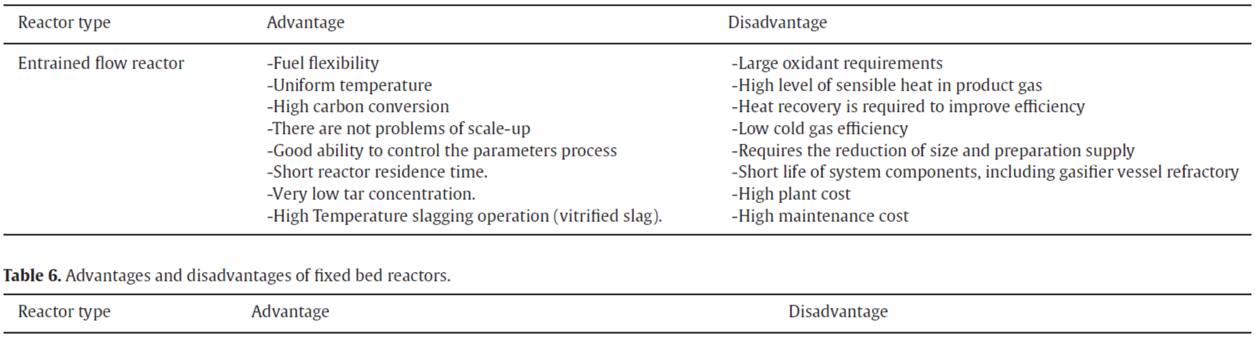
Table-2: Advantages and Disadvantages of Fixed Bed Gasifiers



Reactor type	Advantage	Disadvantage
Fixed bed "Updraft"	-High thermal efficiency -Good contact between the solid material and the oxidizing agent -Can handle materials of different sizes -Can handle materials with high humidity -Reduced entrainment both of dust and that of Ashes -Simple construction	-High content of tar in the syngas -Energy content of tar> 20% -Low production of CO and H_2. -requires a subsequent treatment of the tar cracking -Limited flexibility to load and process (the treated material should have properties homogeneous) -Reduced starting difficulties and temperature control -Need for installation of mobile grates to avoid the formation of preferential paths in the fixed bed -According to catalysts, they may be not usable since syngas energy may be lower than that necessary for the activation, requiring external energy supply -Poisoning deactivation of catalysts may be possible
Fixed bed "Downdraft"	-Robust technology -There are no problems of scale-up - High carbon conversion -Low production of tar -Limited entrainment of ash and dust -High solid residence time -Simple construction -Reliable technology	-Low specific capacity -Need for uniform sizes in input (pellets no larger than 100 mm) -Training of sintered slag on the grid -Requires materials with a low moisture content -Limited flexibility to load and process (the treated material must have the same characteristics) -Low coefficient of heat transfer -Difficulty starting and controlling the temperature -Poisoning deactivation of catalysts may be possible -Limited possibility of scale-up (the dimensions of the reactor are limited by problems of temperature control)

- **Entrained Flow Gasifier**
  - ✓ Reflected by the following Table-3:

Table-3: Advantages and Disadvantages of Entrained Flow Gasifiers



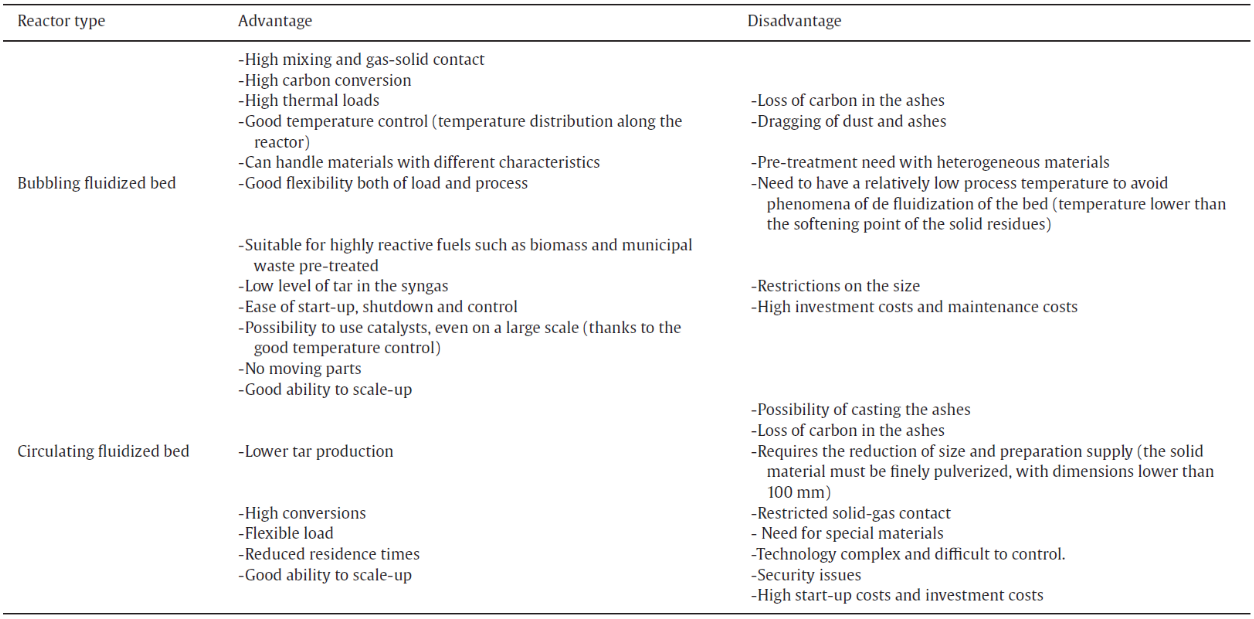
Reactor type	Advantage	Disadvantage
Entrained flow reactor	-Fuel flexibility -Uniform temperature -High carbon conversion -There are not problems of scale-up -Good ability to control the parameters process -Short reactor residence time. -Very low tar concentration. -High Temperature slagging operation (vitrified slag).	-Large oxidant requirements -High level of sensible heat in product gas -Heat recovery is required to improve efficiency -Low cold gas efficiency -Requires the reduction of size and preparation supply -Short life of system components, including gasifier vessel refractory -High plant cost -High maintenance cost

Table 6. Advantages and disadvantages of fixed bed reactors.

Reactor type	Advantage	Disadvantage

- **Fluidized Bed Gasifier**
  - ✓ Summarized in the Table-4, below:

Table-3: Advantages and Disadvantages of Fluidized Bed Gasifiers



Reactor type	Advantage	Disadvantage
Bubbling fluidized bed	-High mixing and gas-solid contact -High carbon conversion -High thermal loads -Good temperature control (temperature distribution along the reactor) -Can handle materials with different characteristics -Good flexibility both of load and process	-Loss of carbon in the ashes -Dragging of dust and ashes -Pre-treatment need with heterogeneous materials -Need to have a relatively low process temperature to avoid phenomena of de fluidization of the bed (temperature lower than the softening point of the solid residues)
Circulating fluidized bed	-Suitable for highly reactive fuels such as biomass and municipal waste pre-treated -Low level of tar in the syngas -Ease of start-up, shutdown and control -Possibility to use catalysts, even on a large scale (thanks to the good temperature control) -No moving parts -Good ability to scale-up -Lower tar production -High conversions -Flexible load -Reduced residence times -Good ability to scale-up	-Restrictions on the size -High investment costs and maintenance costs -Possibility of casting the ashes -Loss of carbon in the ashes -Requires the reduction of size and preparation supply (the solid material must be finely pulverized, with dimensions lower than 100 mm) -Restricted solid-gas contact - Need for special materials -Technology complex and difficult to control. -Security issues -High start-up costs and investment costs

Energies **2009**, *2*, 556-581; doi:10.3390/en20300556

OPEN ACCESS

energies

ISSN 1996-1073

www.mdpi.com/journal/energies

Review

Thermochemical Biomass Gasification: A Review of the Current Status of the Technology

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Received: 13 May 2009; in revised form: 15 July 2009 / Accepted: 16 July 2009 /
Published: 21 July 2009

Abstract: A review was conducted on the use of thermochemical biomass gasification for producing biofuels, biopower and chemicals. The upstream processes for gasification are similar to other biomass processing methods. However, challenges remain in the gasification and downstream processing for viable commercial applications. The challenges with gasification are to understand the effects of operating conditions on gasification reactions for reliably predicting and optimizing the product compositions, and for obtaining maximal efficiencies. Product gases can be converted to biofuels and chemicals such as Fischer-Tropsch fuels, green gasoline, hydrogen, dimethyl ether, ethanol, methanol, and higher alcohols. Processes and challenges for these conversions are also summarized.

Keywords: review; thermochemical conversion; gasification; biomass; syngas; biofuel; chemical; combined heat and power

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1. Bioenergy and the Role of Biomass Gasification

The demand for energy sources to satisfy human energy consumption continues to increase. Prior to the use of fossil fuels, biomass was the primary source of energy for heat via combustion. With the introduction of fossil fuels in the forms of coal, petroleum and natural gas, the world increasingly became dependent on these fossil fuel sources. Currently, the main energy source in the world is fossil fuels. The use of plastics and other chemicals which are derived from these fossil fuels also have increased. These tremendous increases have led to many concerns. Although it is not known how much fossil fuel is still available, it is generally accepted that it is being depleted and is non-renewable. Given these circumstances, searching for other renewable forms of energy sources is reasonable. Other consequences associated with fossil fuel use include the release of the trapped carbon in the fossil fuels to the atmosphere in the form of carbon dioxide which has led to increased concerns about global warming. Also, fossil fuel resources are not distributed evenly around the globe which makes many countries heavily dependent on imports.

Biomass combines solar energy and carbon dioxide into chemical energy in the form of carbohydrates via photosynthesis. The use of biomass as a fuel is a carbon neutral process since the carbon dioxide captured during photosynthesis is released during its combustion. Biomass includes agricultural and forestry residues, wood, byproducts from processing of biological materials, and organic parts of municipal and sludge wastes. Photosynthesis by plants captures around 4,000 EJ/year in the form of energy in biomass and food. The estimates of potential global biomass energy vary widely in literature. The variability arises from the different sources of biomass and the different methods of determining estimates for those biomasses. Fischer and Schrattenholzer estimated the global biomass potential to be 91 to 675 EJ/year for the years 1990 to 2060 [1]. Their biomass included crop and forestry residues, energy crops, and animal and municipal wastes. Hoogwijk estimated these to be 33 to 1135 EJ/year [2]. Biomass included energy crops on marginal and degraded lands, agricultural and forestry residues, animal manure and organic wastes. Parikka estimated the total worldwide energy potential from biomass on a sustainable basis to be 104 EJ/year, of which woody biomass, energy crops and straw constituted 40.1%, 36% and 16.6%, respectively [3]. Only about 40% of potential biomass energy is currently utilized. Only in Asia, does the current biomass usage slightly exceed the sustainable biomass potential. Currently, the total global energy demand is about 470 EJ/year. Perlack estimated that, in the United States, without many changes in land use and without interfering with the production of food grains, 1.3 billion tons of biomass can be harvested each year on a sustainable basis for biofuel production [4]. 1.3 billion tons of biomass is equivalent to 3.8 billion barrels of oil in energy content. US equivalent energy consumption is about 7 billion barrels per year [5]. However, harvesting, collecting and storage of biomass adds another dimension of technical challenges to the use of biomass for production of fuels, chemicals and biopower [6].

Two main ways of converting biomass energy (solid fuel) into biofuels and biopower are biochemical conversion and thermochemical conversion processes. Biochemical conversions convert the biomass into liquid or gaseous fuels by fermentation or anaerobic digestion. Fermentation of the biomass (starch and cellulose) produces primarily ethanol. Anaerobic digestion leads to the production of gaseous fuel primarily containing methane. The details of biochemical conversions are outside the intended scope of this manuscript.

Thermochemical conversion technologies include combustion, gasification and pyrolysis. While combustion of biomass is the most direct and technically easiest process, the overall efficiency of generating heat from biomass energy is low. Gasification has many advantages over combustion. It can use low-value feedstocks and convert them not only into electricity, but also into transportation fuels. In the upcoming years, it will serve as a major technology for complementing the energy needs of the world [7]. Use of advanced technologies such as gas turbines and fuel cells with the syngas generated from gasification results in increased efficiency [8]. For complete combustion of solid fuels, excess air is needed, and high combustion temperatures generate more NO_x and other emissions, as compared with the combustion of products by gasification. During combined cycles for combined heat and power generation, contaminants in the syngas such as sulfur and nitrogen species and trace elements are removed efficiently resulting in much lower emissions [9]. Moreover, liquid and gaseous fuels are more of interest because of their ease of handling and operations, and their applications as transportation fuels.

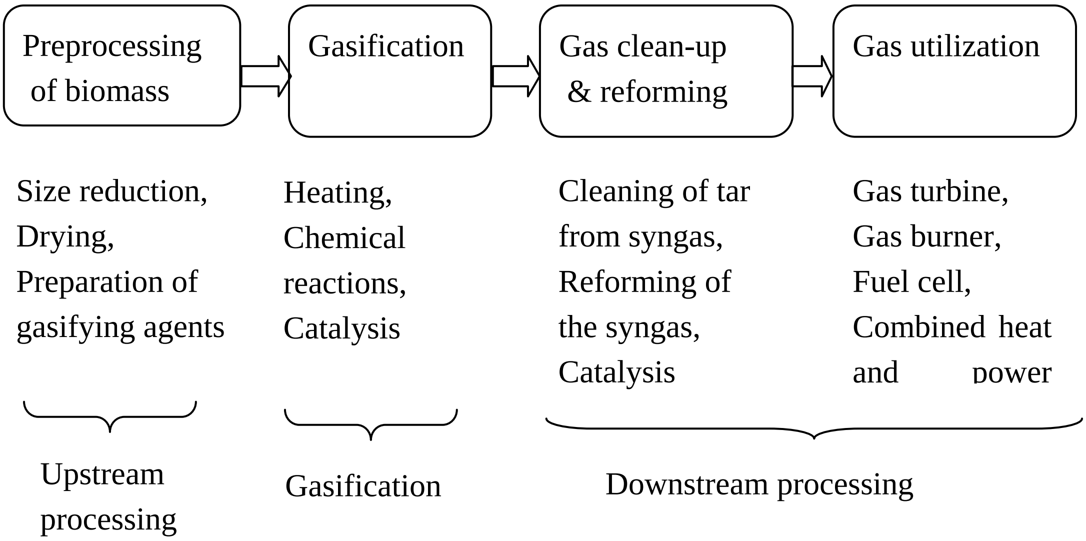
High oxygen content in biomass reduces the energy density of the biomass. The production of hydrocarbons, similar to petroleum transportation fuels, requires the removal of oxygen from the carbohydrate structure. The oxygen may be removed in the forms of CO_2 and H_2O. Thermochemical conversion of biomass to syngas is an attractive route to extract the oxygen from carbohydrate structures to produce intermediate compounds having C_1 (CO and CH_4), which can be further synthesized into hydrocarbons by catalysis or fermentation. Other thermochemical schemes of decarboxylation (CO_2 removal) and dehydration (H_2O removal) from carbohydrates result in higher hydrocarbons (higher than C_2) having undesired properties which require further conversion to be compatible with transportation fuels [10].

Thermochemical conversion technologies have certain advantages and disadvantages over biochemical conversion technologies. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass including agricultural residues, forestry residues, non-fermentable byproducts from biorefineries, byproducts of food industry, byproducts of any bioprocessing facility and even organic municipal wastes; and the product gases can be converted to a variety of fuels (H_2, Fischer-Tropsch (FT) diesels, synthetic gasoline) and chemicals (methanol, urea) as substitutes for petroleum-based chemicals; the products are more compatible with existing petroleum refining operations. The major disadvantages are the high cost associated with cleaning the product gas from tar and undesirable contaminants like alkali compounds, inefficiency due to the high temperatures required, and the unproven use of products (syngas and bio-oil) as transportation fuels. However, research on the optimization of gasifier operating conditions and heat recovery, syngas cleaning, bio-oil stabilization, and efficient product utilization can make the process important for sustainable production of biofuels. With life cycle assessment, Wu concluded that use of cellulosic biofuels (ethanol via gasification and fermentation, FT diesel and dimethyl ether (DME) from biomass, etc) in light duty locomotives results in significant savings of fossil fuel resources and reduction in green house gases [11]. Co-production of cellulosic biofuels and power generation by GTCC consumes the least fossil fuel resources and results in the greatest reduction in green house gas (GHG) emissions on a per-mile basis, of the thermochemical conversion techniques.

There have been substantial efforts to generate both gaseous and liquid fuels from coal gasification during the 1970s oil embargo. However, after that the continued low price of petroleum resources halted the major research, development and commercialization of these technologies. Biomass gasification differs from coal gasification. Biomass is a carbon-neutral and sustainable energy source unlike coal. Because biomass is more reactive and has higher volatiles content than coal, biomass gasification occurs at a lower temperature. Lower temperature reduces the extent of heat loss, emissions and material problems associated with high temperatures. Biomass also has low sulfur content, which results in lower SO_x emission. But the high alkali contents in biomass, like sodium and potassium, cause slagging and fouling problems in gasification equipment [12].

The main steps involved in the gasification process can be categorized as upstream processing, gasification and downstream processing (Figure 1).

Figure 1. Processes involved in biomass gasification.



2. Upstream Processing

Upstream processing includes processing of the biomass to make it suitable for gasification operations. Size reduction is needed to obtain appropriate particle sizes. Drying is needed to achieve appropriate moisture so that the process can work efficiently. Densification also may be necessary due to the low density of biomass.

2.1. Size reduction

Smaller particles have larger surface areas per unit mass and larger pore sizes which facilitate faster rates of heat transfer and gasification [13]. Lv observed that smaller particles resulted in more CH_4, CO, C_2H_4 and less CO_2 which led to higher gas yields, gas energy content (LHV) and carbon conversion efficiency (C_{eff}) [14]. Rapagna reported increases in gas yield and gas compositions of CO, CH_4 and CO_2, when the particle size was reduced from largest (1.090 mm) to smallest (0.287 mm) [15]. By decreasing the particle size from 1.2 mm to 0.075 mm, it was observed that H_2 and CO contents as well as gas yield and carbon conversion efficiencies increased whereas the CO_2 decreased [16]. Higher gas yields and energy efficiencies were attributed to the increased heat transfer in smaller size particles due to the larger surface area.

Hammer-mills, knife mills and tub grinders are typical instruments used for reducing the particle sizes of agricultural and forestry residues. Hammer mills are used both for dry agricultural and dry forestry residues. Tub grinders are small, mobile hammer-mills. Screens are used in the mills to assure the ground particles have certain maximum size [17]. Energy consumption during size reduction depends on the moisture content, initial size of biomass, biomass properties, and screen size of the mill and properties of the mill. Mani conducted tests of grinding performance on corn stover, barley straw, wheat straw and switchgrass, and found that the corn stover consumed the least specific energy during hammer mill grinding [18]. On the other hand, switchgrass used the most specific energy probably because of its fibrous nature.

2.2. Drying

Biomass collected from farm and forest lands may contain high moisture. Drying is needed to obtain a desired range of water content for the gasification processes. Drying is an energy intensive process which may decrease the overall energy efficiency of the process. However, in case of gasification, waste heat can be utilized to decrease the moisture content of the biomass which will increase the overall efficiency of the process. Perforated bin dryers, band conveyor dryers and rotary cascade dryers have been used to dry biomass [17]. In the case of generating combined heat and power, biomass moisture should be as low as possible to increase the overall efficiency and decrease the net cost of electricity. However, for low moisture raw biomass (less than 10%) drying stage may not be needed [19].

3. Gasification

Gasification is the heart of the process. The main operating parameters of the gasifier include type and design of gasifier, gasification temperature, flow rates of biomass and oxidizing agents (air or steam), type and amount of catalysts, and biomass type and properties.

3.1. Types of gasifier

Gasifiers are categorized based on types of bed and flow. The gasifier bed can be a fixed-bed or a fluidized bed. Fixed bed gasifier can be classified further as updraft (countercurrent) or downdraft (concurrent). In the updraft gasifier, the feed (biomass) is introduced from the top and moves downwards while gasifying agents (air, steam, etc.) are introduced at the bottom of the grate so the product gas moves upwards. In this case, the combustion takes place at the bottom of the bed which is the hottest part of the gasifier and product gas exits from the top at lower temperature (around 500 °C). Because of the lower exit temperature, the product gas contains large amounts of tar. In a downdraft gasifier, both the feed and product gas moves downward and the product exits from the bottom at a higher temperature, i.e., around 800 °C. In this case, most of tars are consumed because the gas flows through a high temperature region. However, heat needs to be recovered from high temperature product gas to increase the energy efficiency. These two types of gasifiers, updraft and downdraft, have been used most extensively in the past.

In the fluidized bed gasifier, the feed is introduced at the bottom, which is fluidized using air, nitrogen and/or steam and the product gas then moves upward. There are more particulates in the product gas from this gasifier [20]. Fluidization of the bed enhances the heat transfer to the biomass particle leading to increases in reaction rates and conversion efficiencies. Fluidized beds also are able to tolerate a wide variation in fuel types and their characteristics. A fluidized bed can be either a bubbling fluidized bed or a circulating fluidized bed. In case of the bubbling fluidized bed gasifier, the flow rate of the fluidizing agent is comparable to the minimum fluidizing velocity. Uniform temperature across the bed can be maintained by fluidization resulting in uniform product gases. The fluidizing mediums used are generally silica or alumina materials which have high specific heat capacity and can operate at high temperature. Catalysts also can be added as fluidizing agents which can increase the conversion efficiency and reduce tar formation. However, fluidized catalysts are more susceptible to attrition and poisoning. There is a need for robust catalysts that are effective at high temperature (800 °C or more) in the fluidized medium. Some of the catalysts that have been investigated are discussed in detail in the in-bed catalyst section. Circulating fluidized beds have higher flow rates of the fluidizing agents which move most of the solid and ungasified particles to an attached cyclone separator, from which the solids are re-circulated to the gasifier bed. The higher flow of gasifying agent increases the heat transfer and conversion rate of the biomass.

The advantages and disadvantages of each type of gasifiers have been summarized by Warnecke [21]. Gasifiers also can be categorized by the method of heat source provided for the endothermic gasification reactions. Heat can be supplied to the gasifier indirectly or directly. In a directly-heated gasifier, part of biomass is allowed to combust inside the gasifier. The combustion then raises the temperature and provides the required heat for the endothermic gasification reactions. In the case of an indirectly heated gasifier, biomass or ungasified char is combusted in a separate chamber and heat exchanger tubes conduct the heat from the combustion chamber to the gasification chamber [12].

3.2. Gasification process

Gasification takes place at high temperature in the presence of an oxidizing agent (also called a gasifying agent). Heat is supplied to the gasifier either directly or indirectly which raises the gasification temperature of 600–1,000 °C. Oxidizing agents are typically air, steam, nitrogen, carbon dioxide, oxygen or a combination of these. In the presence of an oxidizing agent at high temperature, the large polymeric molecules of biomass decompose into lighter molecules and eventually to permanent gases (CO, H_2, CH_4 and lighter hydrocarbons), ash, char, tar and minor contaminants. Char and tar are the result of incomplete conversion of biomass.

The overall reaction in an air and/or steam gasifier can be represented by Equation 1, which proceeds with multiple reactions and pathways. Equations 2–8 are common reactions involved during gasification. Among these, Equations 4–7 occur when steam is available during gasification. Many authors have studied the degradation kinetics of various biomass feedstocks (rice husk, pine chips, wheat straw, rapseed straw, pigeon pea stalk, etc.) using thermogravimetric analyses (TGA). TGA provides the weight loss of any material with change in temperature. The weight loss (or thermal degradation) in a nitrogen atmosphere occurred in mainly three stages; with the first stage being dehydration (below 125 °C), the second stage being active pyrolysis (125–500 °C) and the third stage being passive pyrolysis above 500 °C. The dehydration reflects loss of water, the active pyrolysis reflects the loss of the hemicellulose, cellulose and part of lignin, and the passive pyrolysis reflects the slow and continuous loss of residual lignin. The temperature ranges of these stages and the kinetic parameters of the degradations depend primarily on the rate of heat transfer, the composition of the biomass, and the degree of the oxidizing environment [22–25].

$$\begin{gathered}CH_xO_y \text{ (biomass)} + O_2 \text{ (21\% of air)} + H_2O \text{ (steam)} \\ = CH_4 + CO + CO_2 + H_2 + H_2O \text{ (unreacted steam)} + C \text{ (char)} + \text{tar}\end{gathered} \tag{1}$$

$$2C + O_2 = 2CO \text{ (partial oxidation reaction)} \tag{2}$$

$$C + O_2 = CO_2 \text{ (complete oxidation reaction)} \tag{3}$$

$$C + 2H_2 = CH_4 \text{ (hydrogasification reaction)} \tag{4}$$

$$CO + H_2O = CO_2 + H_2 \text{ (water gas shift reaction)} \tag{5}$$

$$CH_4 + H_2O = CO + 3H_2 \text{ (steam reforming reaction)} \tag{6}$$

$$C + H_2O = CO + H_2 \text{ (water gas reaction)} \tag{7}$$

$$C + CO_2 = 2CO \text{ (Boudourd reaction)} \tag{8}$$

3.3. Effects of gasification operating conditions on the product properties

To obtain the desired product gas composition, the least amount of impurities, and to increase the net energy conversion efficiency, the gasification operating conditions need to be optimized. The following section describes the effects of the main operating conditions on the quantity and composition of the product gas and its impurities.

3.3.1. Biomass flow rate, type and properties

Overfeeding of biomass can lead to plugging and reduced conversion efficiencies whereas starve-feeding results in less gas yield. Hence, an optimum biomass flow rate is desired for the gasification system to maximize energy efficiency. Optimum biomass flow rate is dependent primarily on the design of the gasifier and the properties of the biomass.

The main constituents of lignocellulosic biomass are cellulose, hemicellulose and lignin. Cellulose is a linear polymer of D-glucose (a six-carbon sugar) linked with β-1,4 linkages; hemicellulose is a branched polymer with both five carbon and six-carbon sugars, and lignin is a randomly constructed and highly aromatic cross-linked macromolecule. Herbaceous crops and wood contain 60–80% (db) cellulose and hemicellulose, and 10–25% lignin [5]. The composition of these polymers in the biomass affects the product composition. Hanaoka observed that at 900 °C, carbon conversion efficiencies of cellulose, xylan and lignin were 97.9%, 92.2% and 52.8%, respectively [26]. The product compositions from gasification of xylan and lignin were similar. Cellulose resulted in higher CO

(35 vs. 25 mol %) and CH_4 (6 vs. 5 mol %) but lower CO_2 (27 vs. 36 mol %) and H_2 (29 vs. 33 mol %) yields than those of xylan and lignin. Barneto observed that composting of biomass increased the lignin content in the compost, which resulted in up to 20% increased H_2 production at a slow heating rate as compared to the original biomass at a fast heating rate [27].

Co-firing of biomass with coal also is being studied. Kumabe observed that by varying the ratio of coal to biomass for the gasification, the extent of the water gas shift reaction was maximal at the ratio of 0.5 which they attributed to the synergy between the coal and biomass [28]. With increase in biomass ratio, they observed increases in gas and CO_2 yields, decreases in char, tar and H_2 but CO, and hydrocarbons (HCs) were unchanged. Gasification of coal with biomass reduces problems associated with high ash and sulfur contents of the coal [29].

3.3.2. Air flow rate (equivalence ratio, ER or superficial velocity, SV)

Equivalence ratio (ER) and superficial velocity (SV) are measures of the air (or oxygen) flowrate. ER is the ratio of air flow to the airflow required for stoichiometric combustion of the biomass, which indicates extent of partial combustion. The SV is the ratio of air flow to the cross-sectional area of the gasifier which removes the influence of gasifier dimension by normalization [30]. Hence, both ER and SV are directly proportional to the airflow. Air flow influences the gasification products in different ways. Air supplies the O_2 for combustion (and fluidization in the case of fluidized bed) and effects the residence time. By varying amount of the O_2 supply, air flow rate controls the degree of combustion which in turn, affects the gasification temperature. Higher airflow rate results in higher temperature which leads to higher biomass conversion and a higher quality of fuel. But, an excess degree of combustion, on the other hand, results in decreased energy content of the gas produced because a part of biomass energy is spent during combustion. Higher airflow also shortens the residence time which may decrease the extent of biomass conversion.

With an increase in ER (from 0.20 to 0.45), Narváez observed an increase in gas yield, a decrease in lower heating value (LHV) of the gas and decreased contents of H_2, CO, CH_4 and C_2H_2 and tar [31]. Lv reported that with an increase in ER from 0.19 to 0.27, the H_2 content varied a little but gas yield increased and then decreased with an optimal ER of 0.23 [32]. Wang found that with an increase in ER from 0.16 to 0.26, the bed and freeboard temperatures increased resulting in a higher yield and higher heating value (HHV) of the gas, an increase in cold gas efficiency from 57% to 74%, an increase in H_2 content from 8.5% to 13.9%, and an increase in CO content from 12.3% to 14% [33]. Kumar observed increases in gas yields, carbon conversion and energy efficiencies with an increase in ER from 0.07 to 0.25 [34]. All authors reported increases in gas yields with increases in ER (from 0.0 to 0.45). However, contradictory results of decreases in H_2 and CO yields with increases in ER also have been reported [35]. The increase in gas yield with increase in ER implies that an increased airflow increases conversion rate. Some of the contradictory results on the effects of ER on the contents of H_2, CO and CH_4 (%) is logical because the percentage compositions of individual gases depend on both the yield of individual gases and the overall gas yield. If the increase in overall gas yield is more pronounced than the increase in individual gas yield, then the percentage composition of individual gas decreases, even though the individual gas yield may actually have increased. Effects of ER on the product gas composition also depend upon other factors such as temperature and steam to biomass ratio. During steam gasification, at high temperature, the H_2 yield is more pronounced than the increase in gas yield which results in an increase in H_2 content.

3.3.3. Steam flow rate (steam to biomass ratio, S/B)

Supplying steam as a gasifying agent increases the partial pressure of H_2O inside the gasification chamber which favors the water gas, water gas shift and methane reforming reactions (Equations 5–7), leading to increased H_2 production. However, the gasification temperature needs to be high enough (above 750–800 ℃) for the steam reforming and water gas reactions to be favorable [34,36,37]. Catalysts can lower the operating temperature needed for the above reactions to occur. Higher S/B also leads to higher biomass conversion efficiency [38].

Reduction in tar also is observed at higher steam to biomass ratios, which is attributed to steam reforming of the tar with an increased partial pressure of steam. Narváez found that with an increase in H/C ratio (H and C from incoming biomass, moisture and steam) from 1.6 to 2.2, H_2 content increased, LHV increased from 4 to 6 MJ/Nm^3 and tar content decreased from 18 to 2 g/Nm^3 [31]. By varying S/B from 0 to 4.04, Lv observed that with S/B higher than 2.7, the gas composition did not change significantly but, with S/B between 0 and 1.35, CO yield decreased, and CH_4, CO_2 and C_2H_4 yields increased [32]. With S/B of 1.35 and 2.70, the CO and CH_4 yields decreased and CO_2 and H_2 yields increased which implied higher steam reforming reactions. Turn observed that increasing S/B from 1.1 to 4.7 decreased CO, CH_4, C_2H_2 yields, and increased H_2 and gas yields [35]. H_2 increased from 46 to 83 g per kg dry and ash-free (daf) biomass. Since the temperature of the steam supplied to the gasifier is lower than the gasification temperature, a significant amount of heat is needed to raise the steam temperature which, in turn, may lower the temperature of the gasifier bed. Hence an S/B ratio above a threshold, steam had negative effects on the product.

Increasing the temperature of the gasifying agents led to an increase in the heating value of the fuel gas, and reduces the tars, soot and char residues [36]. A preheater is recommended before the introduction of gasifying agents (steam and air) to the gasifier to facilitate higher gasification bed temperature.

3.3.4. Gasification temperature profile

Gasification temperature is one of the most influential factors affecting the product gas composition and properties. Higher temperature results in increased gas yield because of higher conversion efficiency. Since, the reactions (Equations 5–8) occur simultaneously, the contents and ratios of H_2, CO, CO_2 and CH_4 in the product gas are affected by temperature and partial pressures of reactants.

At temperatures above 750–800 ℃, the endothermic nature of the H_2 production reactions (steam reforming and water-gas reactions) results in an increase in H_2 content and a decrease in CH_4 content with an increase in temperature. At temperatures above 850–900 ℃, both steam reforming and the Boudouard reactions (Equations 6–8) dominate, resulting in increases in CO content. High temperature also favors destruction and reforming of tar (Equations 9–10) leading to a decrease in tar content and an increase in gas yield [31,34,37,39,40]. Gupta and Cichonski observed significant increases in H_2 above 800 ℃ for S/B between 0.5 and 1.08 [37]. Maximal H_2 yield was obtained at 1,000 ℃ for a feedstock consisting of paper, and 900 ℃ feedstocks consisting of cardboard and wood pellets.

Gonzálezobserved that in air gasification contents of H_2, CO increased from 700 to 900 °C, whereas contents of CH_4 and CO_2 decreased [40]. They also observed that the CO/CO_2 ratio linearly increased from 0.85 at 700 °C to 2.7 at 900 °C in two segments. At 700–800 °C, the slope was 0.0067 and then almost doubled to 0.113 at higher than 800 °C which showed the predominance of the Boudouard reaction at higher temperatures. It was also observed that higher temperatures (700 to 950 °C) increased the gas yield and overall energy content of the gas [38,41]. Kumar observed that an increase in temperature (furnace set point from 750 to 850 °C), led to increases in energy and carbon conversion efficiencies and percent gas compositions of H_2 [34]. Turn found that with an increase from 750 to 950 °C, H_2 increased from 31% to 45%, CH_4 and CO remained fairly constant, CO_2 decreased and gas yield increased [35]. Boateng reported that with an increase in gasification temperature from 700 to 800 °C, gas yield, gas HHV, energy efficiency, carbon conversion efficiency and H_2 content increased and CH_4, CO and CO_2 contents decreased [42]. The decrease in CO content may have been due to the comparatively lower temperature (than 850–900 °C) for the Boudouard reaction to predominate.

$$C_nH_x = nC + x/2\ H_2 \tag{9}$$

$$C_nH_x + mH_2O = nCO + (m + x)/2\ H_2 \text{ (reforming reaction)} \tag{10}$$

4. Downstream Processing

The product gas from biomass gasification needs to be processed further for effective utilization. The processes involved are, overall, termed as downstream processing. Cleaning of tar and other contaminants from product gas, biopower generation, reforming and conversion to biofuels constitute the downstream processing operations. The product gas contains particulates, tar, alkali compounds, and nitrogen and sulfur containing compounds which typically need to be removed before the product gas is used. Reforming reactions change the gas composition of the product gas as desired for the specific syngas utilization. For example, high H_2 content is desired for fuel cell applications, and specific ranges of CO/H_2 are desired for producing other fuels and chemicals from syngas. Tolerable amounts of the contaminants in the syngas depend on the syngas applications. Combustion systems can work with relatively high amounts of tar but hydrocarbon conversion catalysts and fuel cells need syngas with low levels of tar.

4.1. Syngas cleaning

4.1.1. Particulate removal

The product gas stream from the gasifier typically contains particulates. The particulates consist of unconverted biomass material (ash and char) and bed material. Ash materials are the mineral components of the biomass; char is the unconverted portion of the biomass which is less reactive, resulting in decreased carbon conversion efficiency, and the fines from the bed material also are entrained with the gas stream. Particulate deposition in the downstream equipment causes plugging and results in higher wear.

Cyclone separators are widely and routinely used to separate the larger particulates (above 5 μm in diameter) at the initial cleaning stage with little pressure drop. These are inexpensive to build and operate. The design methodology for cyclone separators is available [43–45]. Generally, multiple cyclones are used to increase separation efficiency. Wet scrubbers, various barrier filters and electrostatic precipitators subsequently separate smaller particulates.

Wet scrubbers remove particulates using liquid sprays (usually water) on the gas stream. These can remove 95–99% of over 1 μm particle size and 99% of over 2 μm with pressure across the venturi of 2.5 to 25 kPa [46]. However, wet scrubbers are used at less than 100 °C which results in loss of sensible heat. Hotter gas is desired, especially, for many applications such as in gas turbines and reforming reactions.

Electrostatic precipitators (ESP) apply electrical voltage to charge and then separate particulates. The separation efficiency depends on particulate resistivity, and sulfur and alkali contents. Because of its large size and high capital cost, it is suited for large-scale operations.

Barrier filters allow the gas to pass through various porous media collecting the particulates of 0.5 to 100 μm. Because of the smaller pore size, it increases the pressure differential across the filter. Common types of barrier filters are (a) metal or ceramic porous candle filters, (b) bag filters, and (c) packed bed filters. Candle filters can operate at high temperature (ceramic more than metallic) which makes them attractive for hot gas cleaning. Ceramic filters have been tested in a gasifier operated at about 700 °C gas temperature. Bag filters are constructed of woven material which collect smaller particles of even sub-micron size, and can operate at temperatures of about 350 °C. Packed bed filters use bed materials such as ceramic spheres and sawdust to capture the particulates as gas flows through it [47].

4.1.2. Alkali removal

Significant amounts of alkali compounds (CaO, K_2O, P_2O_5, MgO, Na_2O, SiO_2, SO_3) are present in biomass. These alkali compounds can vaporize at temperatures above 700 °C during gasification which, when condensed (below about 650 °C), form particles (<5 μm) in the downstream equipment (gas turbine, heat exchanger), stick to the metal surfaces, and result in corrosion. Moreover, alkali salts inactivate the catalysts used in tar cracking, reforming and converting syngas into hydrocarbons. Removal of alkali can be performed by cooling the gas and then passing it through barrier filters. Hot gas removal of alkali compounds holds promise, particularly for high temperature applications. However, research on hot gas alkali removal is still in the experimental stage [47]. Turn reported that a bauxite filter at 650–725 °C removed most of the Na and K compounds [48].

4.1.3. Nitrogen compounds

When gasified, the nitrogen content of the biomass (0.5–3%) results primarily in ammonia (60–65%) and molecular nitrogen. Unlike coal gasification, conversion to hydrogen cyanide is very low in biomass gasification [49]. If not removed, combustion of part of ammonia (occurring at temperatures above 1,000 °C, typical of combustion) results mostly in NO_x formation. If cold product gas is desired, ammonia can be removed by wet scrubbing. Hot gas cleaning for ammonia can be performed by destructing ammonia at higher temperature using dolomites, nickel-based catalysts and iron-based catalysts [50].

4.1.4. Sulfur compounds

Most biomass contains very little sulfur (<0.5%), which, during gasification, is converted to H_2S and SO_2. Because of the low sulfur content in biomass, as compared to coal, the gas sulfur content in the gas is low enough to meet the needs of most applications. But for a few applications, such as methanol synthesis, even a low sulfur level can irreversibly inactivate the catalysts. Fuels cells and some tar catalysts also are sensitive to sulfur. SO_2 in syngas can be removed by wet scrubbing. SO_2 and H_2S are the predominant sulfur compounds in the exit gas, in the cases of coal combustion and gasification, respectively. Limestone, dolomite or CaO are used for SO_2 and H_2S removal because of their low cost and wide availability. Calcination processes are advantageous for SO_2 removal whereas cleaning at 600–900 ℃ and regeneration of sorbents is the best scrubbing process for H_2S removal from hot gas [51].

4.1.5. Tar removal

Tar is a generic term used for all organic compounds found in the product gas with the exception of gaseous hydrocarbons. Tar is the part of the biomass which does not decompose completely into lighter gases. Removal of tar is one of the biggest technical challenges facing the commercialization of gasification technology [52]. The high-temperature product gas from a gasifier contains tar. If not removed, the tar condenses on the wall of the downstream equipment such as heat exchangers, combustion engine, reactors or fuel cells [53]. Measurement of tar has been improved over the years to maintain consistency among different tar measurement techniques [54,55].

The primary organic compounds in tar can be grouped as mixed oxygenates, phenolic ethers, alkyl phenolics, heterocyclic ethers, poly-aromatic hydrocarbons (PAH) and larger PAH. The composition shifts from larger molecules (e.g., larger PAH) to smaller molecules (e.g. mixed oxygenates) with increased reaction severity [46,47]. During gasification, reaction severity can be increased by increasing the temperature, flow of oxidizing agents or amount of catalysts.

Tar is less problematic for combustion of product gas because tar also can combust and add to the calorific value of the fuel, although less readily and at higher temperatures. Other applications, wherein the gas stream is cooled, result in condensation of the tar. Tars also are detrimental to catalysts used for conversion of syngas and fuel cell applications.

Tar removal techniques are categorized as: (a) primary removal techniques and (b) secondary removal techniques. Primary removal techniques refer to techniques that reduce the tar content in the syngas and are employed inside the gasifier without the need of a secondary reactor. Primary removal methods include design and optimization of the gasification operating conditions, and addition of catalysts in the gasifier bed (called in-bed catalysts). Secondary tar removal techniques use a separate reactor to destruct and reform the tar content below acceptable level in the product gas. Secondary tar cleaning techniques are divided further into wet and hot gas cleaning. Devi reviewed the methods for removing tar from syngas, with a focus on primary tar removal methodologies [56].

Effects of operating conditions (A primary removal technique)

Numerous studies have shown that the gasification operating parameters, primarily gasification temperature profile, ER, type of gasifying agent, S/B, total gasifying agent to biomass ratio, and feed rate are effective in reducing the amount of tar in the syngas. Effects of the operating conditions on the amount of tar in the product gas have been described in the previous section. In general, higher temperature, ER, and S/B results in product gas with less tar due to their contributions to destruction of tar. Yamazaki found that, in a downdraft gasifier, a higher SV of 0.7 m/s resulted in higher amount of tar as compared to a lower SV of 0.4 m/s [30]. According to them, higher SV resulted in shorter residence time and channeling which may have led to higher amounts of tar. However, a SV of 0.4 to 0.6 m/s were able to produce gas suitable for use in internal combustion engines. Particle yield also increased with increasing SV. Various gasifier designs, such as secondary injection of air or oxygen into the gasifier and two-stage gasification systems, also can result in lower tar contents [56].

In-bed catalyst (A primary removal technique)

The addition of catalysts such as dolomite, limestone, olivine, alkali carbonates, Ni-based catalysts, metal-oxide catalysts, zeolite or char in the gasifier bed, either with or without sand along with the biomass feed, help reduce tar and increase the extent of reforming reactions in the gasifier, thereby increasing overall carbon conversion efficiency.

Rapagna compared the performances of sand, dolomite and olivine particles as bed materials in a bubbling fluidized bed lab-scale gasifier [57]. They observed that the gas yield increased by more than 50%, tar was reduced by 20 times and char was reduced by 30% when dolomite or olivine was used as a bed material as compared to using sand. However, methane content was almost the same which indicated that the olivine and dolomite catalyzed tar destruction, but not methane reforming. Mechanical strengths of olivine and sand were similar but dolomite resulted in more fines. Asadullah found the amount of tar was negligible when using $Rh/CeO_2/SiO_2$ catalysts as compared to 30, 113 and 139 g/m^3 observed for commercial steam reforming catalyst G-91, dolomite and non-catalyst systems, respectively, in the bed for low temperature (823–973 K) fluidized-bed gasification [58,59]. Deactivation was not severe in the 20 h test probably because carbon conversion efficiency was high leaving less char in the bed.

In-bed catalysts reduce tar content but complete tar removal (satisfactory for downstream processing) is not achieved without the use of secondary reactors [52]. Also, it should be noted that the optimized operating conditions, gasifier designs and the application of in-bed catalysts for tar reduction using primary methods may not be optimum conditions for yield, composition, and energy content of the syngas. Therefore, the process efficiencies also need to be considered in determining the best operating conditions and gasifier design for obtaining desired product composition.

Wet cleaning (A secondary removal technique)

Cold gas cleaning uses water scrubbing and venturi scrubbing to condense the tar compounds from the syngas and simultaneously removing the particulates. It has been demonstrated that tar concentrations below 20–40 mg/Nm^3 can be achieved using a venturi scrubbing system [53]. This technology has been used extensively in coke-oven and gas processing industries, whose details can be found in Baker [46]. The exit gas temperature from wet cleaning methods is 35–60 °C, which results in loss of sensible heat and water condensate which requires treatment before disposal.

The use of barrier filters and cyclone separators have not been effective for tar removal since tar aerosol particles are less than 1µm in size and are sticky in nature which makes them difficult to remove from walls of the cyclone and filter. Electrostatic precipitator (ESP) wet scrubbers can remove most of the tar up to about 150 °C but are more expensive. The tar collected using these physical techniques can be burned to produce heat or re-injected into a gasifier. Bergman developed a wet scrubbing (scrubbing liquid was other than water which was regenerated and recycled) based cleaning technology called "OLGA" [52]. Tar components, which condensed above 25 °C, were heavy poly-aromatic hydrocarbons (PAH) (≥4 rings), light PAH (2–3 rings) and heterocyclic compounds. By removing these three tar components selectively, based on their dew points, the dew point of the resulting tar was less than normal temperature. Hence, the cleaned syngas can be acceptable for most syngas applications.

The disadvantages of wet cleaning are: (a) that since the product gases are at a high temperature, reducing the temperature, during wet cleaning, decreases the net energy efficiency of the process, (b) that the waste water needs to be treated extensively before discharge which is a capital-intensive process, and (c) if the product gas is used for high temperature applications, there will be a net loss of energy in cooling and heating the product gas stream [53].

Reforming for secondary tar removal and increased H_2 production

The drawbacks of wet cleaning have encouraged extensive research on hot gas cleaning technologies. The aim of hot gas cleaning is to crack the tar using high temperature. Without a catalyst, the temperature required for tar cracking is above 850 °C which reduces efficiency, causes material problems and produces soot [12]. Hot gas cleaning also results in increased hydrogen production in the product gas because the destruction of tar yields hydrogen, and the higher temperature and catalysts provide favorable conditions for reforming and shift reactions [53]. Non-catalytic reforming performed by Wang at 800–950 °C indicated that supplying air to the reformer decreased the HHV of the product gas by partial combustion and dilution of the reformed gas [33]. With an increased ER from 0.15 to 0.21, tar concentration decreased from 5.7 to 1.0 Ng/m^3. Supplying steam (up to S/B of 0.5) to the reformer increased the HHV and cold gas efficiency of the reformed gas. H_2, and CH_4 contents increased but CO and tar contents decreased with increasing S/B into the reformer. Supplying steam or/and air to the secondary reactor, in presence of catalysts, enables the tar to react and form CO, H_2, CO_2 and CH_4.

Tar removing catalysts are grouped into mineral and synthetic catalysts. The mineral-based catalysts are naturally occurring minerals and inexpensive. They also have fewer disposal problems. Calcined rocks (calcined dolomite, magnesite and calcite), olivine, clay materials and iron ores are mineral-based catalysts. Among these, calcined rocks are the most efficient catalysts. However, calcined rocks are suited only for fixed-bed secondary reactors as they erode in fluidized bed reactors. Olivine has more mechanical strength for attrition but is less efficient than dolomite. Clay materials generally do not withstand temperatures of 800–900 °C, whereas iron ores are rapidly deactivated.

Fluid catalytic cracking (FCC), char, alkali metal-based, activated alumina, and transition metal-based (Pt, Zr, Rh, Ru, Fe, and Ni) catalysts are synthetic catalysts. Transition metals (Ni, Rh, etc.), as well as other synthetic catalysts, are relatively expensive as compared to the mineral catalysts. FCC deactivate rapidly, alkali metals agglomerate in the bed, and transition metals, although very active (8–10 times than dolomite), need gas with low levels of sulfur, tar and char [60].

Numerous efforts have been made to design catalysts for destructing tar and increasing the extents of reforming reactions at the same time. Using calcined dolomite (120 g per kg/h of biomass) in the gasification fluidized bed and a nickel based catalyst (weight hourly space velocity, WHSV of 2.7 to 10.7 h^{-1}) in a secondary fixed-bed reactor, Lv observed that decreasing WHSV had a positive impact on H_2 content and H_2/CO. CH_4 content decreased by half, H_2 content increased up to 49% (v/v), and H_2/CO increased up to 3.32 at a WHSV of 2.7 h^{-1} [39]. WHSV was defined as the ratio of biomass flow rate to catalyst mass in the secondary reactor. With an increase in catalytic reactor temperature (650 to 850 ℃), H_2 content increased, CH_4 CO_2, C_2 yields decreased but CO content remained the same. Maximal H_2 yield was 130.28 g H_2/kg biomass.

Wang found that activity of Ni/dolomite catalysts in the secondary catalytic reactor were comparable to commercial steam reforming catalysts [61]. Ni/dolomite catalysts are relatively cheaper than steam reforming catalysts and have anticoking properties. With a space time of 0.02 kg of catalyst (m^3/h) and a temperature of 850 ℃, the catalysts were able to convert 98% of the tar while increasing H_2 content. By comparing commercial steam reforming catalysts for naphtha and natural gas, Aznar and Corella concluded that catalysts for naphtha were more effective in destructing tar than catalysts for natural gas reforming [62,63]. A 2 g/m^3 level of tar did not poison the catalysts. Operating conditions such as temperature, space time (mass of catalyst per unit flow rate of product gas), catalyst particle size and gas compositions affected tar conversion efficiencies. Inaba compared two types of supports for production of hydrogen over Ni catalysts [64]. They found that metal oxides produced large quantities of dark-colored tar while zeolite-based support produced carbon deposition without tar formation. Higher temperatures led to higher rates of gasification and H_2 production, and decreased depositions of tar and char on the catalysts. Nordgreen reported improved gas yield, decreased tar (most pronounced decline was for toluene), increased CO, CO_2, H_2 yields and decreased CH_4 yield by using elemental iron as a tar removal and reforming catalyst in a secondary reactor [65]. Corella concluded that the performances of expensive Ni-based monoliths were comparable to cheaper dolomite for tar elimination [66]. The development of more robust and efficient catalysts can improve the tar conversion efficiency. Resistance to coking and sulfur poisoning were reported after adding WO_3 as sulfur-resistant promoter to Ni/MgO-CaO catalysts supported on dolomite [67]. Kimura found that a co-impregnation method resulted in higher performance of the catalysts for steam reforming of tar ($Ni/CeO_2/Al_2O_3$) than sequential impregnation (Ni/Al_2O_3 and $Ni/CeO_2/Al_2O_3$) due to strong interaction between Ni and CeO_2 [68].

4.2. Conversion of syngas to biofuels, bioproducts and biopower

Syngas, primarily a mixture of CO and H_2, is a building block for synthesizing a variety of fuels and chemicals [69]. The main routes of converting syngas to fuels and chemicals, and generating biopower follow.

4.2.1. Biopower

The product gas from biomass gasification can be used to produce heat and electricity using a combined heat and power (CHP) system called integrated gasifier combined cycle (IGCC or BIGCC, Biomass-fired IGCC). The main advantages of producing heat and electricity using gasification over direct combustion are (a) fuel-gas based technologies such as gas engines or gas turbines can achieve higher efficiencies than combustion efficiency, (b) the overall efficiency of gasification is higher because gaseous fuels, having improved combustion characteristics, burn more efficiently than solid fuel, and (c) production of gas provides an opportunity to remove contaminants that ultimately produce NO_x and SO_x emissions [9,70,71]. With an overall efficiency of 35%, 7 billion tons of globally available biomass, with an energy content of 124 EJ, could produce 44 EJ of electricity [72].

Several demonstration and commercial CHP plants have been developed around the world as alternatives to the use of fossil fuel for electricity production [72]. Most remarkable and first BIGCC was demonstrated at Varnamo, Sweden producing 6 MW of electricity and 9 MW of heat primarily from wood chips. This facility operated between 1993 and 1999, and was closed due to unfavorable economic conditions. The 8,500 h of gasification runs and about 3,600 h as a fully operational integrated plant provided valuable experiences. The demonstration proved that the producer gas from a high-pressure circulating bed gasifier could be cleaned using hot cleaning technique and could be burned in a gas turbine under stable conditions even with low-energy of 3.8 MJ/kg. More research initiatives are underway to restart the demonstration plant for increased H_2 production using municipal wastes [73]. Yin reported that a circulating fluidized-bed (CFB) gasifier attached to gas engines and a capacity of 150 t/d of rice husk, located in China, reliably provided 1 MW of electricity at a rice mill with an overall electrical efficiency of 18% with a payback period of less than 2 years [74]. Wu reported that after 8,000 h of operation, the overall efficiency improved to 28% for demonstration plant of BIGCC at the scale of 5.5 MWe [75]. The operating and capital costs were estimated to be 0.079 USD/kWh and 1,200 USD/kW with a biomass price of 35.7 USD/ton.

With an increase in size of the gasification system, the cost of electricity production decreases. Brammer and Bridgwater estimated the cost of electricity (coE) was 8.67 Euro c/kWh for a 2 dt/h system at cost of €30/dt with a rotary dryer reducing the moisture from 50% to 10% [18]. Craig and Mann estimated cost of electricity production to be 0.0655 to 0.0820 USD/kWh, depending on the gasifier design, including high or low pressure, and directly or indirectly heated [76]. Uddin and Barreto, and Rhodes and Keith found that biomass-fired cogenerations systems such as BIGCC, with carbon capture, were energy efficient, emission efficient and cost competitive with natural gas cogeneration systems with carbon capture [77,78]. Tiffany concluded that, for ethanol production from corn, the use of biomass (corn stover and fermentation byproduct such as distillers grains and corn syrup) to produce heat and/or electricity might require high capital cost but the profitability of the process was more resilient to the change in prices of commodities (corn, oil, natural gas, electricity), and these were competitive with the conventional natural gas and purchased electricity [79]. However, issues related to biomass collection and utilization, and commercialization of CHP-BIGCC need to be resolved. High capital costs associated with first generation large-scale gasification of biomass, the technical risks involved, and the unproven technologies of tar cleaning are the main hindrance to the commercialization efforts. The heating value of the product gas needs to be increased, especially in air-blown gasification, to power gas turbines [7,80].

CHP generation from biomass is especially beneficial for rural electrification in developing countries where diesel is the primary fuel. Abe, in a case study of Cambodia, estimated that with the current technology, the cost of electricity from gasification of locally available biomass (agricultural residue, planted trees) was lower than the cost of electricity from diesel engine at the scale of 13.3 kWh electricity usage per household [81]. Gasification has potential to provide electricity to more than 60% of the villages which currently are without electricity. However, the major challenges in the commercialization of small-scale gasification systems are to effectively clean the product gas, at this scale, for proper operation of gas engines; to design the system flexible enough to operate using varying biomass qualities; and to decrease the capital cost [82,83].

4.2.2. Hydrogen

H_2 can be used as a transportation fuel in fuel-cell based automobiles, as a zero-emission fuel. It should be realized that H_2 is not an energy carrier, but rather an energy source. Hence, sources of energy are needed to produce hydrogen. H_2 has the highest energy content on a mass basis. Use of H_2 in fuel cells has gained attention because of its high efficiency (around 60%) as compared to efficiency of IC engines (20–38%). However, more research is needed in the areas of production, storage, transportation and utilization of H_2 for its viable use as an energy carrier [84,85]. Currently, the total production of H_2 is about 9 million tons, 95% of which is produced by steam reforming of natural gas. The H_2 is used for the production of chemicals and intermediate products with 95% being used to produce ammonia (50%), petroleum products (37%), and methanol (8%) [86,87].

Biomass gasification results in H_2 production. As described in the previous sections, changes in gasifier and reformer operating conditions influence the H_2 content of the product gas. Higher temperature, ER, S/R and catalysts all lead to higher H_2 production. However, additional reforming reactions may be needed to further increase the H_2 content in the product gas.

4.2.3. Catalytic synthesis of methanol and higher alcohols

Methanol, produced in large quantity, is used for making various fuels and chemicals. Currently, it is used primarily for making formaldehyde, dimethyether, MTBE (methyl tert-butyl ether, additive for gasoline) and acetic acid. Methanol also is used for converting fats and oil to biodiesel. CO, H_2, CO_2 and H_2O are used to produce methanol using methanol synthesis reactions in the temperature range of 220 to 300 °C and pressures of 50 to 100 bars using Cu/ZnO catalysts (Equations 11 and 12) [12].

$$CO + H_2O = H_2 + CO_2 \tag{11}$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \tag{12}$$

Optimum operating conditions such as temperature, pressure and space velocity (ratio volumetric flow and reactor volume) for the maximal selectivity of methanol from syngas depend heavily on the composition of the syngas. Using a commercial $Cu/ZnO/Al_2O_3$ catalyst, Gerber showed that methanol yield was affected by ratio of H_2 to $CO+CO_2$ but methanol selectivity was more affected by the CO_2/CO ratio [88]. Removal of CO_2 improved both the selectivity and yield of methanol.

In Europe, a number of efforts have been made to produce methanol from biomass. In France and Sweden, methanol production by pressurized biomass gasification was developed and tested [83]. However, the low cost of petroleum-based feedstocks (natural gas and coal) have been detrimental to use of biomass for this application. Recently, increase in the price of fossil fuels and increased awareness about the global warming have led to amplified research efforts for biomass utilization for production of biofuels and chemicals.

Syngas can be converted to higher alcohols using catalysts. After a survey, Gerber reported that catalysts for mixed alcohol synthesis are not commercially available except for one available for methanol synthesis [88]. By comparing 10 catalysts from different classes, they observed that $Rh/Mn/Fe/SiO_2$ catalysts and two modified FT based catalysts had high STY (space-time yields, $g/L_{cat}/h$) of C_{2+} oxygenates (predominantly C_2 to C_5 alcohols, acetic acid, acetaldehyde, and ethyl acetate) with a maximum of 170–400 and 50–830, respectively. Rhodium catalysts seemed to be the best for C_{2+} oxygenate selectivity and STY. Modified FT catalysts were best for best C_2 alcohol selectivity and total liquid STY. Further testing of Rh based catalysts, with different promoters and temperature condition, showed that iridium gave maximum STY of oxygenates of 880 followed by lithium and nickel. Selectivity to C_{2+} alcohols were best by iron and rhenium followed by carbon [89].

4.2.4. Fischer-Tropsch Synthesis (FTS) diesel and gasoline

The Fischer Tropsch (FT) process is a method to produce alkanes from syngas in the presence of Fe, Co and Ru-based catalysts as represented by Equation 13. Co and Fe are more practical to use because of the high cost of Ru. Co also is comparatively more expensive than Fe, but due to its higher activity and longer life, it is the preferred FT catalyst. Co-based catalysts in slurry phase reactors give high wax production from syngas, which is then selectively cracked to diesel fuel [90]. The process takes place at 20 to 40 bars and 180–250 °C. The FT product needs to be hydrocracked with H_2 to reduce the double bonds of unsaturated hydrocarbons producing hydrocarbons in the diesel fuel range. Larger (higher than C_5) hydrocarbons are desired for use as liquid fuels. FT products are free of sulfur. The yield of FT diesel is estimated to be 120 L/mt biomass with a prediction of ultimately reaching 210 L/mt. The research challenge for the FT synthesis process is to narrow the range of resulting hydrocarbons. The chain lengths of FT products vary from 1 to 50 producing hydrocarbons ranging from methane, gasoline range, diesel range, naphtha, kerosene, to heavy waxes.

$$CO + H_2 = C_nH_m + H_2O \tag{13}$$

During World War II, Germany produced these fuels from coal based syngas. Currently, Sasol in South Africa and Shell in Malaysia produce FT fuels from coal and natural gas, respectively. To date, there is no commercial demonstration of FT fuel production from biomass.

Contaminants in biomass-derived syngas need to be removed to suit the FT synthesis process. Around 2.1:1 H_2/CO ratio is desired for FT synthesis depending on selectivity. As syngas from biomass gasification has less H_2/CO ratio, shift reactions are required to increase the H_2 content suitable for the FT process. Higher partial pressures of CO and H_2 are desired for higher selectivity for longer chain hydrocarbons. Other gas components also may reduce the partial pressures of CO and H_2, thereby reducing the liquid selectivity. Hot gas cleaning does not seem very beneficial for FT process because this process operates at lower temperature (200 °C) [12,91]. Detailed reviews of the reactors used in FT process can be found elsewhere [90].

Many authors have suggested that by using FT catalysts on zeolite based supports the selectivity of the product can be narrowed to gasoline range hydrocarbons. The bifunctional catalysts allows two simultaneous reactions (syngas to methanol over the metallic function and methanol to hydrocarbons over acidic function) to take place. With Cr_2O_3-ZnO/ZSM5 as bifunctional catalysts, Ereña observed that conversion of CO increased with pressure (10–50 atm), temperature (300–425 °C) and space time (7.23–62.22 h^{-1}) and decreased with CO/H_2 molar ratio (0.33–2.0) [92]. The gasoline fraction (C_{5+}) increased with space time and CO molar ratio and decreased with pressure and temperature. Methanol content was less than 0.01 wt% in the product, which indicated that the reaction rate was limited by methanol synthesis. The product distribution was nearly constant with 70–75 wt% CO, 22–28% hydrocarbons and a small amount of water.

Cr_2O_3-ZnO, with an atomic ratio of 2.0, was the best catalytic mixture for high CO conversion and high gasoline fraction. Cr/Zn > 2.0 decreased CO conversion. Higher Zn gave higher gas production, especially methane and light paraffins because Zn favored hydrogenation reactions over the gasoline formation reactions. Zeolite, with Si/Al ratio of about 154, was most suitable for production of gasoline range hydrocarbons [93].

4.2.5. Fermentation of syngas to ethanol

Fermentation of synthesis gas (Equations 14 and 15) is an attractive process to produce ethanol as a transportation fuel because the biological catalysts are more specific resulting in less side products [94]. Henstra summarized the micro-organisms used for the fermentation of syngas [95]. Since the fermentation takes place at lower temperature as compared to catalytic conversion of the synthesis gas to liquid fuels, the wet gas cleaning can be used for removal of impurities from the product gas. Moreover, ethanol (blended with gasoline) has been used successfully as a transportation fuel in many countries, most notably in US and Brazil with existing transportation infrastructure and automobile engines. As compared to the biochemical conversion with hydrolysis and fermentation processes, gasification and fermentation have potential to use a much wide variety of feedstock producing ethanol.

$$6CO + 3H_2O = C_2H_5OH + 4CO_2 \tag{14}$$

$$6H_2 + 2CO_2 = C_2H_5OH + 3H_2O \tag{15}$$

Datar demonstrated using the producer gas, generated from gasification of switchgrass, to produce ethanol by fermentation [96]. During their 20-day fermentation study, they alternately used bottled gas (clean gases) from days 0 to 8.5 and days 11.4 to 14.5 and producer gas for the rest of the days. They observed that after introducing producer gas, the H_2 utilization stopped but the CO utilization continued forming primarily ethanol. At the end of the run, ethanol concentration reached 5 g/L.

The major challenge with this process was to increase rate and yield of fermentation by increasing gas to liquid mass transfer rate of CO and H_2 [97,98], and to search for a right microbe having increased ethanol yield and high resistance to the contaminants in the syngas [95,99,100]. Sensible heat from product gas during wet gas cleaning also needs to be recovered to increase the net energy efficiency of the overall process.

5. Conclusions

Biomass gasification is a promising technology to displace use of fossil fuels and to reduce CO_2 emission. Among other alternative energy conversion pathways, it has great potential because of its flexibility to use a wide range of feedstock, and to produce energy and a wide range of fuels and chemicals. Recently, the focus of its application has changed from production of combined heat and power to production of liquid transportation fuel. The technical challenges in commercialization of fuels and chemicals production from biomass gasification include increasing the energy efficiency of the system and developing robust and efficient technologies for cleaning the product gas and its conversion to valuable fuels and chemicals.

Acknowledgements

This project was supported in part with Hatch funds through the Agricultural Research Division of the Institute of Agriculture and Natural Resources at the University of Nebraska.

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Chapter 21

Review of Biomass Thermal Gasification

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/66362

Abstract

Gasification of biomass is one of the most attractive methods for producing hydrogen rich gas. Syngas production from biomass is an attractive solution for energy crisis. The production of energy from biomass reduces the dependence of developing countries on fossil fuels, as ample biomass is available in the developing countries and is renewable. Downdraft gasifiers are fixed bed gasifiers where the gasifying agent and biomass are flowing downwards, developed for high-volatile fuels such as wood or biomass gasification. Cocurrent flow regime throughout the oxidation and reduction zones reduces the tars and particulates in syngas, which will reduce the necessity of complicated cleaning methods compared to updraft gasifiers especially if the gas is used as a burnable gas in a small community. It is important to ensure homogenous distribution of gasifying agent at the downdraft gasifier throat. This chapter presents latest trends in gasification of biomass using downdraft gasification.

Keywords: gasification, hydrogen, agriculture waste, catalysts, downdraft gasifier

1. Introduction

Gasification of biomass is one of the most attractive methods for producing hydrogen rich gas. Syngas production from biomass is an attractive solution for energy crisis. The production of energy from biomass reduces the dependence of developing countries on fossil fuels; as ample biomass is available in the developing countries and is renewable. Downdraft gasifiers are fixed bed gasifiers where the gasifying agent and biomass are flowing downwards, developed for high volatile fuels like wood or biomass gasification. Cocurrent flow regime throughout the oxidation and reduction zones reduces the tars and particulates in syngas, which will reduce the necessity of complicated cleaning methods compared to updraft gasifiers especially if the gas is used as a burnable gas in a small community. It is important to ensure homogenous distribution of gasifying agent at the downdraft gasifier throat [1–3].

Gasification is a process under development to utilize the energy conserved in biomass. Gasification can be used as a source of energy in rural and off-grid areas to fill the power gaps. The limited supply and the increasing demands of fossil fuels have led the world to investigate alternative energy sources. Renewable energy sources have been studied widely, and biomass appears as the most promising renewable energy source. Biomass can be used to overcome the depletion of fossil fuels and to reduce the environmental impact of the conventional fuels such as greenhouse gas emissions using one of these four technologies: direct combustion, thermochemical processes, biochemical processes, and agrochemical processes. Biomass is the third energy source after coal and oil. Biomass covers 35% of the energy demand of the developing countries corresponding to 13% of the world energy demand. Biomass is widely available in quantities enough to meet the world energy demand [1–7].

The oldest way to generate energy is to burn biomass. Due to environmental and technical difficulties associated with burning biomass, innovative processes should be developed to utilize biomass [5, 8–10]. Developing more effective techniques to utilize biomass will reduce the disposal problem and create profits. Hydrolysis, pyrolysis, gasification, and hydrogenation are the principal processes for biomass conversion in the literature [7, 11]. Gasification represents efficient and environmentally friendly method for producing the syngas as a biofuel from different sources of biomass [12–14], and to produce second-generation biofuels such as methanol, ethanol, and hydrogen [8, 10, 12, 15]. Gasification can be defined as the partial (incomplete) combustion of biomass, and gasification could extract up to 60–90% of the energy stored in biomass [16, 17]. To develop second-generation biofuels, economical and Feasible clean technologies of syngas are required. [15]. However, economical gasification of biomass may produce burnable gases, which can be used to provide heat requirements instead of LPG [12]. Gasifiers were developed to replace biomass burners. Gasifiers will prevent the necessity of on-site power generation [18, 19]. Gasification is the conversion of biomass into a combustible gas and charcoal by partial oxidation of biomass at temperature range of 800–900°C [6, 19, 20].

The charcoal is finally reduced to H_2, CO, CO_2, O_2, N_2, and CH_4 [6, 8–10, 21]. Char gasification starts at temperatures above 350°C [7]. The products of gasification consist of the following components: ash, volatile alkali metals, tars, and syngas. Tars represent a challenge for the commercialization of gasification product as an alternative fuel [22]. Frequently using tar may result in complete shutdown and repair of the industrial unit [18, 22]. Tars set and amount vary considerably based on reaction conditions and gasifier type [18]. Gas produced from gasifier can be cleaned by removing tars either physically or chemically [18]. Physical removal can be achieved using bag filters or wet scrubbers. Chemical removal methods depend on converting tars to lighter hydrocarbons either using thermal conversion or catalytic conversion processes [18, 22].

Gasification of such material may help in reducing the gap between electricity requirements and available energy sources. Decentralized power regeneration units will help to fill power gap in rural and off-grid locations [4]. Yet, it is still difficult to develop a decentralized power generation unit based on biomass energy which can be used to fill the gap in energy needs in rural areas and farms [4]. Technical difficulties prevent further commercialization of gasification units in accordance to lower conversion efficiency [23, 24]. Leung et al. [25] proposed a governmental support to accomplish faster steps toward gasification units commercialization. However, all over the world, biomass energy has been widely incorporated in the power generation system; U.S. started partial and full conversion of conventional power plants to biomass [24]. Throughout this chapter, we will discuss the latest trends in agricultural waste gasification. Our goal is to provide a full description of the process starting from basic understanding and ending by design of a gasification unit.

2. Chemistry of gasification

The reactions taking place in the gasifier can be summarized as indicated below [3, 4, 21]:

Partial oxidation:

$$C + \frac{1}{2} O_2 \leftrightarrow CO \quad \Delta H = -268 \text{ kJ/mol} \tag{1}$$

Complete oxidation:

$$C + O_2 \leftrightarrow CO_2 \quad \Delta H = -406 \text{ kJ/mol} \tag{2}$$

Water gas phase reaction:

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = 118 \text{ kJ/mol} \tag{3}$$

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = 170.7 \text{ kJ/mol} \tag{4}$$

The heat required for water gas phase and Boudouard reactions is provided by complete and partial oxidation reactions, and complete oxidation provides around 60% of the heat requirements during gasification [3, 17]. In addition to the previous reactions that are common in combustion and gasification, hydrogen, steam, and carbon monoxide undergo further reactions as shown below [3, 24]:

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -42 \text{ kJ/mol} \tag{5}$$

Methane formation:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H = -88 \text{ kJ/mol} \tag{6}$$

The water gas shift and methane formation reactions are in equilibrium and the governing parameters are: pressure, temperature, and concentration of reaction species.

3. Gasifier design

The unit design is a very important factor in determining the syngas quality and heating value [15]. The gasifier will hold two processes: conversion of biomass to charcoal and then conversion of charcoal to hydrogen and carbon monoxide. The mixture of hydrogen and carbon monoxide can be used for direct heating in rural areas [16]. Leung et al. [25] identified four types of gasifiers: updraft, open core, downdraft, and circulating fluidized bed (CFB) gasifiers. The maximum efficiency of the updraft, downdraft, and CFB gasifiers may reach to 75%, the maximum energy output is 10E6, 4E6, and 40E6 kJ/h, respectively. According to Chopra and Jain [13], the fixed bed gasifiers can be further divided into: updraft, Imbert downdraft, throatless downdraft, cross draft, and two-stage gasifiers. The fixed-bed gasifier is suitable for producing low heating value gas for small and medium applications [13, 26]. The downdraft gasifier is distinguished by a simple design, high carbon conversion, long residence time, low cost, low pressure, relatively clean gas, and low gas velocity. The downdraft gasifier is suitable for producing low heating value burnable gas or for generating electricity of small-scale systems in the range of 10 kW up to 1 MW [12, 26–28].

3.1. Design of downdraft gasifiers

Downdraft gasifiers are fixed bed gasifiers where the gasifying agent and biomass are flowing downwards, developed for high volatile fuels like wood or biomass gasification. Cocurrent flow regime throughout the oxidation and reduction zones reduces the tars and particulates in syngas, which will reduce the necessity of complicated cleaning methods compared to updraft gasifiers especially if the gas is used as a burnable gas in a small community [12, 17]. It is important to ensure homogenous distribution of gasifying agent at the downdraft gasifier throat.

Bhavanam and Sastry [24] provided design procedures for different types of downdraft gasifiers. The gasification reaction in a downdraft gasifier undergoes several steps, starting with drying step at 100°C, followed by pyrolysis step between 200 and 300°C resulting in release of around 70% of biomass weight as volatile matter and tars [16, 24]. After pyrolysis, the remaining biomass and volatile matter react with the incoming oxygen in the combustion step. Finally, various reactions take place in the reduction zone including carbon and steam reaction to produce CO and hydrogen, water-gas shift reaction, and CO and steam to form methane and carbon dioxide [24]. The four gasification reaction steps are illustrated in **Figure 1**. However, a limited experience has been gained in the field of biomass gasification while it represents an attractive renewable energy route [16]. **Table 1** illustrates the design specifications for two types of downdraft gasifiers: Imbert and stratified downdraft gasifiers. **Table 1** is developed based on extensive discussion in Bhavanam and Sastry [24].

Imbert downdraft gasifier is a cylindrical chamber of varying inner diameter across chamber length. The upper part of the cylindrical chamber is loaded with biomass according to

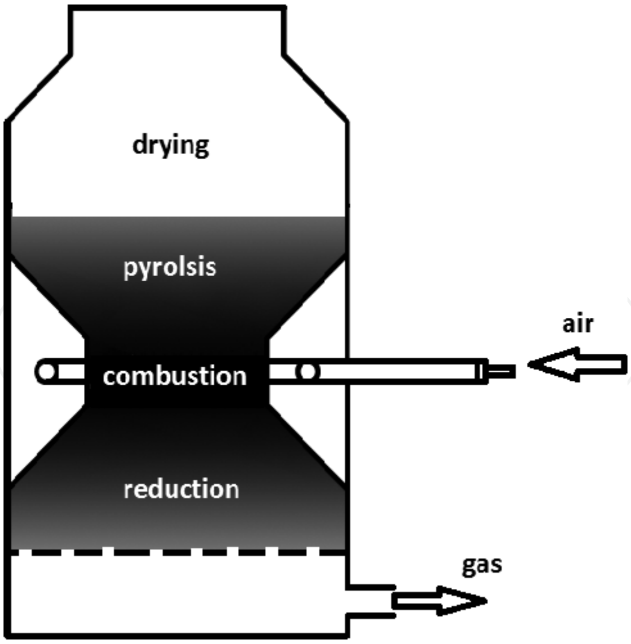

Figure 1. Different reaction zones in downdraft gasifier.

Design considerations		Imbert	Stratified
Biomass	Material	Uniform woody	Small size
	Moisture content	<20%	<20%
	Ash content	<5%	–
Reactor type		Packed bed supported on a throat	No-throat cylindrical packed bed with open top
Biomass feeding		Hopper	Open top
Gas feeding		Nozzle in the combustion zone	Enters from top mixed with biomass
Produced gas		Tar oils <1% $T = 700°C$	Less tar
Maximum capacity		500 kW	Easy to scale up

Table 1. Design consideration for Imbert and stratified downdraft gasifiers.

requirement. Air nozzles, attached to distribution manifold, permit air to be drawn into biomass to improve mixing of gasifying agent and biomass. A charcoal balance is established around the nozzles. Below the air nozzles, a classical Imbert hearth forms the reduction part. Insulating the reduction hearth reduces the amount of tars in the produced syngas and increases gasification efficiency. The hot gases are forced to go through the hot zone due to hearth constriction. The char bed on the grate removes the dust, which should be cleaned eventually to prevent clogging, and dropping in airflow or channeling [17].

Stratified or open-top downdraft gasifier is a uniform diameter gasifier, usually made of a cylindrical vessel with a hearth near the bottom. The stratified gasifier is an improved, easy to design gasifier compared to Imbert downdraft gasifier. The open-top helps in maintaining uniform access of gasifying agent to the pyrolysis zone, which prevents localized heating. Biomass is added through the open-top to the top layer of gasifier. The length of the gasifier can be divided into four reaction zones: unreacted biomass zone at which air enters, the flaming pyrolysis zone at which air reacts with biomass, adiabatic char gasification zone at which gases from flaming pyrolysis zone reacts with charcoal, and finally the unreacted charcoal zone that is located just above the grate which acts as a buffer for ash and charcoal. The stratified downdraft gasifier can be mathematically modeled easily as a plug flow reactor at which air and biomass are uniformly mixed. With such simple design, it is expected that stratified downdraft gasifier will replace the Imbert downdraft gasifier in commercial applications [17].

Wander et al. [29] illustrated the design of 12 kg/h downdraft stratified gasifier for sawmill dust gasification. The reactor is a cylindrical body of 270 mm internal diameter and 1100 mm of height made of SAE 1020 steel. Internal rods are used to mix the sawdust in the reduction zone. Ash box is used to reduce the ash content of the produced syngas. The reactor is insulated using 50 mm of rock wall. Air was introduced from the open top as a gasifying agent and a secondary air was used to provide air required for internal burner. A gas chromatography was used to analyze the gas samples and three water condensers in an ice bath were used to measure tars and humidity content.

Zainal et al. [30] developed a downdraft gasifier for the gasification using around 50 kg/h of wood chips. The temperature in the combustion zone may reach 1000°C, which reduces the tar content of produced syngas. The gasifier is made of mild steel pipe with a diameter of 0.6 m and a height of 2.5 m. A cone structure is used inside the gasifier above the combustion zone with an inclination of 60° to facilitate the wood material movement. The air supply was accomplished using a 40 mm diameter stainless-steel pipe with eight 10 mm diameter nozzles. The air is preheated by positioning the supply tube inside the gasifier. The heating value of the produced syngas was in the range of 4.65–5.62 MJ/Nm^3 depending on operating conditions.

Panwar et al. [31] developed an open-top downdraft gasifier for wood gasification to provide the heat requirement for the food processing industry. The downdraft gasifier was lined with ceramic and designed for a wood input of 60 kg/h equivalent to 180 kW. The gasifier body is made of mild steel. The air distribution system consists of six air tuyeres of 20 mm in diameter. A cyclone was used to remove solid particulates from produced syngas. The complete combustion of the syngas is achieved in a premixed burner to provide heat needed for the food processing industry unit. Note that 30 kg of charcoal and 10 kg of wood were used to provide hear required for gasifier start up.

Sheth and Babu [1] showed a design of an Imbert downdraft gasifier for wood waste gasification with a total height of 1.1 m. The diameter of pyrolysis zone and reduction zone are 0.31 and 0.15 m, respectively. The gasifier has throated combustion zone, a bed of char supported by a grate follows the combustion zone. The air is supplied through two nozzles in the oxidation zone. The high temperature in the combustion zone ensures cracking of tars into volatiles and water. The diameter of pyrolysis, reduction, and oxidation zones is 310, 150, and 53 mm, respectively. The grate is movable to unclog it for removing ash.

Vervaeke et al. [32] illustrated the design of a small-scale pilot plant downdraft gasifier equivalent to 100 kW of electricity generation. The downdraft unit used in this study is a pilot scale of the Xylowatt gasifier. The downdraft gasifier is a batch gasifier with a capacity of 90–105 kg. The gasification system consists of downdraft gasifier and inside it are ash collection container, cyclone, filter, and a scrubber.

Lv et al. [33] developed a downdraft gasifier to produce hydrogen from biomass using air and oxygen/steam as gasifying agents. Total 5 kg of char were supported on the grate to reduce tar content and to act as a catalyst to upgrade syngas. Biomass is pine wood blocks used in cubes cut into 3 cm × 3 cm × 3 cm. The gasifier height is 1.3 m and the diameter is 35 cm. The gasifying agent is preheated in a chamber inside the gasifier. Gas is cleaned using triple-stage spray shower filled with steel wire rings. The internal diameter of the gasifier is calculated according to the power output. The height is calculated based on batch operation time. The internal diameter is calculated in meters using the following equation [26]:

$$D = \left(\frac{1.27 * \mathrm{FCR}}{\mathrm{SGR}}\right)^{0.5} \tag{7}$$

where FCR is the fuel consumption rate (kg/h) and SGR is the specific gasification rate (kg/h/m^2).

The height can be determined in meter using the following equation [26]:

$$H = \frac{\mathrm{SGR} \times t}{\rho} \tag{8}$$

where t is the operation time (h) and ρ is the feedstock bulk density (kg/m^3).

The power output P_0 can be calculated in kW from the following equation [26]:

$$P_0 = \frac{\mathrm{FCR} \times \mathrm{HHV} \times \eta}{3.6} \tag{9}$$

where HHV is the higher heating value of the feedstock in MJ/kg and η is the efficiency of the gasifier usually around 0.7. The amount of air needed during operation can be calculated in Nm^3/h from the following equation [26]:

$$\mathrm{AFR} = \frac{\varepsilon \times \mathrm{FCR} \times \mathrm{SA}}{\rho_a} \tag{10}$$

where ε is the equivalence ratio, FCR is the fuel consumption rate, SA is the stoichiometric amount of air required for chemical reaction, and ρ_a is the density of air (1.18 kg/m^3). Finally, the size of the air nozzle, which is required for uniform air distribution, can be calculated in mm^2 from the following equation [26]:

$$A = \frac{\mathrm{AFR} \times 10^3}{\nu \times 3.6} \tag{11}$$

where ν is the inlet velocity of air (m/s).

4. Factors affecting on the gasification process

Zhou et al. [34] discussed the ongoing gasification projects taking place in China. The biomass gasification units were divided based on scale: small-, medium-, and large-scale biomass gasification and power generation units. Pretreatment of biomass includes size reduction, size screening, separation of magnetic materials, and storing as wet biomass. Then prior to gasification, drying and storing as dry material are accomplished to reduce the moisture content to 10–15% [35]. Feedstock type and feedstock preparation are important factors affecting the yield and quality of produced syngas. Shredding and drying are two processes conducted to prepare the biomass raw material for gasification process [14]. The main parameters affecting the gasification are clarified below:

Equivalence ratio (ER): The equivalence ratio is the air/biomass ratio divided by the theoretical air/biomass ratio. Increasing ER will decrease the heating value of the produced gas due to decreasing H_2 and CO concentration and increasing CO_2 concentration. Higher ER helps in reducing tars and provides more O_2 to react with volatiles. Typical values of ER ranges between 0.2 and 0.4 [24]. Guo et al. [36] reported that increasing ER decreases the concentration of combustible gases (H_2, CO, CH_4, and C_nH_m). The heating value was higher than 4 MJ/Nm^3 when ER is kept lower than 0.4. Increasing ER improves the reaction temperature and carbon conversion, and reduces the tar yield. For a downdraft stratified gasifier, Wander et al. [29] suggested an equivalence ratio of 0.3:0.35 kg-O_2/kg-wood. A higher ratio is required when higher heat loss is expected, an equivalence ratio of 2:2.4 kg-air/kg-wood is optimum for producing a syngas with low heating value of 4–6 MJ/Nm^3. For woody material in a downdraft gasifier, Zainal et al. [30] suggested an equivalence ratio of 0.268–0.43 with 0.38 showed optimum value (corresponding to a heating value of 5.62 MJ/Nm^3). While Sheth and Babu [1] defined that the optimum equivalence ratio for wood gasification in Imbert downdraft gasifier is 0.205.

Effect of biomass characteristics: Biomass characteristic is a major factor affecting produced syngas quality. The physical properties that may have major effect are: absolute and bulk density, and particulate size. The chemical composition parameters that are of major importance to define the syngas [17] quality including volatile matter, moisture content, fixed carbon, ash content, and gross calorific value and the ultimate analysis comprises the carbon, oxygen, nitrogen, and sulfur of the dry biomass on a weight% [19].

Moisture content: The moisture content can be determined by complete drying of biomass sample. The moisture content is calculated by subtracting the sample weight after drying from fresh sample weight. Maximum allowable moisture content in downdraft gasifier is 40% on dry weight basis. Updraft gasifier can handle biomass with higher moisture content. The higher moisture content in biomass will increase the consumed energy for drying, and will reduce the pyrolysis of biomass. As a general rule, increasing moisture content decreases the conversion [1, 24].

Superficial velocity: The superficial velocity is the ratio of the syngas production rate at normal conditions and the narrowest cross-sectional area of gasifier. Lower superficial velocity is linked with high yield of char, and large quantities of unburned tars, which may deactivate catalyst, plug lines, and destroy compressors. On the other hand, higher superficial velocity results in reduced amount of char and low overall process efficiency [24].

Operating temperature: Operating temperature affects conversion, tar content, gas composition, gas heating value, and char conversion. To select the optimum temperature, gasifier type, and biomass source should be considered. Usually, temperature higher than 800°C should be used to obtain high conversion and low tar content in the produced syngas [24]. Low temperature is associated with low tar content, low H_2 and CO content in the produced syngas [12]. Increasing temperature will increase gas yield, hydrogen, heating value, and ash agglomeration. To overcome the ash agglomeration problem, practical temperature does not exceed 750°C [24].

Gasifying agent: Gasifying agents in use are air, steam, steam/oxygen mixture, and CO_2. Gasifying agent affects the heating value of the produced syngas. The heating value increases with increasing steam content of the gasifying agent, while heating value decreases as air increases in the gasifying agent [24]. The steam/oxygen mixture represents a zero nitrogen-gasifying agent which increase heating value and allow liquefying the produced gas after proper treatment [37]. Using almond shells, the lower heating value was 5.9–6.7, 6.3–8.4, and 10.9–11.7 MJ/Nm^3 using the gasifying agent: 35 wt.% O_2 enriched air, 50 wt.% O_2 enriched air, and steam/oxygen mixture, respectively. Campoy et al. [38] reported a heat value of syngas produced from gasification to have an average value of 4–6 and 9–13 MJ/Nm^3 using air and oxygen/steam mixture, respectively. In addition to lower efficiency compared to air/steam mixture, enriched oxygen-air requires high capital cost for oxygen [38]. The addition of steam will shift toward the reforming reaction and heterogeneous gasification reactions.

Residence time: Residence time has a remarkable impact on the composition and produced tars. Increasing residence time decreases the fraction of oxygen-containing compounds, decreases yield of one and two atomic ring compounds, and increases three and four ring compounds [24].

Pressure: Atmospheric and higher pressures are commonly used in gasification process. Selecting the optimum pressure depends on the application of the produced syngas. If the syngas is used for producing methanol or synthetic auto-fuels, higher pressures are preferred to improve the process yield and to reduce tar content. For generating burnable gases, atmospheric pressure should be used [12]. High pressure applications are recommended for large-scale gasification, while atmospheric pressure is recommended for small-scale gasification [35]. High pressure gasification is still not well developed and further research is needed to further commercialize such process [39].

Catalyst: Catalyst type is a very important factor affecting gasification quality and produced syngas. Catalyst affects the composition of the syngas by manipulating the percentage volume of hydrogen, carbon dioxide, methane, and carbon monoxide. Optimum catalyst should play a role in minimizing the gas content of carbon dioxide and maximizing the gas content of hydrogen, carbon monoxide, and methane [40]. The catalyst type and loading on the gasification of cotton stalks and saw dust were studied. The catalysts selected are USY zeolite, dolomite, CaO, granulated slag, red brick clay, olivine, and cement kiln dust. The results demonstrate that the cement kiln dust and calcium hydroxide are more effective for increasing the gas yield and decreasing the char yield [8, 10].

Effect of biomass/steam ratio: Biomass/steam ratio affects hydrogen content in the produced syngas. Contradictory reports are found in literature, while Lv et al. [41] reported a positive effect on hydrogen content when biomass/steam ratio increases. Lv et al. [33] reported a negative effect of biomass/steam ratio increase on syngas hydrogen content. This variation can be understood by considering that biomass/steam ratio effect is altered according to the entire system configuration.

Lower values of biomass/steam ratio shift the reaction to produce more solid carbon and methane, since number of moles of steam increases in the feed. While at higher values of biomass/steam ratio, Co and H_2 are increased in the syngas as carbon and methane produced are decreased consequently.

5. Cost of biomass gasification process

The cost of any industrial process is governed by the capital cost and the running cost. Selection of best gasifier type depends on cost of fabrication, ease of manufacture, tar content, lower heating value, feedstock elasticity, and application of syngas [26]. The fixed bed gasifiers are more suitable for small- and medium-scale applications, while fluidized bed gasifiers are suitable for large-scale applications (equivalent to >15 MW) [25]. For example in China rice hulls, fluidized bed gasifiers are used in a production scale equivalent to 1–1.2 MW while downdraft gasifiers are used in a production scale equivalent to 60–200 kW [42]. The capital cost of the gasifier is divided into three items: gasifier and gas cleaning system cost, fuel gas utilization equipment cost, and fitting and system construction cost [25]. Cleaning systems and removing tars will add a significant cost to the produced syngas, which reduce the feasibility of using syngas in internal combustion engines [12]. Optimizing tar content can be achieved by varying the operating conditions and feedstock [43].

Upgrading using catalytic treatment represents the most economical and efficient method for syngas upgrading since it provides a way for removing tars and other particulates and converting tars to hydrocarbons [12]. Downdraft gasifier represents a reasonable cost production method for generating syngas with low tar content [29]. Especially small gasifiers that has proven economic feasibility [27].Wu et al. [44] recommended implementing biomass gasification depending on the low biomass price. By comparing different technologies to generate electricity based on 1 MW scale, Wu et al. [44] mentioned that the capital cost of fluidized bed gasifier system for biomass gasification-power generation system is 60–70% of the capital cost of coal power station and much lower compared to the capital cost of conventional power station. For producing combustible gases, Bridgwater et al. [45] reported that for syngas produced from fluidized bed, updraft, and downdraft gasifiers: hydrogen volume percentage is 9, 11, and 17%, respectively; CO volume percentage is 14, 24, and 21%, respectively; and a heating value of 5.4, 5.5, and 5.7 MJ/Nm^3, respectively. The downdraft represents the ideal solution to produce combustible (burnable) gases for household uses.

Biomass gasification economics are very sensitive to the scale of produced MW [44]. Leung et al. [25] mentioned two disadvantages of small- and medium-size gasifiers: capital cost limitation that may prevent incorporating important processes like tar removal, and the environmental demands imposed by new regulations which is difficult to be met by different biomass gasification technologies. Wu et al. [44] identified 160 kW as a critical scale of biomass gasification unit, less than 160 kW biomass gasification units loses the economical attraction. Note that 1–5 MW was recommended as the most competitive size for biomass gasification unit. Lower than a unit capacity of 160 kW, the price of kWh increases sharply from 0.4 to 1.8 Yuan RMB/kWh for very small capacities. For unit with capacities higher than 160 Wh, the price will decrease gradually as the unit size increases. At the 600 kW capacity, the price will be around 0.3 Yuan RMB/kWh; while the price may reach 0.25 for a unit capacity of 1000 kW [44].

It is recommended to conduct gasification at pilot plant scale to mimic large scale to figure out the approximate industrial process scale economics [38]. The steam enhances the reforming and heterogeneous gasification reactions, the temperature inside the gasifier should be kept enough to support such reactions [38]. Combining gasification unit with heat and power generation systems will improve the economics of the process [3]. Gasification units combined with heat and power generation systems are expected to have an overall efficiency of 85% compared to a maximum efficiency of 35–55% for conventional power station, in addition to a substantial saving in carbon emissions. Total 1000 kg/year of carbon are saved for each MW when gasification units hybrid with heat and power generation systems [3].

Downdraft gasifiers are economically competitive even to conventional LPG heating unit. Panwar et al. [31] found that replacing LPG heating system with a downdraft wood gasification system could save $13,850 US for 3000 h of operation. The payback period of the gasification system was only 1100 h. According to the extensive study of literature, the recommended gasification process consists of the following steps [13, 17, 19]:

1. Straw collection and preparation (milling and pelletization of straws).
2. Belt conveyor for feeding of the gasifier.
3. Downdraft gasifier.
4. Blower for suction of air and gas produced.
5. Gas cleaning and separation of tars.
6. Gas holder for storage of gas.
7. Gas distribution net.
8. Gas application devices.
9. Gas metering devices.

6. Preliminary techno-economic studies of downdraft gasifier

The aim of this chapter is to illustrate a detailed design of biomass gasification system to generate syngas for household applications. The stratified gasifier is selected based on the

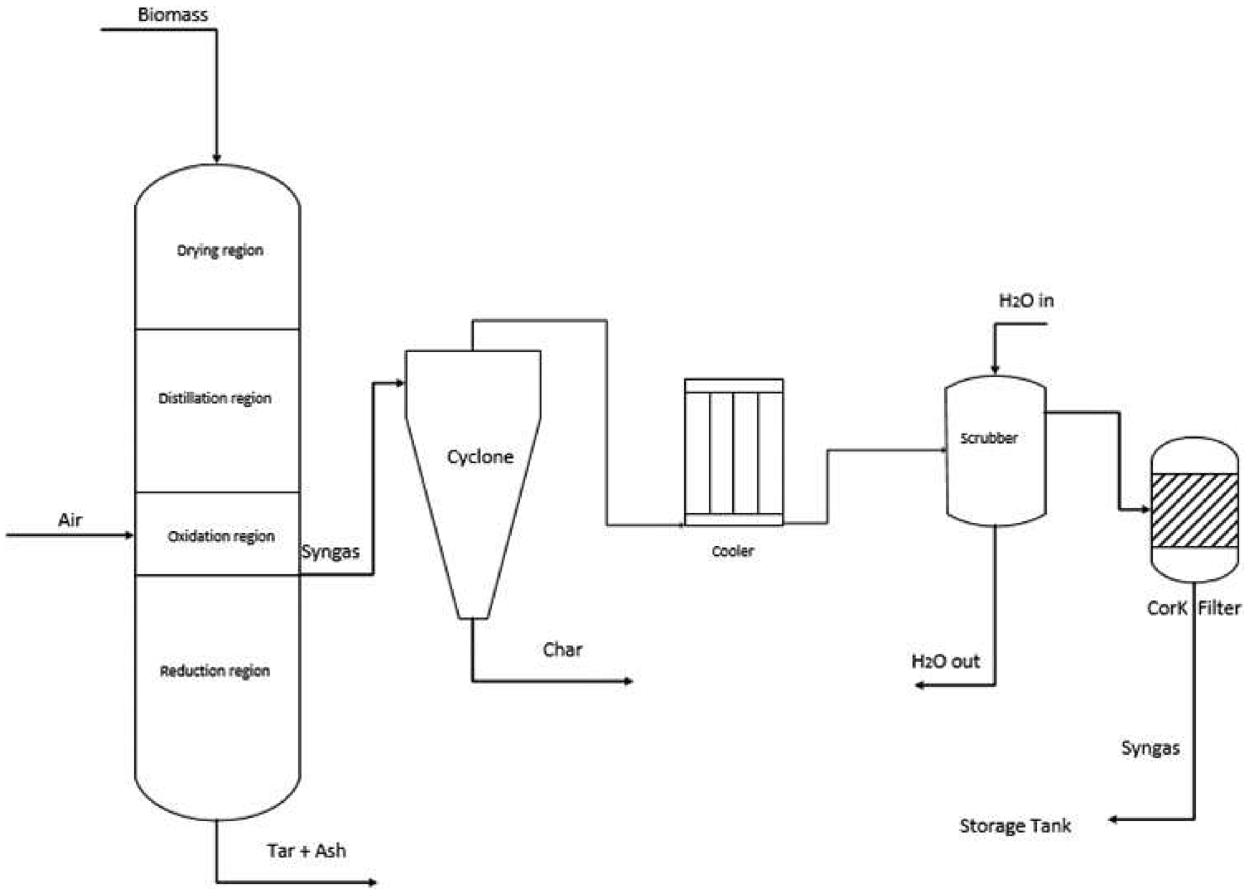

Figure 2. Gasification system for producing burnable gas.

following parameters: easiness in design and scaling up, and production of syngas with tar content lower than that of Imbert gasifier [16–18, 26]. The gasification system comprises of a downdraft burnable syngas gasifier followed by a gas cleaning and distributing system. Throughout this chapter, the design specification of the downdraft gasifier is presented. This system can be used to convert solid agricultural waste to a syngas that is a burnable gas used to provide energy requirements for small communities, as shown in **Figure 2**.

The energy (household) requirements: for 50 families.

The gas demand per day is: 500 m^3/day.

The syngas gas will be produced on two batches: Morning and afternoon (each one will last for 250 m^3/batch).

The first batch will take place from 7 to 10 am.

The second batch will take place from 2 to 5 pm.

The storage unit will hold around 200 m^3 gas and accordingly will provide heating requirements during the period of nonoperation.

The system consists of the following units: biomass shredding, grinding unit, gasification unit, air controlling system, air heating and gas precooling unit, cyclone (acts like cyclone to remove dust), gas cooler, water filter (scrubbing unit), gas distribution system, control system, cork filter, and storage tank.

No.	Object	Cost, Egyptian pounds
1	Gasifier with control system	30,000
2	Gas cleaner	10,000
3	Belt conveyor	15,000
4	Milling and pelletization of biomass	50,000
5	Gas holder	15,000
6	Gas distribution system 100 × 500	60,000
7	Gas stoves 100 ×350	35,000
8	Gas meters 100 ×400	40,000
9	Erection	10,000
10	Contingency (10%)	26,000
	Total	2,90, 000

$ = 8.5 Egyptian pounds.
Assume that:
Cost of material = 300 L.E/ton
Cost of preparation = 100 L.E/ton
Cost of raw materials = 0.25 ×400 × 360 = 36 000 L.E/year
Labors required = 2 ×1500 = 3000 L.E/month = 3000 ×12 = 36000 L.E/year
Income gas production = 500 m^3/day
≈60 kg L.P.G/day
= 60 × 360 = 21,600 Kg/year
= 21,600 × 7 = 151,200 L.E/year
Profit = income − raw material − depreciation
Profit = 151,200 – 36,000 – 36,000 – 29,000 = 49,400
Return on Investment = profit/initial cost
Return on Investment = (49,400/290,000)×100 = 17%
Therefore, the payback period is about 6 years based on the international prices of L.P.G.

Cost of equipment for gasification system.

The cost of land required for erection of the plant is not included in this calculation of the feasibility study.

7. Conclusions

Gasification represents a viable solution to overcome the energy shortage by developing commercial gasification units in rural and off-grid areas. An integrated system comprising a gasification-electrical generation method represents an ideal solution from the technical and economical points of view.

However, due to the wide varieties of available biomass feedstock, it is recommended to manipulate different systems in each location depending on the feedstock, produced syngas, and energy demands. Downdraft gasifier is recommended for small-scale applications in rural areas. The co-current nature of air and biomass flow reduces the tar content and increases CO and H_2 in the produced syngas. The syngas produced from downdraft gasifier can be used after a simple purification process in thermal applications. From a cost study, the payback period of a gasification system is around 5 years.

Acknowledgements

The authors would like to express deepest thanks for the Science and Technology Development Fund (STDF Egypt) for financing and supporting the development of the thermal gasification of biomass.

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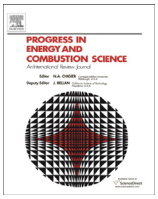

Review

New concepts in biomass gasification

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ARTICLE INFO

Article history:
Received 28 January 2014
Accepted 29 May 2014
Available online 2 July 2014

Keywords:
Biomass
Gasification
Process intensification
Process combination
Polygeneration

ABSTRACT

Gasification is considered as a key technology for the use of biomass. In order to promote this technology in the future, advanced, cost-effective, and highly efficient gasification processes and systems are required. This paper provides a detailed review on new concepts in biomass gasification.

Concepts for process integration and combination aim to enable higher process efficiencies, better gas quality and purity, and lower investment costs. The recently developed UNIQUE gasifier which integrates gasification, gas cleaning and conditioning in one reactor unit is an example for a promising process integration. Other interesting concepts combine pyrolysis and gasification or gasification and combustion in single controlled stages. An approach to improve the economic viability and sustainability of the utilization of biomass via gasification is the combined production of more than one product. Polygeneration strategies for the production of multiple energy products from biomass gasification syngas offer high efficiency and flexibility.

Contents

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http://dx.doi.org/10.1016/j.pecs.2014.06.002
0360-1285/

1. Introduction

Global warming and climate change concerns result in efforts to reduce CO_2 greenhouse gas emissions by increasing the use of renewable energies and increasing the energy efficiency. Besides solar and wind energy, biomass is considered as a main renewable energy source. In the renewable energy mixture of solar, wind and biomass energy, biomass can be used as adjustable, controlled energy which will be supplied in increased amount when wind and solar energy supply is low.

Since the discovery of the mankind how to make fire, biomass has been the main energy source for thousands of years and still today it contributes in the range of more than 10% to the world energy supply and ranks as the fourth source of energy in the world [1]. In rural agricultural areas, biomass is still the main energy resource for heating and cooking and often it is the only available energy source there. In developing countries in Asia and Africa more than one-third of the total energy consumption is based on biomass. A big advantage of biomass is that it is available at every place all over the world which is in contrast to coal or natural gas. For example, in India which has very large coal reserves of more than 250 billion tons, the coal deposits are just located in the state of Bihar and northeast. Transportation costs play a major role in the distribution of the coal. Biomass in contrast is uniformly and widely distributed over the country [2].

Gasification is a key technology for the use of biomass. It offers a high flexibility in using different kind of feedstock materials as well as in the generation of different products. In principal, all different types of biomass can be converted by gasification into syngas mainly comprising hydrogen, carbon monoxide, carbon dioxide and methane. From this syngas, all kinds of energy or energy carriers – heat, power, biofuels, hydrogen, biomethane – as well as chemicals can be provided. Synthesis of Fischer–Tropsch (FT) diesel, dimethyl ether (DME), methanol and methane are established technical processes. The use of the available biomass resources needs to be highly efficient and sustainable. Gasification offers a high potential and a high process efficiency for the use of biomass [3]. Gasification of biomass is performed by partial oxidation of the carbon contained in the biomass at high temperature using a controlled amount of an oxidant which can be air, pure oxygen or steam. The composition and properties of the syngas depend on the biomass feedstock, the gasifier type and the operation conditions of the gasifier, such as the used oxidant, the temperature and the residence time in the gasifier. Gasification with air leads to a syngas with a heating value of 4–7 MJ/m^3 whereas using pure oxygen or steam as an oxidant leads to significantly higher heating values of the gas of 10–18 MJ/m^3 [4,5].

Biomass comprises a broad range of different kinds of bio materials, such as wood, forest and agricultural residues, waste from wood and food industry, algae, energy grasses, straw, bagasse, sewage sludge etc. The use of different kinds of biomass results in different challenges and solutions for transportation, storage and feeding of the biomass, for operation of the gasifier and for cleaning of the produced syngas. Most commonly used types of biomass gasifiers are fixed bed and moving bed, fluidized bed and entrained flow gasifiers. Fluidized bed and entrained flow gasifiers provide an intensive contact between the gas and the solid biomass which results in high reaction rates and conversion efficiencies. Fixed bed gasifiers typically have a lower heat and mass transfer and often generate higher amounts of tar and char. However, operation and design of fixed bed gasifiers are simpler and they are preferably used in small size. Performance data of the mentioned gasifier types are given in Table 1.

Depending on the use of the syngas, its cleaning needs to be very efficient. Catalytic synthesis reactions or the use in fuel cells for examples require high purity of the syngas. Main impurities in the syngas are fly ash particles and tar. Other impurities in the syngas are typically sulphur compounds (e.g. H_2S, COS), hydrogen chloride, alkalines, and ammonia. Tar formation is a main problem in biomass gasification. Tar condensation at lower temperatures can cause clogging or blockage of pipes, filters, catalyst units or engines. Tar formation also lowers the syngas yield and the heating value of the gas. Tar removal has been the subject of many researches leading to the development of primary and secondary measures for tar reduction. Overviews on this topic are recently given e.g. by Han and Kim [13], by Aravind and de Jong [14] and by Shen and Yoshikawa [15].

In order to promote the utilization of biomass gasification, advanced concepts are required which have to maximize the syngas yield, optimize the gas quality, increase the gas purity, increase the overall process efficiency and improve the economic viability by decreasing system and production costs.

This paper aims to provide a detailed review on such new concepts in biomass gasification. Process integration and combination, polygeneration strategies as well as new gasification concepts are presented as follows (see also Table 2):

- An interesting example for process integration is the recently developed UNIQUE gasifier concept which integrates gasification, gas cleaning and conditioning in one reactor unit. This

Table 1
Performance data of most commonly used gasifier types.

Gasification technology	Gasification temperature/°C	Cold gas efficiency/%	Char conversion/%	Tar content in raw producer gas/g/m^3_N	References
Fluidized bed (FB) gasifier	800–900	<70	<70	10–40	[6]
Circulating fluidized bed (CFB) gasifier	750–850	50–70	70–95	5–12	[7,8]
Fixed bed downdraft gasifier	Max. bed temp.: 900–1050 gas exit temp.: 700	30–60	<85	0.015–0.5	[9,10]
Fixed bed updraft gasifier	Max. bed temp.: 950–1150 gas exit temp.: 150–400	20–60	40–85	30–150	[9,11,12]

Table 2
Overview of the presented gasification concepts.

Concept	Characteristics	Benefits	Current state
UNIQUE gasifier	Integrates gasification, gas cleaning and conditioning in one reactor unit	Compact design with decreased requirements for footprint as well as reduced investment costs	Lab-scale testing of the concept successful.
Multi-stage gasification combining pyrolysis and gasification	Separate and combine pyrolysis and gasification in single controlled stages	High process efficiencies and high quality syngas with low tar concentration	Realization of concepts from 100 kW to 6 MW successful.
Combination of pyrolysis and gasification at different locations	Produce concentrated oil-char slurries by decentralized pyrolysis plants and gasification of the slurries and production of biofuels in a large centralized plant	Transportation of the biomass as well as biofuel production becomes more economical	Start of a 5 MW demonstration plant
Combination of gasification with a partial oxidation stage	Gasification is combined with a subsequent partial oxidation stage	Tar reduction by partial oxidation	Used in multi-stage gasification processes of small scale
Indirect biomass co-filing in coal fired boilers	biomass is gasified and the produced gas is co-fired in a boiler with coal	Easy and cost-effective way to reduce fossil CO_2 emissions	Used in large scale
Polygeneration – combined heat and power	Combined production of heat and power	High overall process efficiency	Used in scales up to a few MW
Polygeneration – combined SNG, heat and power	Combined production of SNG, heat and power	High overall process efficiency; high flexibility possible; transportation fuel	Tested in smaller scale; large scale application planned
Polygeneration – combined biofuels, heat and power	Combined production of biofuels, heat and power	High overall process efficiency; high flexibility possible; transportation fuel	Tested in smaller scale; large scale application planned
Polygeneration – combined hydrogen and heat	Combined production of hydrogen and heat	High overall process efficiency; renewable hydrogen production	First tests in smaller scale started
Plasma gasification	Gasification is performed in a plasma	Decomposition of any organic material into its elemental molecules	Mainly used for waste treatment
Supercritical water gasification	Gasification is performed in supercritical water	Wet and liquid biomass can be treated without pre-drying	Lab-scale testing and research

concept offers a compact design with decreased requirements for footprint as well as reduced investment costs.

- New advanced multi-stage gasification concepts separate and combine pyrolysis and gasification in single controlled stages. This enables to achieve high process efficiencies and a syngas with low tar concentration. On the other hand, the complexity of the process is increased by combining different reactors.
- A special approach performs pyrolysis and gasification at different locations. The concept aims to produce concentrated oil-char slurries by decentralized pyrolysis plants and gasification of the slurries and production of biofuels in a large centralized plant. In this way, transportation of the biomass as well as biofuel production becomes more economical.
- Other concepts combine gasification with a combustion stage. In this way unreacted char can be combusted to increase the overall process efficiency.
- By combination of gasification with a partial oxidation stage, tar can be converted.
- Indirect biomass co-firing in coal fired boilers by gasification of the biomass is an easy and cost-effective way to reduce fossil CO_2 emissions.
- Polygeneration strategies for the production of more than one product in a combined process can significantly improve process efficiency, economic viability and sustainability of the use of biomass. Combined heat and power production is a classic example for a polygeneration process, but also new approaches, such as combined SNG, heat and power production, or biofuels, heat and power production as well as hydrogen and heat production attract increasing interest.
- New gasification concepts, such as plasma and supercritical water gasification, provide interesting advantages for special kinds of biomass.

2. Advanced process integration and combination concepts

2.1. Compact UNIQUE reactor concept – integrated gasification, gas cleaning and conditioning

In existing gasification plants, abatement of particulate (char, fly ash) and tar (high molecular weight hydrocarbons) content of the raw syngas is normally done by filtration and scrubbing: in this way the clean fuel gas is made available at temperatures close to ambient, and the most immediate option for power generation is gas engine. Such process configuration does not allow high electric conversion efficiencies: reported values are close to 25% [16], that is what is also obtainable with modern combustion plants coupled with steam turbines. This penalizes notably the overall economic balance of the plant, which would benefit of a higher share of electricity against heat production, due also to the incentives for green electricity offered in most countries. In addition, tar separation is sometimes not as effective as it should be, reduces the gas yield, and generates waste streams difficult to dispose or recycle properly.

High temperature gas cleaning and catalytic conditioning is the focal point to promote more efficient industrial applications of biomass gasification for energy and chemicals: gas treatments should be strictly integrated with biomass conversion and carried out at a close temperature range, to preserve the thermal energy content of the biomass gas. This is even more true in the case of steam gasification and its coupling with a high temperature fuel cell or downstream catalytic processes, to avoid loss by condensation of the significant amount of water vapour contained in the gas stream, useful to reform CH_4, shift CO towards H_2 and prevent carbon deposition on the catalytic surfaces.

The application of such fundamental process integration concepts not only allows to realize more simple, efficient and cost effective gasification plants, but offers the opportunity to overcome some major obstacles still preventing a large market diffusion of such technologies, specifically at the small to medium scales (less than 10 MW_{th}) amenable to vast economic contexts of developed and developing countries. It needs to be stressed that the integration of a biomass steam gasifier with a high temperature fuel cell (more specifically, a solid oxide fuel cell) appears most suitable to realize very efficient bio-energy systems at relatively small scale. It is almost universally recognized that power generation by means of a fuel cell can compete in terms of efficiency with large IGCC installations; high temperature fuel cells are able to utilize the major fuel species obtained from the biomass gasification process (H_2, CO, CH_4). Although they are much more resistant to contaminants than low temperature fuel cells, provision should be made however to drastically reduce the fuel gas content of alkali and sour gas compounds.

Recent developments in innovative catalysts, sorbents and high temperature filtration media offer the opportunity to integrate in one reactor biomass gasification and gas cleaning and conditioning processes needed to obtain a clean fuel gas from biomass that would allow immediate and efficient conversion into power (high temperature fuel cells; micro gas turbines; combined, strictly integrated heat and power plant schemes) and further catalytic gas processing addressed to second generation bio-fuels (liquid fuels, hydrogen) and chemicals, allowing to implement diversified polygeneration strategies.

The *UNIQUE* gasification technology, developed by means of joint R&D efforts by several research organizations and private companies throughout Europe, did provide the opportunity to develop technical innovations addressed to existing and new industrial installations. Their effectiveness was tested at real industrial conditions, over a significant range of scales, from lab facilities to output slip streams of industrial gasifiers. Both authors of this paper are directly connected to the developments of the so called UNIQUE gasifier: although such a circumstance may well explain why it is described in some details within this survey about innovative biomass gasification concepts, it should be mentioned here that additional, complementary reviews stress in their conclusions the potential of hot gas cleaning for efficient tar reforming, especially since the particulate filter combined with a catalyst can be a key component of the gasifier itself [17].

2.1.1. The UNIQUE gasifier concept

This new concept for a compact integration of biomass gasification and hot syngas cleaning and conditioning systems was originally outlined in patents [18,19], deeply investigated in its different technical aspects by means of a collaborative R&D European project [20] and applied in further developments [21] and industrial testing campaigns.

Catalytic filter elements for particle and tar removal (see e.g. Refs. [22,23]) are directly integrated into the freeboard of a fluidized bed steam gasifier. Fig. 1 shows schematically the principle of this new gas cleaning concept. Remarkable system simplification is achieved by housing the whole gas conditioning system in the gasifier, reducing thermal losses, equipment and plant space, and allowing for a very compact unit: the activity of catalysts and sorbents is increased, while keeping high the thermal efficiency of the whole conversion process as no cooling step is included, and avoiding particle entrainment in the product gas at the reactor outlet. As a result, some major advantages of traditional primary and secondary hot gas treatments are combined together, without their well-known respective drawbacks (catalyst clogging by solid particles, loss of gas chemical and thermal energy, etc.).

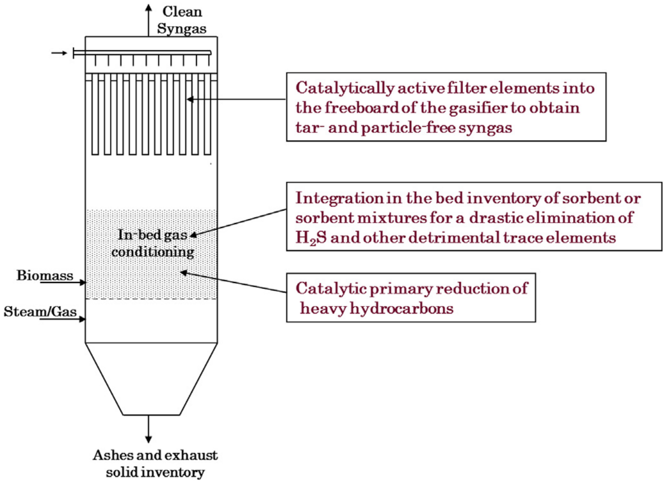

Fig. 1. The UNIQUE concept for integration of gasification with hot gas cleaning and conditioning in one reactor vessel [20].

As a result, this arrangement (integration of catalytic filtration and biomass gasification in one reactor vessel) allows for the conversion of tar, elimination of trace elements and an efficient abatement of the particulate, delivering high purity syngas, suitable to assure a high share of power generation even in small- to medium-scale (few MW_{th}) combined heat and power production and power plants, and to increase the overall economic revenue. The *UNIQUE* concept for hot gas cleaning and conditioning provides a concrete contribution to the target of reducing the cost of electricity obtained by means of advanced biomass energy systems.

2.1.2. In bed primary catalytic reduction of tar

As it is well known, the main problems to improve industrial viability of biomass gasification processes are related to the presence of tar in the product gas. Steam reforming of high molecular weight hydrocarbons is considered the most appropriate way for their elimination [24], however chemical kinetics of the gaseous phase homogeneous reactions are satisfactory at high temperatures, above 1200 °C, due to high activation energies, in most cases greater than 250–350 kJ/mol. With the use of catalysts, steam and dry reforming reactions become an effective way to remove tar components from the fuel gas at lower temperatures, compatible with those adopted in gasification processes.

One of the most important advantages of a fluidized bed gasifier is given by the possibility to utilize a low cost mineral bed material catalytically active for such reactions, in presence of steam as a gasification agent [25,26]. The catalyst to be utilized should be at the same time efficient in the reforming of hydrocarbons, has high selectivity for syngas, and high resistance for attrition and carbon formation. It should also satisfy the requirement of relatively low cost, because the formation of ash and char obliges to discharge used material and reintegrate the bed inventory continuously with a fresh/regenerated charge. A detailed analysis of the performance of primary tar removal catalysts applied at lab to industrial scale is beyond the scope of this work; a comprehensive review of the primary measures (including gasification conditions and gasifier design in addition to bed additives) for tar elimination in biomass gasification processes has been published by Devi and co-authors [27], and a more general and recent examination of different strategies for tar reduction in the biomass product gas via mechanical, catalytic and thermal methods [28] also provides quantitative and comparative figures about catalytic hot gas conditioning performed within the gasifier bed itself.

A large number of investigations deals with dolomite, $(Ca,Mg)CO_3$, or olivine, $(Mg,Fe)_2SiO_4$. Calcined dolomite, limestone or magnesite have been found able to increase the gas hydrogen content [29–33]. Olivine shows a slightly lower activity in biomass gasification and tar reforming, but higher attrition resistance than dolomite [34–36]. Adding calcined dolomite to the fluidized bed inventory of the gasifier allows to reduce the tar content in the dry product gas from two digit numbers down to 1–2 g/Nm^3, while with olivine the corresponding average value is 5–7 g/Nm^3.

Ni-based reforming catalysts show higher activity and selectivity for tar conversion to hydrogen-rich gas, increasing noticeably the gas yield at the expense of char and tar, but suffer from (i) mechanical fragility, (ii) rapid deactivation mostly due to sulphur, chlorine, alkali metals, coke, (iii) metal sintering, altogether resulting in limited lifetime [37]. Ni-based catalysts are also very effective to reduce the NH_3 content in the product gas. Very positive results with respect of all points just mentioned were obtained by impregnation of olivine with nickel [38]. The mechanism of the active phase formation in Ni-olivine under biomass gasification conditions is well understood [39] and the large scale preparation controlled. The positive features of natural olivine (mechanical resistance and activity in tar reforming) are combined with those of nickel catalysts (high activity in reforming of hydrocarbons), without the disadvantages encountered with commercial products. The Ni-olivine catalyst showed very good resistance to attrition and coke formation, with an order of magnitude reduction in the tar content of the product fuel gas, when utilized instead of a bed made entirely of olivine, in a pilot scale (100 kW thermal) dual fluidized bed gasifier as primary catalyst for tar destruction and methane reforming [26]. The major drawback to an extensive utilization of Ni-olivine in the fluidized bed of biomass gasifiers is represented by existing stringent constraints on nickel manipulation and discharge, Ni being a heavy metal. Its use would increase considerably the cost of disposal of contaminated biomass ash.

It is well known that olivine samples with similar general composition and phase structure may show different catalytic activity depending on the degree of integration of iron into their respective crystalline structure [40]. Calcination of iron-bearing olivines in air leads to the oxidation of iron and formation of iron free oxides, the presence of which affects the olivine activity. The amount of iron oxides formed is dependent on calcination time and temperature [40,41]. Recently, using an optimized impregnation method, the Fe content of olivine was enriched with an additional 10 wt% (corresponding to a total iron weight percentage of about 16 wt%), and catalytic biomass gasification experiments were performed at bench scale [42]. The abatement of tar content is shown qualitatively (by visual comparison of liquid samples collected in the tar condensers) and quantitatively in Fig. 2, as a function of the gasification temperature, in relation to fully similar tests with sand (catalytically neutral) and olivine. The Fe–olivine material has a double effect on tar destruction: on one hand, it acts as a catalyst for tar and hydrocarbon reforming; on the other hand, it is also active in relation to water gas shift reaction, at high temperature.

When 10 wt% Fe–olivine was utilized in a pilot gasifier instead of olivine, the gas yield increased on average by 40% and the hydrogen yield by 88%; correspondingly, the methane content in the syngas was reduced by 16% and tar production per kg of dry ash free (daf) biomass by 46% [43]. Complete characterization and micro-reactor reactivity data are also available for Fe–olivine materials containing up to 20 wt% of iron [44] and definitively confirm the interest of addition of iron on olivine.

2.1.3. In bed abatement of detrimental trace elements

Studies were performed on high temperature separation of H_2S, HCl and other detrimental trace elements, like alkalis, and heavy metals, by means of appropriate sorbents to be added to the fluidized bed inventory of the *UNIQUE* gasifier [45,46]. Thermodynamic process models assuming Gibbs free energy minimization were utilized to investigate the fate and removal of sour gases and alkali species in the biomass gasification process, as a function of different composition of inlet streams and gasifier temperature [47,48]. To confirm theoretical findings, experimental tests were performed on conventional and innovative synthetic solid sorbents suitable to be utilized at the operating conditions of the gasifier and able to assure very low concentration levels of these contaminants in the gas phase, comparable with threshold values recommended for solid oxide fuel cells and production of biofuels by chemical syntheses (see also the following Section 3 about polygeneration strategies).

Contaminants are typically removed in downstream equipment. Adding suitable sorbents to the fluidized bed inventory of the gasifier (see Fig. 1) allows for an additional beneficial effect: the improvement of catalyst activity for tar reforming in the filtering elements placed in the freeboard of the gasification reactor.

2.1.3.1. Sour gases. The experimental evidence indicates that Ni-catalysts are suitable to convert tarry fuel gases into a clean syngas even if hydrogen sulphide is present: with H_2S concentrations below 100 ppmv, as it is the case of most biomass gasification processes, the catalyst activity is slightly reduced, however the remaining activity is constant, even after substantial operation time, and complete conversion of naphthalene (a key tar

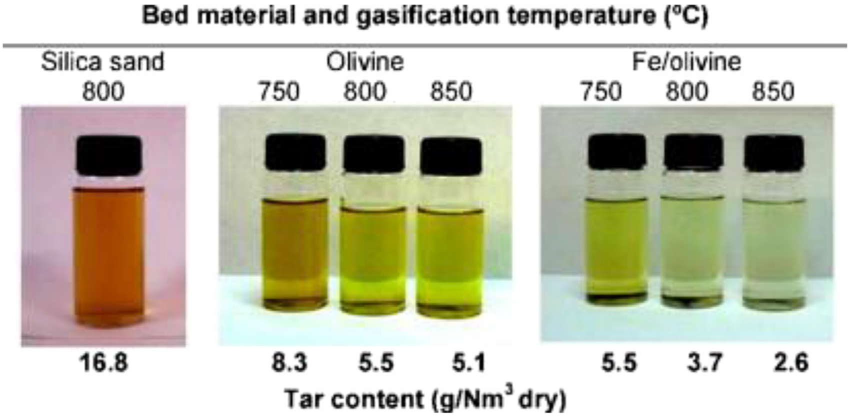

Fig. 2. Effect of bed material and gasification temperature on tar content. Reproduced from Virginie et al. [42].

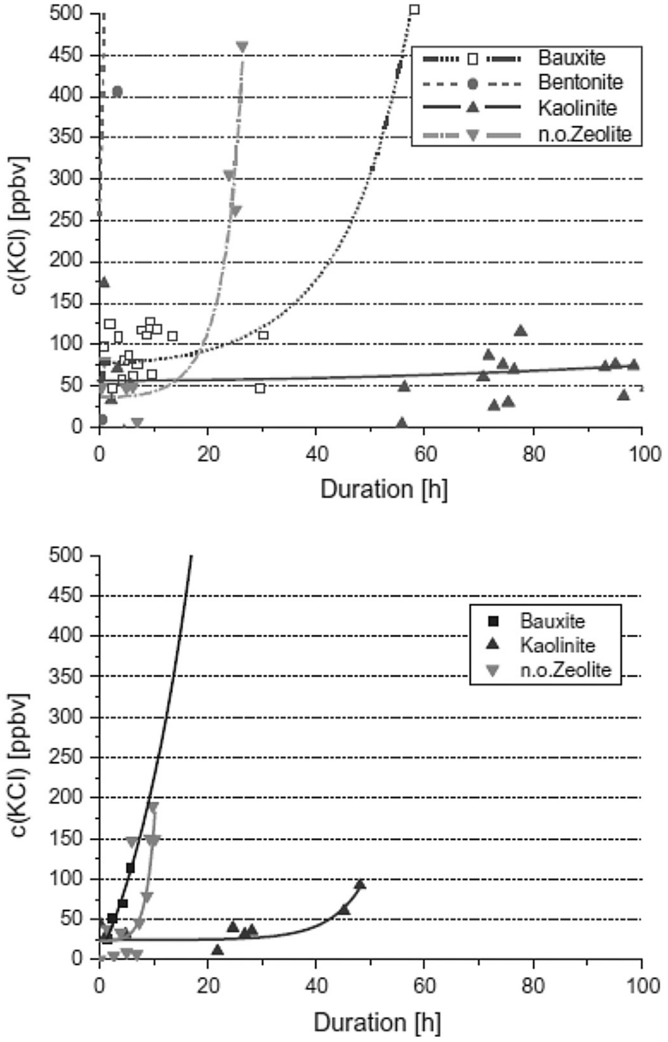

Fig. 3. KCl concentration in the gaseous stream leaving the sorbent sample: a) 800 °C; b) 900 °C [46].

component) has been demonstrated with model gases treated by a catalytic filter in these condition [49–51]. Of course, the presence of H_2S at such levels is expected to determine serious problems for downstream chemical syntheses and at the fuel cell anode, especially for fuel cell operation at temperatures below 1000 °C [14]: for most applications of the product gas the utilization of appropriate sorbents is therefore required, the development of which is described below in this chapter.

An additional issue is that of separation of the sorbents from the remaining constituents of the gasifier bed inventory, with the aim to perform regeneration and cyclic utilization of them: classification based on particle size appears as the most appropriate means.

Calcium based sorbents have been recognized for a long time as effective media to capture H_2S at high temperature; the sulphidation of both, calcined and uncalcined limestone, has been studied extensively [52,53]. However, thermodynamic limitations, especially in presence of a considerable content of steam in the gas phase, can hardly allow to reach H_2S concentrations as low as those required by SOFC. Alternative systems are all characterized by drawbacks of different nature, spanning from reduction of sorption capacity with temperature (iron oxide), metal vaporisation (zinc oxide), oxide reduction by H_2 and CO (copper oxide) [14]. Combinations of different metal oxides and high dispersion of the active phase on a support are the strategies commonly explored to overcome these problems.

Experimental work done at real conditions for the H_2S removal or with simulated coal gas has led to the conclusion that fuel gas composition does not have a large influence on the desulphurization performance, except for the minimum residual H_2S level. The thermodynamic equilibrium is worse when CO, CO_2, H_2O are present [54]. With CeO_2, it is indicated that the presence of H_2O has no negative impact [55], and this seems to be true also with CuO–Al_2O_3 sorbents [56].

Data of H_2S sorption experiments on packed beds of Ca- and Cu-based sorbents (Fig. 4) show that these are not suitable to reduce the H_2S concentration below 1 ppmv at 700–900 °C. The sorbent composition has an influence on the achievable H_2S reduction: slag lime, which contains several oxides beside calcium oxide, achieves the best H_2S reduction (down to 50 ppmv) of all Ca-based sorbents.

In order to meet the requirement of 1 ppmv H_2S, a new sorbent was synthesized according to thermodynamic predictions indicating that stabilized, Ba-based sorbents should be effective; the "CaBa" sorbent was prepared from a mixture of 10 mol-% $BaCO_3$ and 90 mol-% $CaCO_3$.

The CaBa sorbent allowed to achieve H_2S concentrations lower than 0.5 ppmv (the detection limit in these experiments) in the temperature range of 800–900 °C [46]. The stabilization effect was confirmed by the XRD spectra showing the occurrence of a BaS phase. At temperatures below 760 °C the H_2S concentration in the effluent stream raises up to 175 ppmv due to carbonation of the sorbent: the CaBa sorbent regeneration could therefore be possible by cooling the saturated sorbent under non-oxidizing atmosphere. The sorption data also showed that the CaBa sorbent is able to reduce the HCl gas content below 1 ppmv over the temperature range 800–900 °C [46]. The formation of $BaCl_2$ phases is confirmed by the XRD spectra.

Fluidized bed gasification tests at pilot scale (100 kW_{th}) done at Vienna University of Technology with the CaBa sorbent, confirmed the tendency toward lowered H_2S content in the product gas. However, such tests show only qualitative trends; the operating conditions, like sorbent particle size and amount charged into the gasifier, still need to be optimized.

2.1.3.2. Alkali species

2.1.3.2. Alkali species. Alkalis and heavy metals cause fouling and corrosion by condensing. As a result of the potassium and chlorine content of biomass, KCl is the most important compound released during biomass gasification. Aluminosilicates have shown the

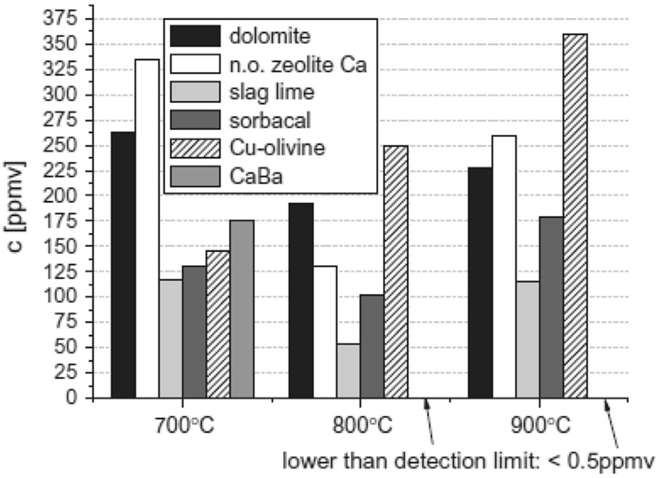

Fig. 4. H_2S concentration in the gaseous stream leaving the sorbent sample [46].

ability to reduce the alkali concentration to the ppb-level under gasification conditions [57]. In addition, aluminosilicates rich in alumina remove chlorine [57] and heavy metals like zinc [58]. Alkalis contaminated gases have high condensation temperatures, so that the attention is often focused on the analysis of the sorbent capacity more than on the gas purity at the outlet of the sorption treatment, the latter being rarely determined in a direct way and more often back-calculated from the sorbent conversion.

The thermodynamic calculations of KCl sorption on aluminosilicates show that the alkalis concentration in the gasifier derived gases can be limited to values of 100 ppbv to 4 ppmv depending on the biomass type. Although KCl is the most abundant of all alkali species in the syngas, NaCl is the alkali species with the highest concentration in the cleaned gas. Thus, the condensation temperature decrease depends on the residual NaCl concentration in the cleaned gas. This ranges from 530 to 630 °C, resulting in a drastically reduced risk of fouling and corrosion downstream the gasifier, specifically when a SOFC is operated (at temperatures of about 800 °C).

The sorption experiments reported in Ref. [46] were performed at packed bed conditions and atmospheric pressure. The inlet gas stream was laden with KCl by overflowing a KCl source set at 700 °C; the KCl gas concentration was about 20 ppmv, determined by the change in weight of the KCl source at the end of each experiment. At a space velocity of 9800 h^{-1} no evidence of kinetic limitation was observed. The results of the KCl sorption tests confirm that aluminosilicates are suitable sorbents for KCl removal below 100 ppbv at 800–900 °C (Fig. 3).

Fluidized bed gasification tests at atmospheric pressure in presence of bauxite for the removal of the most abundant alkali halides, i.e. KCl (and NaCl), confirmed the suitability of aluminosilicate sorbents for the removal of alkali halides released during gasification processes [59]. These materials (bauxite, bentonite, kaolinite and naturally occurring zeolites) are easily available, cheap and without environmental implications for their disposal when exhausted.

2.1.4. *Tar and dust abatement by catalytic filter candles in the gasifier freeboard*

Laboratory tests at real process conditions (a 400 mm high filter candle segment integrated in the freeboard of a 100 mm ID gasifier electrically heated) and proofs of concept at the Güssing dual fluidized bed gasification plant, run by Biomasse Kraftwerk Güssing GmbH & Co. KG (a prototype candle inserted in the gasifier freeboard and processing a slip stream of raw syngas) confirmed that nickel-based catalytic filters of different design can be used successfully in integrated high temperature reforming of tar and removal of particles from biomass gasification product. Fig. 5 shows the arrangement of the bench scale facility used for the lab tests [60], while Fig. 6 shows a sketch and the P&I flowsheet of the test module realized in Güssing [61]; in the latter case, the filter candle is cleaned periodically from the dust cake by means of a rather conventional back pulsing system for rigid hot gas filter elements. Nitrogen is used as the blowback gas for regeneration, properly preheated to overcome possible condensation problems.

Both types of test showed that the particulate content of the cleaned gas is practically brought to zero, making it compatible with the most sophisticated applications (fuel cells): in the Güssing test the reference values were 56.3 and 23.6 g/Nm^3, respectively for the dust and char content of the raw gas in the gasifier freeboard. Tar content reduction is as high as 95%; at bench scale a greater methane conversion was obtained (with a maximum value of 40%; at plant scale methane content decreased only from 10.1 to 8.1%). The reference values are in both cases those obtained with olivine fluidized bed and without filter candle. The dry gas yield improvement obtained with the catalytic filter candle and quantified in the bench scale tests is in the range 70–100%, and the total carbon in the permanent gaseous phase per kg of biomass is increased on average by 30% as a result of tar conversion in smaller molecules. This substantial increase in the gas yield is partially counterbalanced by a reduction in the LHV of the fuel gas by 13–16%.

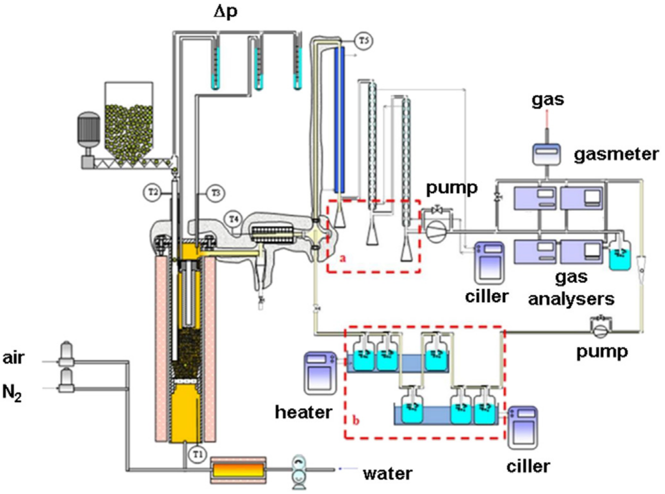

Fig. 5. Scheme of the continuous fluidized bed biomass gasification plant: (a) Tar in the condensate samples determined by total organic carbon (TOC) analysis; (b) Tar fraction sampled in 2-propanol, according to the Technical Specification CEN/TS 15439 analysed by GCMS or HPLC/UV. Adapted from Rapagnà et al. [60].

Fig. 7 shows the characterization of tar samples obtained from bench gasification runs with catalytic candles, compared to the reference test without candle [62]. The experimental rig is always that schematized in Fig. 5; all tests were performed with a fluidized bed of olivine particles; in the catalytic tests, the product gas is made to percolate through an Al_2O_3 based catalytic filter candle positioned in the gasifier freeboard. Test I is characterized by a gasification time of 6 h, while the overall duration of Test II is 20 h (three consecutive periods called a, b and c, with intermediate char burning steps). The catalytic filter candle used in Test II contained additional catalyst integrated in the hollow cylindrical space within the porous candle structure. Tar samples were collected in 2-propanol according to the UNI CEN/TS 15439 protocol and analysed by HPLC/UV. Quantitative determination was carried out by using calibration curves of pure standard tar compounds: phenol (Ph-OH), toluene (Tol), styrene (Styr), indene (Ind), naphthalene (Nap), biphenyl (Bph), diphenyl ether (DphE), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla) and pyrene (Pyr) [55]. Among different tar species, toluene appears as the prevailing compound after the catalytic reforming treatment.

In the reference test (without candle) less than 60% of the hydrogen content of the biomass was found in the product gas as H_2, while in each test with the catalytic candle this value greatly exceeded 100% as a result of enhanced hydrocarbon reforming reactions with steam. To quantify the reforming activity of the catalytic candle, the values of steam conversion detected experimentally were compared with corresponding thermodynamic equilibrium values calculated at the test respective conditions for biomass steam gasification: in the latter case, char and hydrocarbons are completely converted and concentrations of carbon monoxide and dioxide, hydrogen and steam in the fuel gas are fixed as a result of equilibrium attained for the water–gas shift (WGS):

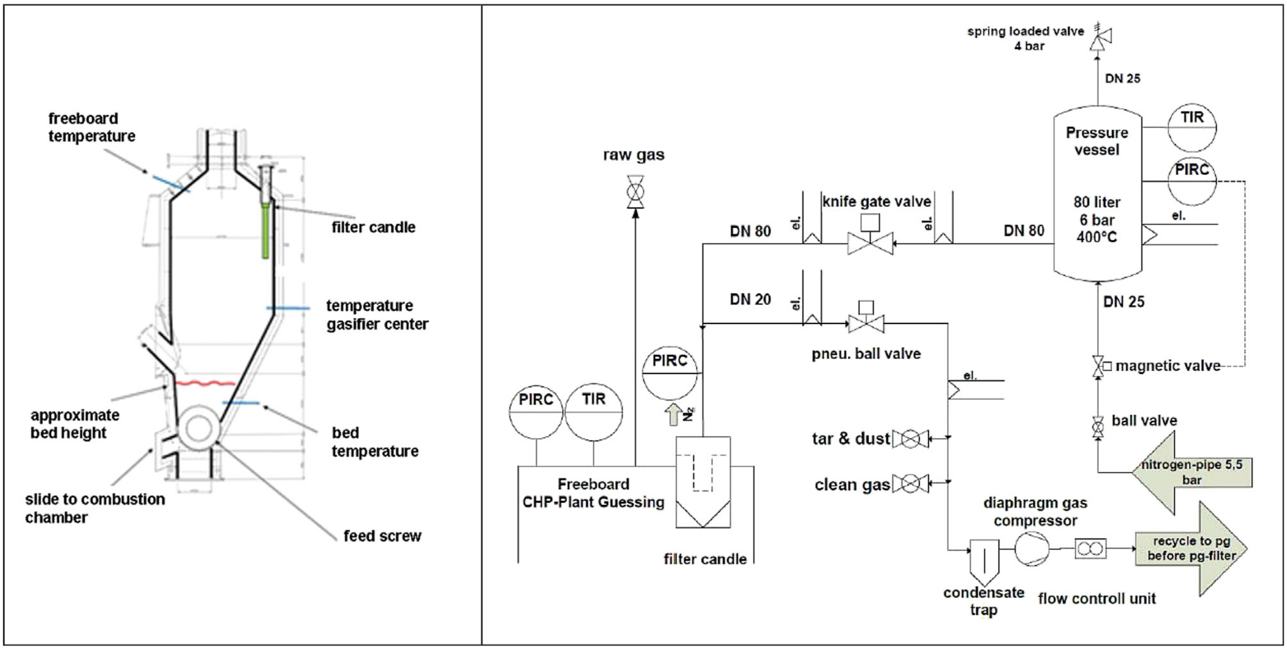

Fig. 6. Sketch and P&I flow-sheet of the test module realized in Güssing for gas filtration inside the gasifier freeboard [61].

$$C_{21}H_{30}O_{14} + 7H_2O \rightarrow 21CO + 22H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

where the empirical formula chosen for biomass ($C_{21}H_{30}O_{14}$) agrees with the composition of almond shells utilized in the experimental tests.

As shown in Fig. 8, the water conversion obtained experimentally is quite close to equilibrium values in almost all tests with a catalytic candle. This is a noteworthy result, as low water conversion is often considered as a drawback for steam gasification [63].

In the catalytic candle, methane and tar steam reforming takes place together with WGS: from the experimental results and thermodynamic calculations it is estimated a corresponding thermal energy demand of the order 0.5 MJ/kg of biomass. The enhancement of the reforming reactions inside the gasifier vessel allows to optimize the supply of this thermal load, provided by gasification itself, with respect to alternative process layouts with downstream equipment for gas conditioning treatments, where energy from additional sources is often required [64].

Pressure drop measurements through the catalytic filter candle fitted in the reactor freeboard were performed on the empty system (without the particulate bed in it) at different temperature levels, and as a function of the filtration velocity (Fig. 9A). The data reported here are generally higher than those exhibited by a non-catalytic filter of the same structural characteristics, the reduction of porosity brought about by impregnation and the presence of more rough surfaces being the main reasons for this effect [63]. The figure shows an increase of pressure drop with temperature at the same filtration velocity, mainly ascribable to the increase of gas viscosity. On the other hand, data in Fig. 9B were obtained during different gasification runs (about 800 °C) and show the increase of pressure drop with time due to the build-up of a dust cake on the filtration surface. Two different filtration velocities are considered: the pressure drop measured at the beginning of each test (clean filter candle) is quite compatible with that reported previously in

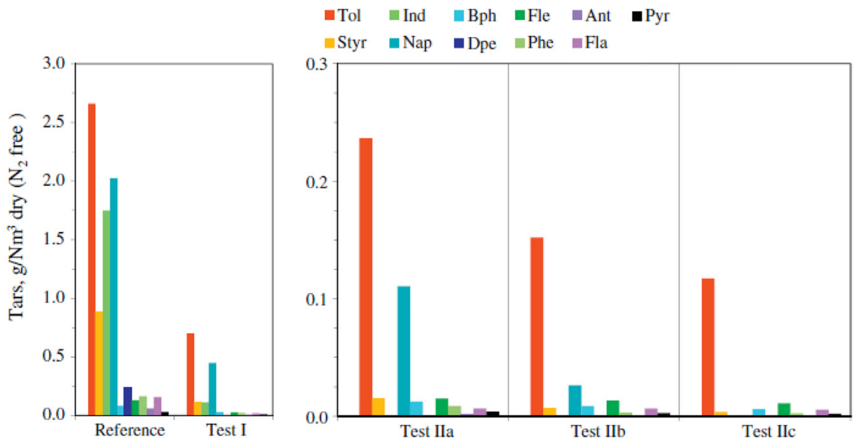

Fig. 7. Characterization of tar samples from gasification tests. Reference: test without filter candle; Test I: with catalytic filter candle and S/B = 0.84; Test II: with catalytic filter candle and S/B = 1.1. Reproduced from Rapagnà et al. [62].

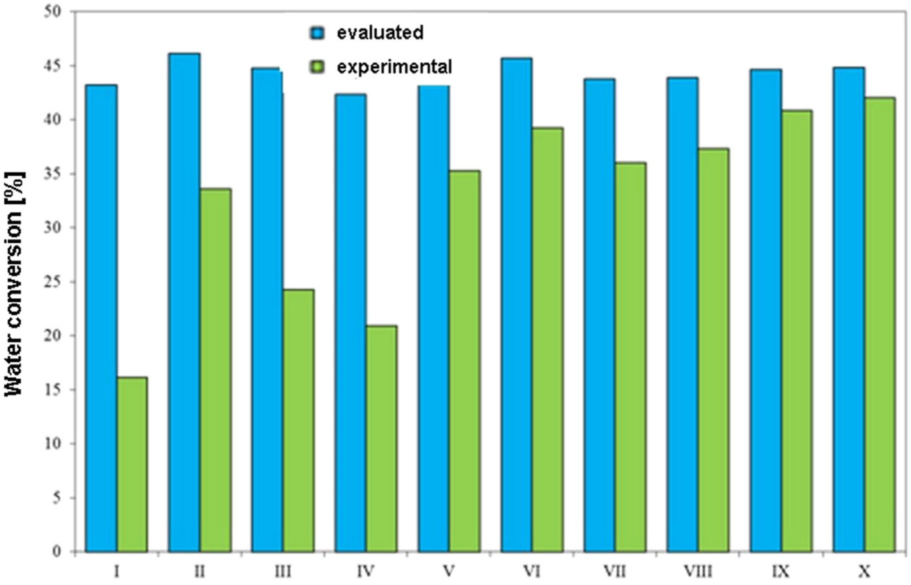

Fig. 8. Experimental and theoretical water conversion values. Test I: without filter candle; Tests II–X: with a catalytic candle in the reactor freeboard [63].

Fig. 9A at the corresponding filtration velocity (and temperature). After substantial gasification time, the data points seem to reach a plateau suggesting that the thickness of the powder cake tends to a stable value; in industrial applications, pressure drop across the filter candle is controlled by a periodic blowback of clean gas, as was shown in Fig. 6. As a whole, the operation of the filter candle in the gasifier freeboard appears to be a promising option for hot gas cleaning toward tar and particulate. However, the overall technical feasibility is not yet proven as the long term behaviour at industrial conditions is still an outstanding issue: innovative ceramic porous structures resistant to the gasifier freeboard environment and temperature peaks were recently developed by Pall Filtersystems GmbH and fully assessed at laboratory scale [65] and tests are in progress at the Güssing plant to verify the long term reliability required by commercial applications.

2.2. Combination of pyrolysis and gasification

Gasification as a thermochemical process to convert carbonaceous material into gas by using a gasifiying agent comprises several overlapping process steps, such as heating and drying, pyrolysis, oxidation and gasification. The overlapping of these process steps makes it impossible to control and optimize the different steps separately in a one-stage gasifier. Moreover, interaction between volatiles and char can have negative impact on the reactivity and gasification of the char [66]. Thus, char gasification should be performed in the absence of the volatiles in order to increase the gasification efficiency. Modern, advanced gasification concepts separate the pyrolysis and the gasification steps in single controlled stages which are combined in a multi-stage gasification process. High gas purity with low levels of tar and high process efficiencies with high char conversion rates are possible.

There are two different approaches which have been followed. The first one combines pyrolysis and gasification directly in a two or three stage gasification process. The different stages can be combined in one unit with separated pyrolysis and gasification zones or in separate reactor units combined in a series. The second approach performs pyrolysis and gasification at different locations. In this concept pyrolysis aims to concentrate biomass at decentralized small pyrolysis plants for an economical transport of the biomass pyrolysis products (liquid and solid) to a centralized large gasification plant in order to produce biofuels.

2.2.1. First approach – multi-stage gasification

Multi-stage gasification processes perform pyrolysis and gasification controlled in separated zones in the gasifier or in single

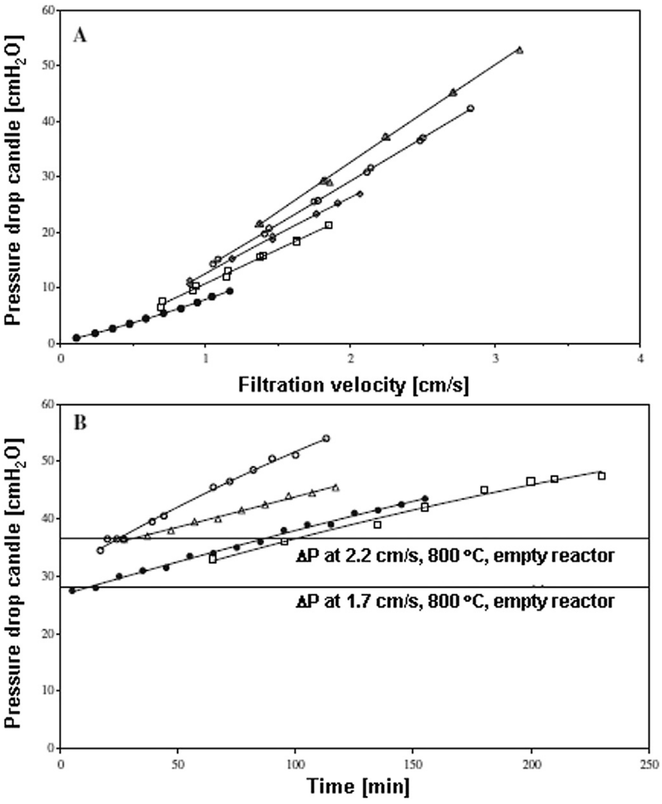

Fig. 9. (A) Pressure drop across the catalytic filter candle with the reactor empty of particles; temperature levels:(●) 20 °C, (□) 300 °C, (▩) 450 °C, (○) 600 °C, (△) 800 °C. (B) Pressure drop across the catalytic filter candle, as a function of time on test; filtration velocity: (○) 2.3 cm/s, (Δ) 2.2 cm/s, (●) 1.8 cm/s, (□) 1.7 cm/s. Reproduced from Rapagnà et al. [63].

combined reactors. This enables conversion of the biomass under optimized operating conditions for the single steps. Main reason for the development and use of a multi-stage gasification process is that a clean syngas with low tar content can be achieved. Furthermore, the overall process efficiency and the product quality and quantity can be enhanced compared to a one-stage gasification.

Several gasification processes according to the multi-stage gasification concept separating pyrolysis and gasification zones have been developed recently. Some examples are the 75 kW_{th} Viking gasifier developed at the Danish Technical University [67], the FLETGAS process developed at the University of Sevilla in Spain [6] and the LT-CFB (low temperature circulating fluid bed) gasification process developed by Dong Energy company from Denmark [68].

The Viking gasifier (see Fig. 10) is a two-stage process with a screw pyrolysis reactor followed by a fixed bed downdraft gasification reactor. The outlet of the pyrolysis reactor is directly combined to the gasification reactor. Between the pyrolysis and the gasification zone air is added to partially oxidize the pyrolysis products. By the partial oxidation and by passing the char bed, the tar content in the syngas is reduced to less than 15mg/m_N^3. The produced gas contains about 32% H_2, 16% CO, 20% CO_2, 30% N_2, and a small amount of CH_4 of about 2%. The higher heating value of the gas is about 6.6mg/m_N^3 [67]. A cold gas efficiency of 93% has been reported for the process [69]. The Viking gasifier has recently been upscaled to a 200 kW_e gasifier and work is in progress for a 500 kW_e gasifier [3].

The FLETGAS process (see Fig. 11) is a special designed three-stage gasification process. In the first stage, devolatilization in a fluidized bed reactor takes place with low conversion of tar and char at temperatures between 700 and 750 °C. Air and steam can be added in this stage at reduced amount to keep the temperature low to have just the devolatilization. High amount of reactive tar is produced. In the second stage, the tar is reformed with steam at high temperature of 1200 °C. In the third stage, the char generated in the first stage is gasified in a moving bed downdraft reactor. The gas coming from the second stage flows through the char bed which serves as a catalyst for further tar reduction. The char produced in the first stage is directly transported from the first stage to the third stage via a gas seal solid transport part [70,71]. Some modelling work [6] has been performed showing the advantages of the process compared to one-stage fluidized bed gasification. A significant decrease of the tar concentration to 10mg/m_N^3, char conversion of 98% and gasification efficiency of 81% compared to tar concentration of 31g/m_N^3, char conversion of 59% and gasification efficiency of 67% for the one-stage fluidized bed gasification has been shown which is an interesting result of this new concept. The composition of the gas was calculated on a dry basis with: 55 %N_2, 13% CO, 15% CO_2, 4% CH_4, 8% H_2, and 2% C_2H_6. The higher heating value was calculated with 6.4MJ/m_N^3. Some experimental work [72–74] has also been performed to develop the process. The process is still under development at pilot scale [6]. Besides the proof of the concept by operation of a pilot unit a techno-economical assessment would also be needed to prove the economical benefit of this concept. A drawback seems to be the high complexity of the reactor set-up.

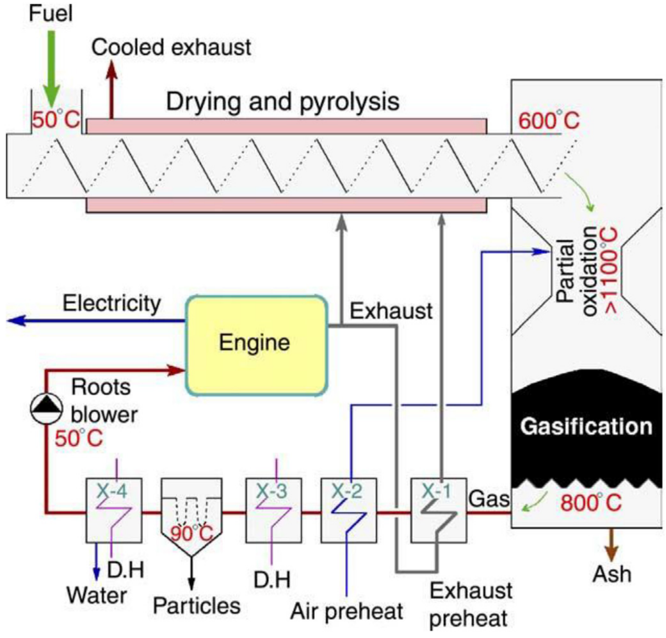

Fig. 10. Scheme of the Viking gasifier [67].

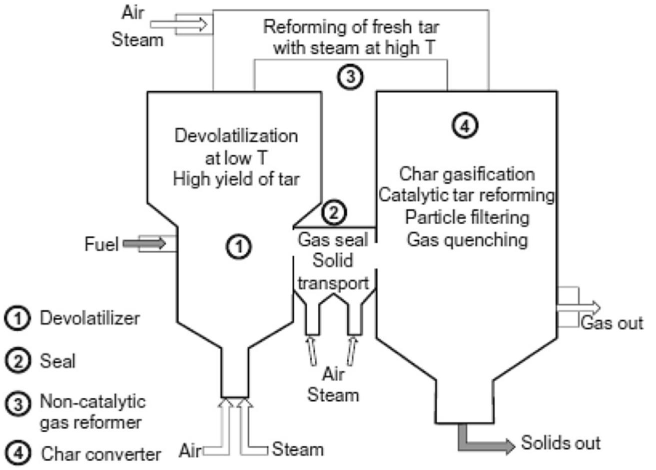

Fig. 11. Principle scheme of the three-stage FLETGAS gasification process [73].

Fig. 12 shows the schematic principle of the LT-CFB gasifier. The gasifier has two stages. The first stage is a circulating fluidized bed pyrolysis reactor operated at about 650 °C. The second stage is a bubbling fluidized bed reactor operated at about 730 °C for the gasification of char. Gasification of char is possible at this low temperature since the residence time in the gasifier is high. The gasifier is autothermally operated by using air as an oxidizing medium. Sand and ash are recirculated from the bottom of the gasifier to the pyrolysis reactor carrying the heat for the pyrolysis of the biomass. Additionally, the char gas is redirected to the pyrolysis reactor. In between the two reactors, a cyclone is installed to separate char and sand from the gas. Char and sand enter the gasifier and pyrolysis and char gas are cleaned in a second cyclone from the ash [68]. After testing the process in a 100 kW_{th} [75] and a 500 kW_{th} unit [3], a 6 MW_{th} demonstration plant has been built and is in operation since 2012 in a power plant owned by Dong Energy where the produced gas is co-fired with coal [68]. The LT-CFB gasification process has been developed for the use of more difficult biomass feedstocks, such as straw, manure fibres, sewage sludge and different organic wastes [3]. Cold gas efficiencies of 87–93% have been achieved in tests with the 500 kW_{th} unit [3]. A gas composition of 3.5% H_2, 16.3% CO, 14.5% CO_2, 59% N_2, 4.3% CH_4 and higher heating values between 5.2 and 7MJ/m_N^3 have been achieved [76]. It is reported that the two-stage process is robust, the

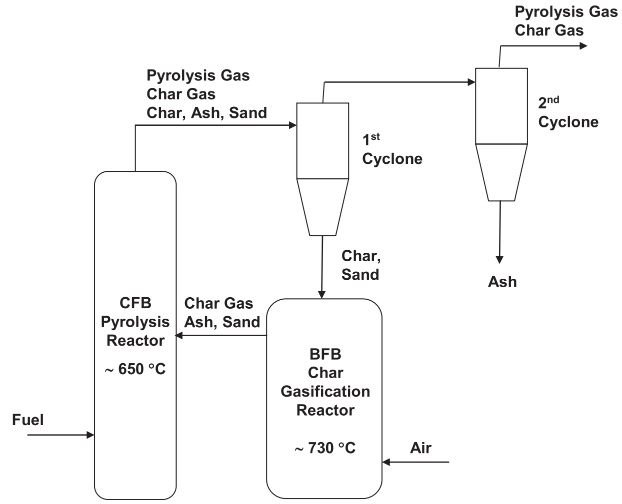

Fig. 12. Simplified principal scheme of the LT-CFB gasifier.

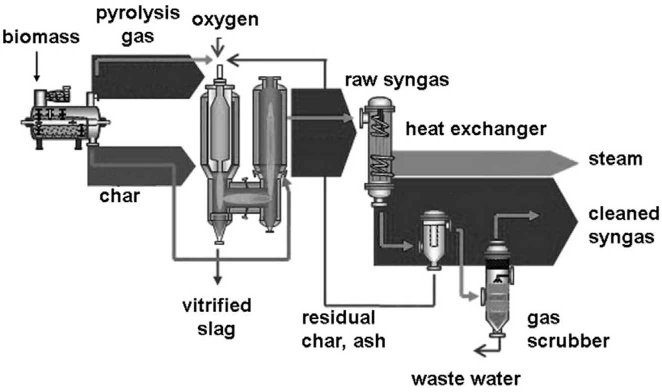

Fig. 13. The Carbo-V gasification process [79].

construction is cheap and requires low maintenance. Alkalines are maintained in the ash due to the low process temperature [77]. However, the produced gas has a high tar content ($>4.8 g/m_N^3$) [76]. Thus, use of the gas in engines, fuel cells or for biofuel production is not possible without further gas cleaning.

Besides the recent new developments, there has been so far one multi-stage gasification process separating pyrolysis and gasification in different reactors which has been built and operated in large scale – the three-stage Carbo-V process developed by the Choren company in Germany [78–80]. Fig. 13 shows the Carbo-V process schematically. The first process stage is a pyrolysis reactor, called low temperature gasifier. The second process stage is a combustion chamber where the pyrolysis gas and recycled char from the deduster is oxidized with pure oxygen. The third process stage is a gasification reactor. The char produced in the pyrolysis reactor is gasified in this stage by using the combustion gas from stage 2 as a reacting agent. Since the reactions in the third stage are strongly endothermic, this stage is also called chemical quenching [79]. The process has been demonstrated in a 1 MW_{th} plant in long-term operation for the production of biofuels. A cold gas efficiency of 82% and an almost tar free gas has been reported for the process [80]. The gas composition was 34.6% H_2, 36.8% CO, 22.6% CO_2, 1.7% N_2, 0.4 CH_4, and 3.9% H_2O [81]. An upscale of the process to a 45 MW_{th} plant was commissioned and a test program was started but not completed due to insolvency of Choren in 2011 [82]. Main reasons for the stop of the 45 MW plant have been seen in problems related to the scale-up of the new technology. This extended the commissioning of the plant far beyond the planned schedule and increased the costs so that the investors decided to stop their funding [83,84]. The technology has been acquired by the German company Linde in 2012 [85]. Linde reported about 1 year after the acquisition of the Carbo-V technology that they have refined the process to a level that demonstration with a partner can commence [86]. Forest BtL Oy from Finland has recently bought a licence from Linde for using the Carbo-V process in a new BtL (Biomass to Liquid) plant with a gasification capacity of 480 MW. Forest BtL Oy selected the Carbo-V technology since this multi-stage gasification process offers a high fuel conversion to syngas and a high syngas quality [87].

An overview of the described multi-stage gasification processes is given in Table 3. It can be concluded that very low tar concentrations in the producer gas are achieved by the different multi-stage gasification processes. Also higher char conversion and gasification efficiencies are achieved compared to one-stage gasification processes (see Table 1). The complexity of the gasification process is increased by combining different reactors. However, this can be compensated by a simpler subsequent gas cleaning process.

2.2.2. *Second approach – use of pyrolysis and gasification at different locations*

A special concept to use pyrolysis and gasification at different locations has been developed under the name bioliq process by the Karlsruhe Institute of Technology (KIT) [88–90]. In the bioliq concept (see Fig. 14), biomass is concentrated into an oil-char slurry in multiple decentralized small pyrolysis plants. The concentrated oil-char slurry is then transported to a large central process plant

Table 3
Overview of multi-stage gasification processes.

Number of stages	Process stages	Cold gas efficiency/%	Tar content in the producer gas/mg/m_N^3	Gas composition	Higher heating value/MJ/m_N^3
2	• Screw conveyor pyrolysis reactor • Downdraft fixed bed gasifier • Partial oxidation by air addition between the 2 stages	93	<15	32% H_2 16% CO 2% CH_4	6.6
3	• Fluidized bed pyrolysis reactor • Steam reformer • Moving bed downdraft gasifier	81	10	8% H_2 13% CO 4% CH_4	6.4
2	• CFB pyrolysis reactor • BFB gasifier	87–93	>4800	3.5% H_2 16.3% CO 4.3% CH_4	5.2–7
3	• Pyrolysis reactor • Partial combustion chamber • Entrained flow gasifier	82	Tar free	34.6% H_2 36.8% CO 0.4% CH_4	High

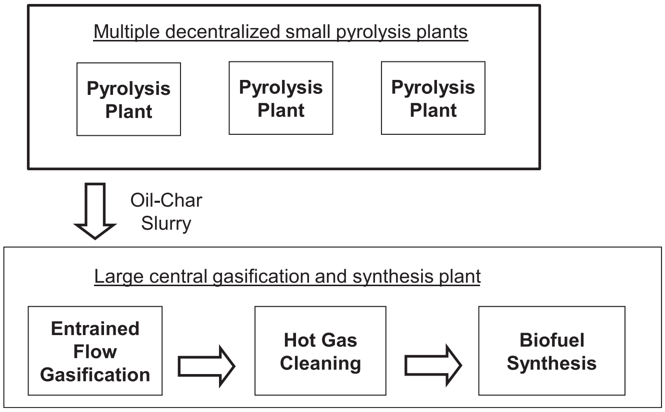

Fig. 14. Schematic principle of the bioliq concept.

for gasification of the slurry and synthesis of biofuels. The concept is based on the use of low-grade lignocellulosic biomass, such as straw or forest residues. The energy density of the oil-char slurry is increased by about ten times compared to the initial energy density of straw. Thus, transportation of the oil-char slurry is much more economical than that of the untreated biomass [91].

A demonstration plant of the bioliq process has recently been built at KIT in Germany [92]. The process comprises the following 4 process steps: 1) Fast pyrolysis to produce the oil-char slurry in a separate decentralized pre-step, 2) Gasification of the slurry to produce syngas, 3) Hot syngas cleaning and conditioning, 4) Synthesis of the biofuel.

Fast pyrolysis has been chosen since short reaction times give higher yields of pyrolysis oil [93]. The slurry is gasified in a 5 MW_{th} Lurgi entrained flow gasifier at an operating pressure of 8 MPa [92]. Even if entrained flow gasifiers are widely used for gasification of water based coal slurries or refinery residues, the gasification of such pyrolysis oil-char slurry is new and part of several experimental investigations related to the atomization of the oil-char slurry as well as to the modelling of the gasification of the slurry [94].

The syngas is cleaned in a completely dry hot gas cleaning process [95]. First the syngas is filtered at 800 °C in a special designed ceramic hot gas filter, where the filter elements are horizontally installed [96]. In a typical hot gas filter design, filter candles closed at one end are installed vertically hanging in a tubesheet [97]. An advantage of the design with horizontally installed filter elements is a more compact design of the filter with a smaller footprint and size of the filter vessel. A problem can be the regeneration of the filter elements which requires a very efficient backpulse system to remove the dust cake also from the top side of the horizontally installed filter elements. Downstream of the filter, chloride and sulphur gas components, such as HCl and H_2S, are removed by sorbents and tars are catalytically reformed in a following step.

Open issues which need to be addressed by further research are how storage (storage conditions and duration) influences the properties and composition of the bio-oil and accordingly the atomization and the gasification behaviour of the oil slurry. Due to the composition, bio-oil generally tends to change during its storage. Bio oil from pyrolysis of biomass is a mixture of different components, such as furfural, phenols, aldehydes, ketones, esters, ethers etc. [98], having a quite high content of oxygen and water. Depending on the biomass feedstock, oxygen content is usually in the range of 35–40% and the water content is between 15 and 30% [99].

Furthermore, the properties of different oil-char slurries coming from different locations and different biomass feedstocks have to be tested and stable atomization and gasification have to be proven for these different slurries.

An economical assessment of the bioliq concept has shown that the production of gasoline and olefins from biomass by this process is not competitive compared to current market prices. Only subsidies, e.g. from tax reduction and CO_2 certificates, could currently enhance the competitiveness of the biofuels [91].

2.3. *Combination of gasification and combustion*

Concepts which combine gasification with a combustion stage aim on one hand at increasing the overall process efficiency by combining combustion of unreacted char for additional heat production or on the other hand for the conversion of tar by partial combustion to achieve a product gas with a lower tar concentration.

A third concept is to implement the gasification process for co-firing of the product gas in a coal combusted power plant. This option reduced the requirements with regard to the gas purity significantly and needs no additional gas cleaning and conditioning equipment downstream of the gasifier. Thus, the process set-up can be kept very simple and cost-effective.

2.3.1. *Dual fluidized bed process with internal combustion*

Biomass gasification is globally an endothermic process, so that it requires providing thermal energy to the reactor. This can be done in different ways that in most practical applications involve burning part of the gasification products, including sometimes auxiliary fuels made available by downstream purification treatments. In this context, air is the most common gasification agent utilized in gasification plants: the excess of thermal energy available in industrial installations allows to heat up the air stream to the gasifier above ambient temperature and to close the energy balance satisfactorily. The ratio between biomass and air fed to the gasifier, commonly related to what would be needed by a stoichiometric biomass combustion process, is expressed as a fraction of it and called *equivalence ratio*. In the case of fluidized bed gasifiers, the air flow rate should also comply with an adequate fluidization regime.

A major drawback of this simple and cost effective arrangement is contamination with nitrogen of the product gas, with N_2 molar fraction values of 50% and more, resulting in a substantial reduction of the gaseous fuel heating value (LHV) down to 4–5 MJ/Nm^3, still acceptable for generating power with internal combustion engines, although unsuitable for more sophisticated and efficient energy applications (fuel cells) and chemical syntheses. To avoid this problem, air could be replaced by oxygen (enriched air) and steam mixtures, with the additional benefit to enhance tar reforming reactions and char gasification. However, this choice implies oxygen (enriched air) availability. With small to medium size biomass gasification units (operating at ambient pressure) and readily available gas separation systems, air enrichment would be mainly accomplished by selective nitrogen–oxygen sorption systems requiring feed gas compression, that is compression of a volumetric gaseous stream up to 5 times larger than the oxidant used in the gasification process, with a substantial penalty of the whole energy efficiency.

With fluidized bed gasification systems, a more efficient arrangement is obtained by physically separating gasification and combustion reactions and utilizing the mineral particle bed (sand, olivine) to transfer heat between them. Fig. 15 illustrates thermal and mass fluxes within the system [100], while Fig. 16 shows schematically the application of this principle to biomass gasification [101]. This is realized by means of dual fluidized bed (DFB) systems. Relevant DFB biomass gasifiers and their major features

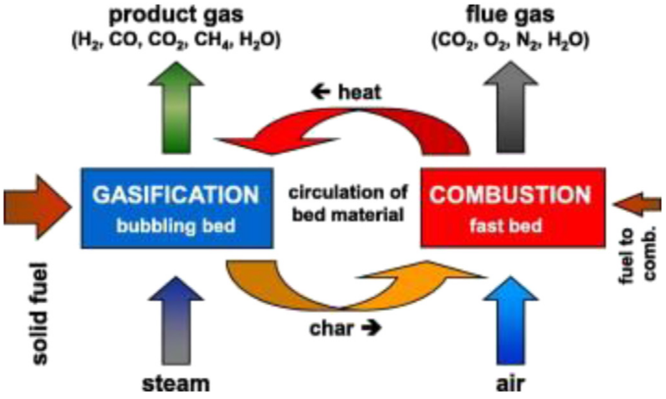

Fig. 15. Heat and mass fluxes in a dual fluidized bed (DFB) gasification system [100].

have recently been reviewed by Kaushal et al. [102] and Goransson et al. [17].

The well-known CHP plant in Güssing is the prototype industrial application of dual fluidized bed biomass gasification: the gasifier is a bubbling bed fluidized by steam, where the biomass feedstock is devolatilized, and organic vapours and char are properly steam reformed to obtain permanent gases (CO, CO_2, H_2, CH_4); the granular bed material is continuously circulated by means of a chute (and a loop seal) to a fast circulating bed fluidized by air, where any non-gasified fuel particles transported along with the bed material are fully burnt, together with additional fuel properly injected, determining an increase in temperature of the particulate solid of 50–100 °C above that in the gasifier; solid and gaseous phases are then separated at the top of the riser/combustor in a cyclone-type device, and hot particles are brought back to the gasification chamber by means of a second loop seal that avoids gas mixing between gasifier and combustor, to provide the heat required by the gasification reactions. By adjusting properly the solid circulation rate, steady state behaviour is obtained at the desired gasification temperature. As a result, air and steam can be used as gasification agents while keeping a very low nitrogen concentration in the fuel gas, permitting LHVs of about 12–14 MJ/Nm^3 and the utilization of steam as an additional gasification agent that improves gas quality (lower tar content). In comparison to more traditional installations, the complexity of plant layout and operation is increased, however the syngas quality is also increased remarkably, opening the way to more diversified utilization options and to polygeneration strategies.

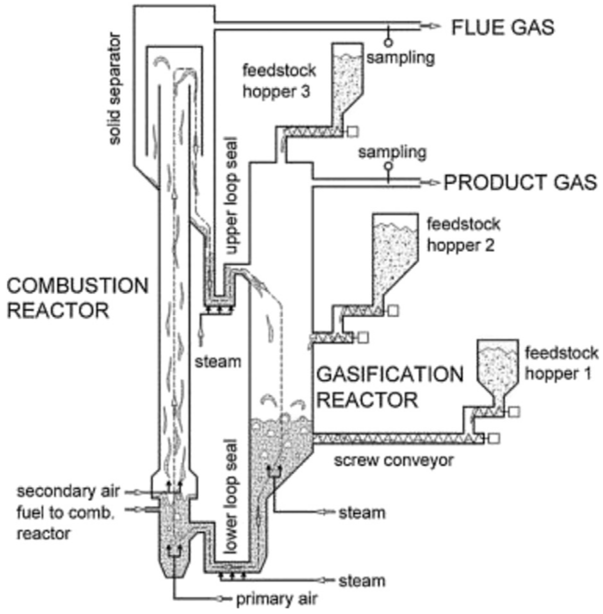

Fig. 16. Scheme of the DFB reactor system [101].

The capacity of the Güssing plant is about 8 MW (electrical output of 2 MW$_e$ and district heating output of approximately 4.5 MW$_{th}$). This dual fluidized bed reactor was developed at the Institute of Chemical Engineering of Vienna University of Technology (TUV) in cooperation with AE Energietechnik, and known internationally under the name FICFB (fast internally circulating fluidized bed) gasification system [103–105]. The construction of the Güssing plant was started in September 2000, and electricity was first generated in April 2002; since then, the plant has been operating regularly, and the present utilization index is above 7000 h/year. A number of literature references about dual fluidized bed systems for biomass gasification can be found in Koppatz et al. [101]. Recently, the TUV FICFB CHP technology has been applied in a number of gasification installations in Austria, Germany and Sweden.

The gas cleaning (Fig. 17 [103]) has been investigated and developed by RENET Austria (Energy from Biomass Network of Competence): it is made in three different and integrated ways. Fine hydrated lime is injected into the system to obtain a primary reduction of tar to less than 1 g/Nm^3, which allows enhanced recovery of sensible heat from the product gas stream; particulate filtration is operated smoothly at about 150 °C; the fuel gas is then contacted with biodiesel (RME) in a scrubbing column, to reach a tar content of about 20mg/m$_N$^{3} and a temperature of about 50 °C. Exhausted biodiesel is used as an additional fuel in the combustion section of the gasifier, and condensed water recycled to the gasification section, so that disposal of liquid streams is avoided.

Finally, the dual fluidized bed gasification system is well suited to exploit the advantages brought about by a reduction of CO_2 content in the product gas by absorption on basic oxides [106]: the use of a CO_2 sorbent minimizes carbon oxides and enhances the equilibrium conversion of catalytic tar and CH_4 steam reforming allowing to clean the gaseous fuel and improve the H_2 yield. The practical feasibility has been demonstrated by adding calcined limestone or dolomite to the reactor bed inventory. The sorbent circulates between the gasifier – CO_2 capture bubbling bed, and the combustor – calciner riser: in the reactor chamber devoted to biomass gasification and CO_2 capture, the endothermic gasification and the exothermic solid carbonation processes combine well together and their coupling reduces the amount of the solid circulation rate required to sustain thermally devolatilization and gasification reactions. On the other hand, the riser provides the calcined solid sorbent and the remaining thermal loading. When oxygen (instead of air) is utilized for combustion reactions in the riser, a CO_2 stream is easily obtained (by steam condensation), available for storage and sequestration.

The thermodynamic constraints of the reaction between CO_2 and CaO impose, at ambient pressure, a temperature level for gasification somewhat lower (650–700 °C) than the usual one (800–850 °C). However, the experimental evidence at pilot and industrial scale [107,108] does not show substantial increase of tar content in these conditions. The H_2 yield in the dry product gas is increased up to 70%.

2.3.2. *Gasification with partial combustion*

Thermal treatment of tar is one method for the reduction of tar concentration in biomass gasification gas [28,13]. At high temperature, the stability of tar is reduced and tar can be converted or cracked into lighter gases. However, thermal reduction of tar is a

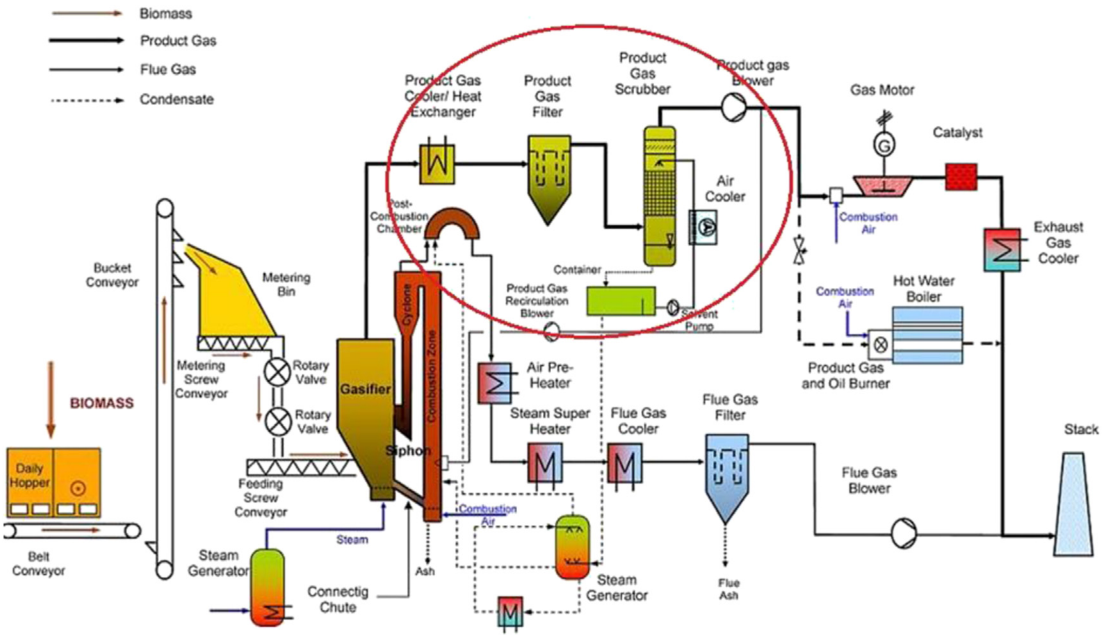

Fig. 17. Fuel gas cleaning with dry dust precipitation and wet RME scrubbing in Güssing [103].

quite complex process and the result depends highly on the process parameters. For example, it has been shown that just heating a tar containing gas by an external heat source to a temperature of 900–1150 °C leads to polymerization reaction of light tar components and to the formation of soot instead of the cracking of the tars [109].

Partial combustion has been attracting increasing interest of researchers in recent years as a method to achieve thermal tar conversion. Air/fuel ratio, hydrogen concentration, methane concentration, temperature and free radicals produced during the combustion influence the cracking or polymerization reactions of the tar components.

Houben et al. [109] investigated tar reduction by partial combustion by using naphthalene as model tar component at a very low concentration of $2.6 \text{mg}/\text{m}_\text{N}^3$ in a mixed gas stream of hydrogen, methane and nitrogen. It has been shown that without oxygen addition polyaromatic hydrocarbons (PAH) and soot were formed. Also, if too much oxygen was added, PAH and soot were formed. For a very low air to fuel ratio of $\lambda = 0.2$, the partial combustion reduced the tar content by more than 90%. For $\lambda > 0.2$, the tar concentration increased. Thus, an optimum was found in the amount of air added for the reduction of the naphthalene. For $\lambda > 0.4$, polymerization to higher tar rings and sooting prevailed. It has also been found that hydrogen and methane have an influence on tar reduction. Hydrogen acts as an inhibitor for the formation of soot. With increasing hydrogen concentration, the amount of higher tar ring components decreased. At hydrogen concentrations higher than 20% nearly all naphthalene was converted to benzene or permanent gases. For higher methane concentrations and very low hydrogen concentrations, polymerization to higher tar ring components and soot formation was observed.

Naphthalene as model tar component doesn't simulate the tar composition of real gases correctly. Real tar is composed of a lot of different components and has typically high concentrations of benzene and toluene which are the most stable tar species and require high temperatures above 1200 °C for their effective reduction (see e.g. Ref. [110]). At the same time, high temperatures favour the formation of coke. Zhang et al. [110] showed that coke formation starts at 900 °C having a maximum at 1100 °C.

The influence of the hydrogen concentration on the presence of free radicals in the partial combustion process has been studied by van der Hoeven et al. [111]. Their investigation showed that a higher hydrogen concentration has positive influence on tar cracking due to increased reaction rates, higher amounts of free radical generated, and longer residence times of the radicals.

Svensson et al. modelled soot formation during partial oxidation of gasifier product gas [112]. They simulated different gas compositions and used naphthalene as a tar component. The simulation results showed decrease of soot formation with increasing the hydrogen concentration in the gas as well as an increase of soot formation in the case of increased methane concentration. This is in qualitative agreement with the experimental results by Houben et al. [109]. However, the influence of the hydrogen concentration on the soot formation was very low in the simulation which requires further investigations. In all simulated cases soot was formed and could not significantly be reduced expect when no naphthalene was added to the gas. In this latter case about 50% less soot was formed compared to the base case where naphthalene was added in an amount of 0.5 mol% of the total incoming gas flow.

Ahrenfeldt et al. [113] showed higher tar reduction with increasing air ratio for the partial oxidation of real gas from the pyrolysis of wood pellets. They showed complete conversion of phenol for $\lambda > 0.3$ and temperatures above 950 °C. For lower air ratios higher temperatures were required to get the same result. Above 900 °C phenol and other primary tars were converted into low molecular weight PAH, primarily naphthalene. The tar concentration in the raw pyrolysis gas was quite high (above 200 $\text{g}/\text{kg}_\text{wood}$).

Investigations of Brandt et al. [114] showed a minimum of the tar concentration at an air ratio of $\lambda = 0.5$ for partial oxidation of gas from the pyrolysis of straw. For higher air ratios the tar concentration slightly increased. The tests were performed at 800 and 900 °C. The tar reduction was nearly comparable for both temperatures. Composition of the tar downstream of the partial oxidation reactor as well as soot formation has not been investigated.

Su et al. [115] investigated the partial oxidation of gas from the pyrolysis of rice straw. Maximum tar reduction has been achieved at an air ratio of $\lambda = 0.34$ at a temperature of 900 °C. Phenolic compounds were completely converted for $\lambda > 0.2$. It is reported that oxygen increases the reaction rate and can promote the formation of free radicals for initial tar cracking reactions. For air ratios above 0.278 only PAHs – naphthalene, fluorine, phenanthrene and pyrene – can be found in the gas. Higher air ratios lead to formation of higher PAHs. This agrees with the results of Houben [109] (see above).

Partial combustion for tar reduction has already been applied successfully in some recent multi-stage gasification concepts, such as the Viking gasifier (described in Section 2.2) for which a tar reduction by partial combustion by a factor of 100 has been reported [67] or the newly developed Fraunhofer ISE gasification process for production of synthesis gas with tar contents below $50 \mathrm{mg/m_N}^3$ [116]. The partial combustion in these multi-stage gasifiers aims to increase the temperature of the pyrolysis gas required for the subsequent endothermic char gasification reaction. In a single stage gasification process, a partial combustion stage downstream of the gasifier is typically not used since the high temperature required for an efficient conversion of tars reduces the energy efficiency of the process. Additionally, it reduces the syngas yield.

2.3.3. *Implementation of gasification in coal fired power plants*

Co-firing of biomass in coal fired power plants is a simple way to substitute fossil fuels by renewable ones [117–119]. At the first sight, the easiest and least expensive way is direct co-firing of biomass in the boilers. Up to about 3% of biomass on energy basis can be directly co-fired with minimal additional investment costs [1]. However, the properties of biomass as fuel are quite different compared to coal. Biomass has lower ash content, higher oxygen content, higher content of volatiles, lower density and heating value, grinding is more difficult due to fibre structures and some have high alkali and/or halogen content [120]. Thus, direct co-firing of biomass can result in several problems, especially if higher amounts of biomass shall be co-fired. These problems are mainly related to the different properties of the biomass ashes due to high alkaline and chlorine contents. Main problems which are reported are corrosion, slagging and fouling in the boiler as well as in the heat exchanger and in the piping, poisoning of DeNOx catalysts and performance problems in electrostatic precipitators [121–124].

One approach to overcome these problems is indirect co-firing of biomass by biomass gasification. Biomass is gasified in a gasifier and the produced gas is co-fired in a coal fired boiler [125]. Up to 10% of the thermal capacity of the boiler can be co-fired without the need of reconstruction of the boiler and auxiliary devices. For higher ratios major changes of the boiler would be required [117].

The first power plant where this concept has been used was the Kymijärvi power plant in Lahti (Finland) [126,127]. The power plant has an electrical power production capacity of 167 MW and a district heat production capacity of 240 MW. A Foster Wheeler CFB (circulating fluidized bed) gasifier was started-up at the beginning of 1998. Depending on the feedstock and its moisture content the capacity of the gasifier is 40–70 $\mathrm{MW_{th}}$ (nominal capacity 50 $\mathrm{MW_{th}}$). Raskin et al. [127] reported on the successful operation of the plant. Wood chips, wet and dry waste wood, saw dust, bark, shredded tires, plastics as well as recycled fuels were successfully gasified. The recycled fuels comprised mainly paper, cardboard and wood, and about 5–15% plastics. It was demonstrated that the concept of indirect co-firing of biomass by gasification is a successful way to generate heat and power by using different types of biomass and a way to operate an existing coal fired boiler with only small modifications. The power plant could be operated in a flexible way by adjusting the amount and the type of biomass which was co-fired.

Based on the successful operation in Lahti, the concept of indirect co-firing of biomass by gasification using a CFB Foster Wheeler gasifier similar to the one in Lahti has been applied at the coal fired Ruien power plant of Electrabel in Belgium [128–131]. The gasifier was commissioned in December 2002 and commercial operation started in May 2003. The gasifier is installed at the boiler of unit 5 of the power plant. Unit 5 has a power output of 190 $\mathrm{MW_e}$ on coal. No pre-treatment (drying, grinding) of the biomass as well as no cleaning and conditioning of the produced gas are required. The quality of the gas is sufficient to be burned in two burners, which are installed below the coal burners in the boiler. Wood residues from the local wood industry as well as fresh wood chips are used as a feedstock. About 9% of the coal is substituted by gas from the biomass gasification and 120 000 t/year CO_2 emissions are saved [131].

In the Netherlands, an 85 $\mathrm{MW_{th}}$ CFB Lurgi gasifier is in operation for indirect co-firing of biomass since 2002 at unit 9 (net production capacity: 600 $\mathrm{MW_e}$ and 350 $\mathrm{MW_{th}}$) of the Amer power station of Essent in Geertruidenberg [132,133]. Low quality demolition wood is mainly used as a feedstock. About 90 000 t biomass was gasified in 2010 generating an electric capacity of about 33 $\mathrm{MW_e}$ [133].

In Austria, a 10 $\mathrm{MW_{th}}$, CFB biomass gasifier designed by Austrian Energy was installed for indirect co-firing of biomass with coal at the Zeltweg power plant (137 $\mathrm{MW_e}$, 344 $\mathrm{MW_{th)}}$ [134,135]. The gasifier was commissioned in 1997 and shut down in April 2001 due to shut down of the power plant. Mainly bark and wood chips were gasified.

After 2003, the interest in the concept of indirect co-firing of biomass by gasification declined. However, recently the interest in this concept increased again and new biomass gasifiers were installed at coal fired power plants. In Denmark, Dong Energy installed a 6 $\mathrm{MW_{th}}$ LT-CFB biomass gasifier (see Section 2.2), which is in operation since 2011, at its Asnaes power plant [68]. Straw is mainly used as a feedstock. In Finland, the so far world's largest biomass gasifier has been inaugurated in March 2013 [136]. The gasifier, a 140 MW CFB gasifier designed and supplied by Metso, was installed at the 560 $\mathrm{MW_{th}}$ coal fired power plant of Vaskiluodon Voima Oy in Vaasa [137]. Between 25 and 40% of the coal consumption of the plant will be substituted by biomass.

Indirect co-firing of biomass by gasification is a concept which is well proven by long-term operating experience in large coal fired power plants, as mentioned above. This concept has several advantages which can be summarized as follows:

- Easy and cost-effective way to reduce fossil CO_2 of coal fired power plants
- Purity and quality of the produced gas can be low to be burned in the boiler. Thus, no high efficient gas cleaning and conditioning or cooling equipment is required and the investment costs are lower than in cases where high gas quality and purity are needed.
- High flexibility in using a broad range of biomass feedstocks, including low quality biomass as well as RDF (refuse derived fuels).
- Biomass which generates problems in direct co-firing, e.g. straw, can be used.
- Compared to direct co-firing, no drying or grinding is required.
- High biomass conversion; residual fine char particles and tars are burnt in the boiler.
- No operating dependency on availability of biomass; biomass can be substituted by fossil fuel.
- No influence on the operating availability of the power plant by possible problems with the gasifier.

- Less coal ash pollution than in direct co-firing (coal ash is often used in concrete production). Less biomass ash enters the boiler since coarser ash particles are removed in the cyclone of the CFB gasifier and returned into the gasifier where they accumulate and are removed as bottom ash. If higher percentages of biomass are co-fired or higher coal ash purity is needed, a hot gas filter [97] can additionally be used to remove fine ash particles from the produced gas without energy loss due to cooling.

3. Polygeneration strategies

Polygeneration is an approach to improve the economic and sustainability of the utilization of biomass via gasification. Polygeneration refers to the combined production of at least two products. The goal is to maximize the transformation efficiency of the energy and material of the feedstock into products. Syngas from biomass gasification can be converted into a broad range of products, e.g. electricity, heat, gaseous or liquid fuels or chemicals. As an additional advantage, polygeneration offers flexibility with regard to changes of market demands. For example, a polygeneration process for the combined production of biofuels, heat and power could be used as a back-up power plant. If the current electricity consumption increases, the production of biofuels can be switched to the production of power.

However, higher flexibility comes with higher capital investment costs as well as higher operation and maintenance costs.

Combined heat and power production is a classical example for a polygeneration process. Newer approaches aim to combine SNG (synthetic natural gas) or hydrogen and heat production, or biofuels, and heat and power production.

3.1. Combined heat and power production (CHP)

Power production is generally coupled with the production of heat. If the heat can be used, the overall process efficiency can be significantly increased. Whereas electricity can be easily transported and distributed, heat has to be produced close to the user. For this reason, decentralized heat and power production by smaller units is preferred, and larger units of several hundreds of MW as typically used for power production are not an option. Interesting ways to use the heat are for example CHP plants of a few MW coupled to district heating systems, CHP plants below 1 MW for heating large public or commercial buildings, public swimming pools, hospitals, hotels or apartment buildings, or CHP plants installed at pulp and paper plants, at saw mills etc. where biomass waste can directly be used to produce electricity, heat or steam for the local plant. Combined heat and power production by biomass combustion is already widely used [138]. However, CHP by biomass gasification offers some advantages, such as higher biomass to power efficiency [3,139], and higher flexibility concerning the used feedstock as well as the applied electricity generation process [140]. First CHP applications by biomass gasification started at the beginning of the 1990s [141]. CHP biomass gasification plants with capacities of a few MW of biomass input have demonstrated several years of successful operation showing the overall reliability of the technology and the achievable high process efficiency. Some examples are the 5.2 MW_{th} Harbøøre plant (start-up in 1993) [3,142,9] and the 26 MW_{th} Skive plant (start-up in 2006) [9] in Denmark, the 8 MW_{th} plant in Güssing (start-up in 2002) [143], the 2 MW_{th} plant in Wiener Neustadt (in operation from 2003 to 2007) [144,145], the 8.5 MW_{th} plant in Oberwart (start-up in 2008) [9] and the 15 MW_{th} plant in Villach (in operation from 2010 to 2013) in Austria as well as the 15 MW_{th} plant in Ulm (start-up in 2012) in Germany [146]. In most of the plants just mentioned, overall process efficiencies of about 90% and biomass to electricity efficiencies from 25 to 31% are reported. In all cases gas engines are used for electricity generation showing increased efficiency of newer gas engine types. The produced heat is used for district heating.

An approach to increase the amount of generated electricity is applied in the 15 MW_{th} plant in Ulm in Germany where in addition to 2 gas engines an organic Rankine cycle (ORC) is installed for electricity production [146]. By using ORC, some of the heat (10–15% of the heat) [9] can be additionally converted into electricity. Combining gas engines with ORC, biomass to electricity efficiencies of more than 40% are achievable.

Another approach to increase the electricity efficiency, is the integrated gasification combined cycle (IGCC) process, where a gas turbine and a steam turbine are combined to generate electricity. The IGCC process has been used for coal gasification since the mid-1990s, showing electricity efficiencies of up to 46% for plant sizes of 200–300 MW [147,148]. Theoretical investigations (see e.g. Ref. [149]) show that even overall electrical efficiencies of up to 53% could be possible with an IGCC process. For biomass, the IGCC process has been applied in the 18 MW_{th} (6 MW_{el} and 9 MW_{th} for district heating) demonstration plant in Värnamo in Sweden [150,151]. The plant was operated from 1993 to 1999 when the demonstration program was completed. The plant had a net electrical efficiency of 32% and a total net efficiency of 83% [150]. Since small steam turbines have a low electrical efficiency [152], an IGCC process is only interesting for larger scales.

A technology for electricity generation which has already gained a high interest is the fuel cell technology. Fuel cells offer the advantages of very high electrical efficiencies, an environmental friendly operation and they can be used from some hundreds of kilowatts down to 1 kW for very small scale applications. Solid Oxide Fuel Cells (SOFCs), which operate at high temperatures with hydrogen, carbon monoxide and methane and their mixtures as fuel [14] are specifically considered as a good option to be combined with biomass gasification. For application as CHP, the high exhaust temperature of the SOFC is an advantage to use the heat. However, even if the biomass gasification syngas composition is generally well suitable as fuel for a SOFC, it has to be cleaned to achieve the high requirements of the fuel cell with regard to impurities. Aravind and de Jong [14] gave a very comprehensive literature review of the different contaminants in the raw syngas, their influence on the performance of a SOFC and techniques to remove them. They concluded that it is possible to clean the syngas to meet the requirements of a SOFC. They proposed a gas cleaning set-up comprising a series of fixed bed reactors and 2 ceramic hot gas filters.

Many performance models and theoretical analyses of the combination of SOFCs and biomass gasifiers show the high potential of this combination with electrical efficiencies from 34 to 45% and CHP efficiencies from 74 to 80% [153–157].

A further increase of the electrical efficiency is possible by combining a SOFC and an additional Micro-Gas Turbine (MGT) with a biomass gasifier. By adding the MGT, the excess fuel in the exhaust gas from the SOFC can be used to generate additional electricity. The combination of a SOFC and an MGT with a biomass gasifier offers a very efficient power production solution for small decentralized CHP plants. Recent modelling studies of Bang-Møller et al. [158] showed an electrical efficiency of 58% and a CHP efficiency of 87.5% for an optimized process using the two stage Viking gasifier combined with a SOFC and an MGT. Morandin et al. [159] have recently modelled nine different system configurations using either an internally circulating fluidized bed gasifier or the Viking two stage gasifier and different combinations as CHP unit, just a SOFC, a SOFC combined with a steam cycle and a SOFC combined with an MGT. Their thermo-economic analysis showed that the combination of a fast internally circulating fluidized bed gasifier with a pressurized operated SOFC and MGT is the most promising configuration with an electrical efficiency of 65%.

However, combination of SOFC and biomass gasification has not been demonstrated on full scale and for long-term operation yet. Experimental investigations have only been performed with single cells or very small stacks, and for short test durations of about 5–150 h (see e.g. Refs. [160–162,69,163]). Only one test has been performed for longer test duration of 1200 h [164].

Based on the published experimental results, the following conclusions can be drawn:

- SOFCs can successfully be operated by using cleaned biomass gasification syngas. General feasibility of the combination of biomass gasification with a SOFC is shown. However, demonstration on full scale and for long-term operation is still missing.
- The cell performance depends on the syngas composition and fluctuations of both can be correlated [161].
- The risk of carbon deposition increases with higher concentration of methane and tars. However, carbon deposition can be prevented by addition of steam.
- However, if steam content is too high, the risk of nickel oxidation of the anode is increased resulting in cell performance degradation [163].
- Inefficient particle removal from the syngas causes ash deposits and prevents a smooth long-term operation [160]. For this reason fly ash and char particles have to be removed efficiently from the syngas.
- Besides particle removal, efficient removal of gaseous impurities, such as tars, sulphur compounds, alkalines, chlorides and ammonia, is important to prevent poisoning of the anodes [14].
- Attention has to be taken on the syngas composition. Higher concentrations of methane, propane and higher hydrocarbons in the biomass syngas increase the rate of internal reforming, if no separate external reformer unit is used, and cause thermal stress which may result in cracking of the cells [161].

Finally, it can't be concluded which one of the available technologies for combined heat and power production should be favoured. It depends on case specific conditions which CHP technology is preferred. One important condition beside investment costs, earnings or incentives for heat and power supply and availability and cost of biomass is the local annual heat demand. Gas engines are well proven and have a relatively high electrical efficiency at relatively low investment costs. SOFCs and the combination of SOFCs with MGTs are promising technologies which offer very high power generation efficiencies even at very small size. However, long-term testing on full scale size is still missing and will be an important topic for future investigations.

3.2. *SNG, heat and power production*

SNG from biomass is considered as a renewable clean fuel substitute for fossil fuels in heating, CHP and transportation systems. Bio-SNG is also regarded as a flexible renewable energy carrier. The existing natural gas pipeline system offers the advantage for an easy transportation and storage of the SNG. Gas heaters, boilers and engines as well as natural gas cars and buses are available as established clean technologies for the use of SNG. Several methanation processes were developed in the past for the production of SNG from coal gasification syngas. One of these processes is e.g. the well-known Lurgi process using a series of adiabatic fixed bed reactors. A comprehensive review on methanation technologies has been given by Kopyscinski et al. [165].

Before the methanation reaction can be performed, the produced syngas has to be cleaned and conditioned. The gas cleaning aims to remove particulates, tars, alkali and sulphur components. The removal of these components has to be very efficient in order to protect downstream catalysts from poisoning. Conditioning of the gas comprises typically a water–gas shift to adjust the needed H_2/CO ratio of 3 or more for the methanation reaction. After the methanation, water and CO_2 as well as unreacted hydrogen and impurities of ammonia are removed from the SNG to achieve the required gas quality, for example to deliver the SNG to the gas grid. More details of the process are given in the literature (see e.g. Refs. [165–167]).

In the last 10 years, the production of SNG from biomass gasification syngas has gained increasing interest and has been investigated by some research groups such as the Energy Research Center of the Netherlands (ECN) and the Paul-Scherrer Institute (PSI) in Switzerland [165].

Recently, the feasibility to produce SNG from biomass gasification syngas has been demonstrated in a 1 MW scale at the Güssing plant [168]. ECN operates a 0.8 MW_{th} SNG pilot unit [169]. A thorough investigation by Wirth and Markard showed that Bio-SNG plants require a size of 20 MW or larger to be economical since the process including gasification, gas cleaning, catalytic methanation and CO_2 separation is complex and expensive [170].

The first commercial Bio-SNG plant of a size of 100 MW will be built in the GoBiGas project in Göteborg in Sweden [171,172]. In the first phase of the project, a 20 MW plant has been erected. In the second phase a 80 MW plant will be built which shall start operation in 2016. There are further plans for large commercial Bio-SNG plants, e.g. the 200 MW Bio2G project of EOn in Sweden [173].

Finally, there is the question whether the effort to produce SNG from the syngas is valuable. If the SNG is used for domestic heating and cooking, it would be a shorter chain to use the syngas directly instead of having an additional production step to produce SNG and to increase the costs and drop the process efficiency. The reason why the additional step to produce SNG is taken is that the existing distribution system for natural gas can easily be used for SNG which is a big advantage and justifies the higher effort. In areas where no natural gas distribution system is available it would be more beneficial to use the cleaned syngas directly for household heating and cooking like it has already been practised e.g. in China in rural areas [174]. However, a risk of the direct use of the syngas is the toxicity of the CO contained in the gas.

Compared to domestic heating by wood combustion, Bio-SNG is less efficient and about twice the wood quantity would be required to produce the same quantity of heat [175]. Also power production by using Bio-SNG is less efficient than using the syngas from biomass gasification directly.

However, Bio-SNG as renewable fuel for transportation can have an efficiency advantage. Felder and Dones [176] showed in their evaluation of the ecological impact of Bio-SNG that the preferential use of SNG is as a transport fuel for cars to substitute oil based fuels. Fahlen and Ahlgren [177] concluded in their study that it is more economical to use Bio-SNG as vehicle fuel than to use it for power and heat production. Ahman [178] showed in his assessment of Bio-SNG as a transport fuel that Bio-SNG can be produced cost efficiently already at low to medium scale plants of 20–100 MW whereas the production of liquid biofuels require larger scale plants to be competitive. Additionally he stated that the production efficiency of Bio-SNG is higher than for DME, methanol or Fischer–Tropsch diesel.

Production of Bio-SNG in a polygeneration plant offers several process possibilities with high overall process efficiencies of up to 90%. For example, excess heat of the process can be used for district heating [177] or part of the excess heat can be transformed in a Rankine cycle to co-produce power [179]. The integration of SNG and electricity via biomass gasification in a district heating system offers economic benefit and reduces CO_2 emission [180]. Polygeneration of Bio-SNG can offer a high flexibility on market demands by adjusting the requested amounts of Bio-SNG, heat and power or just balancing the demands by producing the Bio-SNG as an energy storage.

In a polygeneration system there is also the possibility to operate the gasifier with the aim to produce a syngas with a higher content of methane and to separate this methane directly from the syngas avoiding the need of a subsequent methanation process. The remaining syngas can then be used for heat and power generation for example.

3.3. *Biofuels, heat and power production*

Comparable to Bio-SNG, biofuels, such as FT diesel, DME and methanol, are considered as renewable clean fuel substitutes for fossil transportation or heating fuels. Additionally, liquid biofuels generate less emissions than oil based fuels.

Since the use of liquid fuels for cars and trucks is state of the art, and accordingly an expanded infrastructure of oil based re-fuelling stations exists globally, liquid biofuels can be relatively easily introduced and used in the market. This is the main advantage for the use of liquid biofuels for transportation compared to SNG or hydrogen from biomass.

Polygeneration of liquid biofuels, heat and power offers as main advantages high process flexibility and process efficiencies up to about 90% [3] which is similar to the polygeneration of Bio-SNG, heat and power described in the previous section. The advantage of a polygeneration versus a stand-alone production has been concluded from several technoeconomic analyses.

Narvaez et al. [181] showed in a recent case study that a polygeneration plant for the production of methanol and power has a better performance and higher flexibility compared to the separate stand-alone production plants. Furthermore, they showed savings of the syngas consumption as well as the possibility to compensate a decrease of the catalyst activity by an increase of the syngas feed rate for the methanol production route and using the unreacted syngas afterwards for power production.

Haro et al. [182] concluded in their assessment of 12 different process concepts based on DME as intermediate and considering ethanol, methyl acetate, DME, H_2 and electricity as final products that the highest internal rate of return is given by a concept of producing methyl acetate, DME and electricity and that the polygeneration is more profitable than a single product plant.

Meerman et al. [183] concluded in their study that the economics of a flexible polygeneration FT-liquid facility is better than its stand-alone counterpart.

Djuric Ilic et al. [184] showed in their study that polygeneration of biofuels with co-production of heat and power has a higher reduction of greenhouse gas emissions than the stand-alone production of biofuels.

Comparing the production costs of biofuels to fossil fuels, different techno-economic analysis have shown that biofuels have to be supported by tax or CO_2 incentives in order to be competitive (see e.g. Refs. [185,91]). The production costs decrease with increasing size of the production plant [186].

3.4. *Hydrogen and heat production*

Hydrogen generated from biomass can be an interesting environmental friendly and renewable energy carrier mainly for the use in fuel cells in stationary as well as transportation applications. Gasification of biomass produces a syngas rich in hydrogen if steam or oxygen and steam are used as a gasification agent. If air is used as a gasification medium, the nitrogen dilutes the syngas leading to a low hydrogen concentration and a high effort of hydrogen purification.

In order to separate and purify the hydrogen from the syngas pressure swing adsorption or membranes can be used. To achieve high hydrogen content in the syngas a reforming stage and additionally a water gas shift stage typically follows the gasifier.

Toonssen et al. [187] modelled 10 process configurations with and without heat recovery based on different gasifiers. They calculated exergy efficiencies between 45 and 50% for the cases of hydrogen production without heat recovery and between 62 and 66% with heat recovery. The hydrogen yield for the different gasifiers was between 97 and 106 g per kg of dry biomass. Bhattacharya et al. [188] calculated in their model for an oxygen blown gasification process a similar hydrogen gas yield of 102 g per kg dry biomass.

Tock and Marechal [189] compared in their thermo-economic modelling the hydrogen production from natural gas and from biomass with regard to energy efficiency optimization by polygeneration of hydrogen, heat and power and including CO_2 capture. They concluded that the system performance is improved by process integration maximizing the heat recovery and valorizing the waste heat. They calculated an energy efficiency of 60% for hydrogen production by biomass gasification compared to 80% efficiency for hydrogen production by steam reforming of natural gas.

Shabani et al. [190] investigated hydrogen production by gasification of rice husk combined with heat recovery for electricity generation by 2 Rankine cycles. They used a GE gasifier operated at 1200 °C and 3 MPa with oxygen as gasification medium in their model. Hydrogen efficiency of 40% and net electrical efficiency of 3.25% has been calculated if CO_2 is not compressed for capture and storage. With CO_2 capture and storage the net electrical efficiency drops to 1.5%.

Abuadala and Dincer [191] modelled a quite complex integrated system for polygeneration of hydrogen, heat and power. They considered a system comprising steam gasification of saw dust, a coupled SOFC–SOEC (solid oxide electrolyser cell), steam reformer, water gas shift reactor, compressors, gas turbine and burner. They concluded that their results give an indication for hydrogen production costs which are quite favourable and have potential for practical applications.

Beside the aforementioned theoretical studies, an experimental investigation of an efficient integrated process to produce hydrogen is developed in the frame of the UNIfHY research project funded by the European Commission [21]. The system developed in this project comprises a UNIQUE gasifier (described in Section 2.1), a water gas shift reactor and a pressure swing adsorption unit. Purge gas is recirculated to the gasifier to be used as a heat source for the endothermic reactions in the process. It is predicted that the process with the integration of several subsystems will achieve high hydrogen conversion efficiencies of higher than 66% [21].

4. New gasification concepts

4.1. *Plasma gasification*

In a plasma, gas molecules are ionized by electric discharges. A plasma is highly reactive due to the electrons, ions and the high energy density in the gas. To generate a plasma, direct current (DC) discharge, alternating current (AC) discharge, radio frequency (RF) induction discharge or microwave discharge are typically used. Thermal and cold plasmas can be distinguished. Cold plasmas are generated at vacuum pressure whereas thermal plasmas are achieved at atmospheric pressure. As plasma gases argon, nitrogen, hydrogen, water vapour or gas mixtures are used. The temperatures of thermal plasmas can be 5000 K and higher. Thermal plasma gasification units often use DC or AC arc plasma torch generators. Fig. 18 shows 2 different DC arc plasma torch generator concepts [192]. Generators up to 10 MW power are commercially available [193]. Fig. 19 shows as an example a plasma gasification reactor where the reactor chamber is connected to a non-transferred DC arc plasma torch generator [194].

The very high temperatures of thermal plasmas enable an efficient decomposition of any organic material into its elemental molecules. For this reason plasma gasification has gained interest for the treatment of toxic organic wastes as well as for rubber and plastic waste. Inorganic matter is recovered as a vitrified slag. Energy can be generated from the gasification of the waste. For example, a plasma gasification plant in Utashinai (Japan) is in operation since 2002 gasifying up to about 300 tons per day of municipal solid waste and automobile shredder residues and producing 7.9 MWh electricity with a net production of 4.3 MWh delivered to the grid [192].

Even if the main application for plasma gasification is waste treatment, the use of plasma gasification has gained attraction for syngas production from biomass. Gasification of injected biomass in the plasma takes place within milliseconds without any intermediate reaction at the very high temperatures [195]. Advantages of plasma gasification are syngas with high hydrogen and CO content, low CO_2 content, low tar concentration, high heating value, useable for wet biomass, such as sewage sludge [196,197], no influence of particle size and structure of the biomass.

Disadvantages are the high electricity consumption to operate the plasma, high investment costs, and lower efficiencies.

Plasma gasification of biomass has been investigated by several researchers recently. Hlina et al. [198] have investigated the gasification of wood saw dust, wood pellets, waste plastics and oil from the pyrolysis of waste tires in a DC electric arc plasma with a torch input power of about 100 kW. A mixture of water vapour with a small amount of argon was used as plasma gas. CO_2 or water vapour was added as an oxidizing medium. For all 4 feedstocks, a syngas of high quality with about 90 vol% H_2 and CO was produced. They evaluated the efficiency of the process by comparing the low heating value of the produced gas to the torch input power. Due to the high electricity input the efficiency of the process is low. For the gasification of the pyrolysis oil the energy efficiency of the process is even negative.

Rutberg et al. [199] evaluated plasma gasification of wood for combined heat and power production. By using an AC air plasma with a power input of 2.2–3.3 MJ/kg they produced a syngas with 13.8–14.3 MJ/kg. By calculations they showed the potential to achieve a net electric energy conversion of 46%.

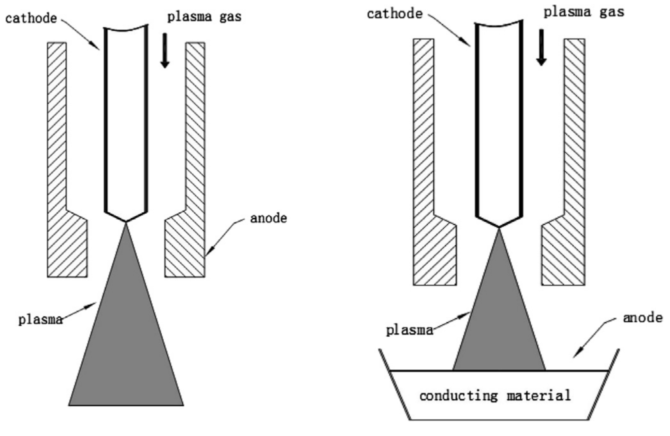

Fig. 18. Scheme of a DC non-transferred arc plasma torch (left) and of a DC transferred arc plasma torch (right). Adapted from Tang [192].

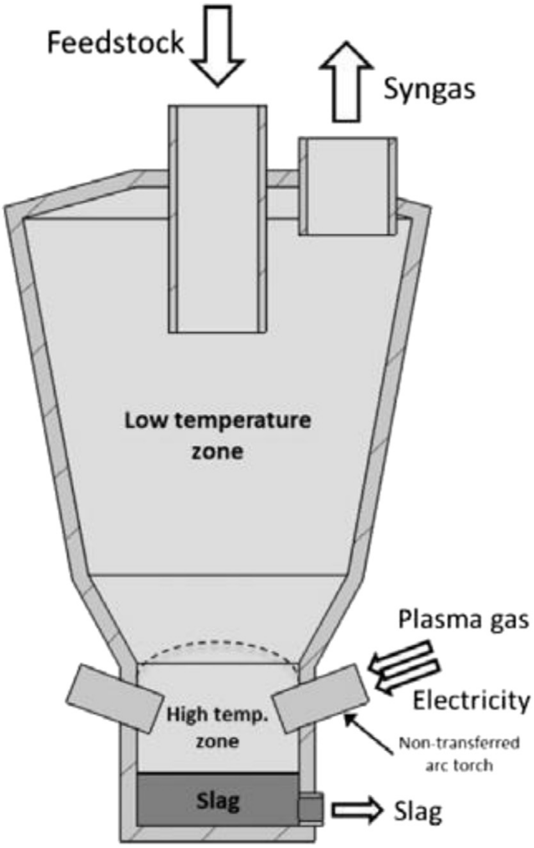

Fig. 19. Scheme of a plasma gasification reactor [194].

Tang and Huang [200] investigated a lab-scaled RF plasma reactor for biomass pyrolysis operated at low pressure (3000–8000 Pa). They produced two products, a gas of 66 wt% of the biomass feed as well as char. The gas was a mixture of H_2, CO, CO_2 CH_4, light hydrocarbons and almost no tars. The energy loss of this lab reactor was quite high and the energy input to the biomass feedstock accordingly low.

A comparison between DC arc plasma gasification and conventional air gasification has been modelled based on non-stoichiometric chemical equilibrium for different feedstocks by Janajreh et al. [194]. Air gasification showed a higher efficiency than plasma gasification. They calculated an average process efficiency of plasma gasification of about 42% compared to a process efficiency of 72% of air gasification. The difference is caused by the high energy consumption of the plasma.

Plasma gasification of distiller grains residues has been investigated in a 10 kW plasmatron reactor by Shie et al. [201]. A syngas with 50–55 vol% H_2, 40–44 vol% CO, 2–3 vol% CO_2 and 1.4–2.5 vol% CH_4 was achieved.

In order to overcome the high energy consumption and high investment costs of DC plasmas, several researchers have investigated the use of microwave plasmas for gasification of carbonaceous feedstocks (see e.g. Refs. [202–205]). All these investigations were performed on small lab-scale with power inputs from 1 to 5 kW. Gasification of glycerol from biodiesel production in a microwave plasma was performed by Yoon et al. [203]. They produced a hydrogen rich syngas with 57% H_2 and 35% CO without any oxygen feed. The carbon conversion was 80% in this case. Feeding oxygen decreased the hydrogen content and the heating value of the gas and increased the CO_2 content and the carbon conversion. Quite similar results were also reported for the gasification of coal and charcoal [204].

Even if lab studies showed that a syngas with high hydrogen content can be achieved by microwave plasma gasification, the possibility of an upscale to technical gasifiers with high throughputs seems very unlikely.

4.2. Supercritical water gasification

Conversion and gasification of organic hydrocarbons in supercritical water has already been fundamentally investigated since the mid of the 1970s. In the last 10 years interest in supercritical water gasification of biomass increased and progress has been made in the investigation of technical processes. Several review papers on supercritical water gasification of biomass have been published giving overview of the fundamentals and reactions as well as details and problems of the process (see e.g. Refs. [206–208]). Furthermore, several studies on the usability of different feedstocks, such as e.g. agricultural wastes, leather wastes, switchgrass, sewage sludge, algae, manure, olive mill wastewater and black liquor, have been performed (see e.g. Refs. [209–215]).

Water in its supercritical condition – above its critical point of $p = 22.12$ MPa and $T = 374.12$ °C (see Fig. 20) – has unique properties as solvent and as reactant. Solubility of organic materials and gases is significantly increased and materials which are insoluble in water or water vapour can be dissolved whereas solubility of inorganic material is decreased.

Main components in the produced gas are H_2, CH_4 and CO_2. CO content is typically low since CO reacts further by water gas shift and methanation reaction [209]. Tar and coke formation is inhibited by fast solution of the formed gas components in the supercritical water. At reaction temperatures below 450 °C, CH_4 is the main component in the produced gas, whereas at reaction temperatures above 600 °C hydrogen is dominant [216]. At temperatures above 600 °C, water is a strong oxidant and reacts with the carbon and releases hydrogen [217].

Main advantages of biomass gasification in supercritical water are: wet biomass can be treated without pre-drying, even liquid biomass waste can be treated – e.g. olive mill wastewater [214], production of hydrogen-rich gas, high gasification efficiency, low tar formation. Main disadvantages are: high investment costs due to the need of special corrosion and high pressure and high temperature resistant materials, and high energy need to heat up the water to the reaction temperature.

The use of catalysts can reduce the reaction temperature and thus the equipment and operating costs. Furthermore, they can enhance the conversion rate and the hydrogen yield. Several catalysts have been tested for supercritical water gasification of biomass including the typical reforming catalysts, such as Ni and Ru, activated carbon, Pt-based catalysts, alkali metal based materials, such as trona, KOH, NaOH, K_2CO_3. Overviews are recently given e.g. in the papers of Elliott [218], Guo et al. [216], and Azadi and Farnood [219].

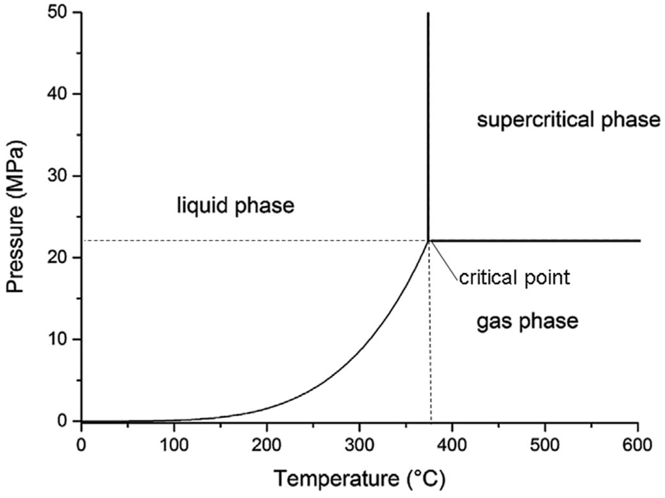

Fig. 20. Schematic phase diagram of water. Adapted from Yakaboylu et al. [213].

The energy efficiency of the supercritical water gasification of biomass has been studied by different researchers. Marias et al. [220] modelled the gasification of vinasse in supercritical water. They showed that the best gasification efficiency of their process of about 87% was achieved at a reaction temperature of 600 °C. By thermodynamic modelling of a supercritical water gasification process for hydrogen production from wet biomass, Lu et al. [221] showed an energy and exergy efficiency of their process of more than 40%. Energy loss results from heat transfer mainly in the heat exchanger, the cooler, the preheater and the reactor. High heat transfer efficiency increases the energy efficiency of the system. As an alternative to very efficient heat exchangers, oxygen can be added to the process in a small amount to make the process energetically self-sustainable with only a small loss of the heating value of the produced syngas [222]. A polygeneration process for the production of methanol and power by supercritical water gasification of glycerol has been studied by Gutierrez Ortiz et al. [223]. Power was produced by a turbine and a fuel cell in their study. They calculated an overall net energy efficiency of their proposed process of 38% for a gasification temperature of 1000 °C.

Even if progress has been made in supercritical water gasification of biomass in recent years and this technology seems to be very interesting especially for wet biomass, technical solutions still need to be developed for large-scale production.

5. Conclusions

Biomass is one of the main renewable energy sources beside wind and solar energy. In contrast to wind and solar energy, renewable energy production from biomass can be adjusted to current consumption need. Gasification is a key technology for the use of biomass offering high flexibility and efficiency. New knowledge and more efficient and cost-competitive industrial applications are required for the long run, showing evidence of promising developments and cross-fertilization with sectors other than energy, which may provide ideas, experiences, technology contributions, new approaches, innovative materials and skills.

The detailed survey of this paper showed some very interesting new concepts and strategies in biomass gasification. These concepts and strategies aim to promote the application of biomass gasification in the future. New advanced process integration and combination concepts enable higher process efficiencies, better gas quality and purity, and lower investment costs. Polygeneration biomass gasification facilities for the production of more than one product in combined processes achieve a highly efficient use of biomass. Furthermore, these facilities offer the flexibility to produce electricity when it is needed and if it is not needed to produce biofuels or chemicals from the syngas. This flexibility is not free of charge. It is coupled to higher investments in both the reactors as well as in the power generation equipment. However, back-up power plants are needed at all and the required investments can be made in polygeneration plants.

In this frame, the development of innovative catalysts, sorbents and high temperature filtration media was shown to represent a fundamental requirement to increase yield and purity of the biomass gasification product, to allow efficient conversion into power (high temperature fuel cells; gas turbines; combined, strictly integrated heat and power plant schemes) and further catalytic processing addressed to second generation bio-fuels (liquid fuels for transportation, hydrogen) and chemicals. Thanks to developments in new materials preparation, characterization and testing at real industrial conditions, poly-generation strategies focussed on biomass, adaptable to different demands and markets, can be implemented and enforced with success.

High temperature gas cleaning and catalytic conditioning is the focal point to promote industrial applications of biomass for energy and chemicals. To avoid unacceptable increase of plant and operating costs, gas treatments should be strictly integrated with biomass conversion and carried out at a close temperature range, to preserve the thermal energy content of the biomass–gas.

Polygeneration by biomass gasification offers high potential and flexibility, however, development and realization of polygeneration strategies is highly influenced by national governmental energy strategies. According to current prices of fossil based fuels and electrical energy, CO_2 incentives and tax supports are required to achieve an economically competitive production of biomass based fuels and power.

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Chapter 1

Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.74191

Abstract

Biomass gasification has been regarded as a promising technology to utilize bioenergy sustainably. However, further exploitation of biomass gasification still needs to overcome a significant number of technological and logistic challenges. In this chapter, the current development status of biomass gasification, especially for the activities in China, has been presented. The biomass characters and the challenges associated with biomass collection and transportation are covered and it is believed that biomass gasification coupled with distributed power generation will be more competitive in some small communities with large amount of local biomass materials. The technical part of biomass gasification is detailed by introducing different types of gasifiers as well as investigating the minimization methods of tar, which have become more and more important. In fact, applying biomass gasification also needs to deal with other socio-environmental barriers, such as health concerns, environmental issues and public fears. However, an objective financial return can actually accelerate the commercialization of biomass gasification for power and heat generation, and in the meantime, it will also contribute to other technical breakthroughs.

Keywords: biomass gasification, gasifiers, tar removal, socio-environmental impact

1. Introduction

Fossil fuel is on the verge of depletion in this century. Scientists and governments around world are looking for new energy resources which could be used safely and efficiently with enough amount for deployment and security. Bioenergy is a renewable energy, which is stored in the organic form in the chemical state and supports human beings' daily life since our ancestor apes knew how to use fire to cook. In these millions of years, bioenergy was mostly used in small scale like household cooking. Now, people have realized that efficient exploitation of biomass resource can actually reduce their dependency over fossil fuel. Biomass gasification has been regarded as an effective pathway to utilization of bioresource. It takes biomass as raw materials and employs pyrolysis or thermal cracking under anoxic conditions. This is an energy conversion process including a group of complex chemical reactions that large organic molecules degrade into carbon monoxide, methane and hydrogen and other flammable gases in accordance with chemical bonding theory. Biomass feedstock with the gasification agent is heated inside an integrated gasifier. With temperature increase, biomass goes through dehydration, volatilization and decomposition. Eventually, the produced gases are used for central gas supply and power generation. This technology has already been developed over several decades and progressively achieved commercialization all over the world, especially in Sweden, Germany, Canada, the United States, India and China. In the early stage, downdraft gasifier had been implemented at a large scale in China and India due to its relatively low tar production. Recently, the development of circulating fluidized bed (CFB) gasifier makes it adaptable for both biomass quality and the raw particle size. Besides, CFB is also easy for scale-up and ash cleaning.

China, as a large agricultural country, produces a large number of crop straw, poultry manure, agricultural by-products and other plant biomass every year. Thus, research and development on key technologies and integrated peripherals of biomass gasification become very necessary. China has already developed various gasifiers, the size of which range from 400 KW to 10 MW. However, compared with fossil fuel, biomass has lower bulk density and energy density, which make it uneconomic for collection and transportation. Therefore, biomass gasification coupled with distributed power generation in small communities with abundant biomass resource would be the way out in future [1].

In recent years in China, the yield of domestic waste has increased every year and exceeds 400 million tonnes per year. Chinese government's 13th five-year plan proposed that the proportion of waste harmless treatment should be no less than 70% by 2020. But waste landfill is still the primary method used to deal with waste in rural areas. Compared with landfill, gasification has advantages of lower environmental impacts and does not consume land resource. When contrasting gasification with incineration, the gasification technology has better quality of gaseous emissions with much lower capital input, which makes gasification more suitable for distributed deployment in rural area. Therefore, there will be a great demand for deployment of waste gasification treatment plants in Chinese rural areas, and more and more people are now focusing on the development of more efficient small-scale gasifiers with capacity under 300 tonne/day. The relevant equipment has also been deployed in Iran, Thailand, Burma and Laos. However, several technical barriers are still there such as effective removal of tar with low cost, environmental influence, accuracy control of gasifier inner temperature, solidification of fly ash and so on.

Therefore, this chapter introduces both technological and logistics challenges of biomass gasification via introducing biomass characters and gasifier technologies. The details of tar minimization and socio-environmental impacts of biomass gasification are also presented as main contents to help understand the primary barriers for the deployment of biomass gasification.

2. Biomass characteristics and general conversion

2.1. Composition of biomass and its common characteristics

Biomass includes all the living or recently living organisms, like land plants, grasses, water-based vegetation and manures [2], and these organisms consist of a number of major elements such as C, H, O, N, P and S. The classification of biomass into different categories is based on their properties. One feasible way is based on the appearances and the growth environment of biomass: woody plants, herbaceous plants/grasses, aquatic plants, manures and wastes [2]. Biomass could also be divided into two types: low moisture content and high moisture content. The low moisture content biomass can be used in thermo-chemical processes (i.e., gasification, combustion and pyrolysis), while the high moisture content plants are more suitable to be used in some wet processing technologies (i.e., fermentation and anaerobic digestion) [3]. Such high moisture contents would consume a large amount of energy for the drying process if employed as resources for thermo-chemical processing.

Biomass is derived from solar energy via photosynthesis. Under a good illumination condition, carbon dioxide in the atmosphere can be converted into organic materials or, in another way, the solar energy is stored as chemical energy, which existed as chemical bonds in the organisms [4]. The said chemical energy is released when these bonds are broken either via thermo-chemical or wet processing. This is an ongoing energy transfer from the sun and hence the sustainability of biomass resource could be ensured. As we have known, the total energy captured annually in biomass is more than that of the annual energy consumption globally [5]. On the other hand, biomass is clean as it is carbon neutral. On the view of carbon network, the net emission of carbon dioxide into the environment during the harvesting of energy from biomass is zero. The final products of conversion of biomass (CO_2 and H_2O) are originally absorbed into the plants from the atmosphere during photosynthesis. The conversion of biomass also has less harmful releases such as NO_x and SO_x compared with fossil fuels [6].

However, the characters of biomass also create many barriers during its actual application. On the aspect of species diversity, biomass usually does not behave as steady as fossil fuels, which causes a lot of difficulty during project planning stage including gasifier type, plant size and the way of energy output. On the other hand, the varieties of biomass resource also lead to different heating values and moisture contents. Compared with other energy carriers, biomass has much lower heating values. Taking wood and wheat straw as examples, their lower heating values are only 18.6 and 17.3 MJ/kg, respectively, while the lower heating value of coal is as high as 23–28 MJ/kg [2, 7]. The reason for this disparity is that the oxygen content of biomass carbohydrates is very high while the combustible elements such as C and H are low. In addition, the intrinsic moisture content in biomass is also very high, which requires more energy for drying before further processes take place [3]. Hence, use of biomass requires the complexity in material handling, pre-treatment and the design of processing facilities [3]. For the purpose of transportation and collection, biomass is unlike any other renewable resources (solar, wind, hydropower) where it is able to be stored directly and transported somewhere else. However, biomass is highly dispersed in regional distribution and the low volumetric of biomass makes it a bit more difficult for the collection and transportation. Therefore, small-scale gasification unit operated in small communities with abundant biomass resource or domestic waste would be the way out in future.

2.2. General conversion technologies of biomass except gasification

For the utilization purpose, the conversion technologies of biomass could be classified in three categories: mechanical extraction; thermo-chemical conversion; and biological conversion, as illustrated in **Figure 1** [3, 8]. Among them, direct combustion, gasification and pyrolysis are considered as the thermo-chemical processes; fermentation and anaerobic digestion are regarded as biological conversion.

2.2.1. Direct combustion

The direct combustion of biomass is widely applied in small-scale cooking and domestic heating by converting chemical energy stored in biomass into heat [9]. In modern industrial technology, combustion is also employed in large-scale applications to produce mechanical power and electricity with the aid of boilers, steam turbines and turbo-generators. The temperature range of biomass combustion is within 800–1000 °C. Materials with the moisture content higher than 50 wt% are not suitable for combustion processes [3]. The net efficiency of electricity generation from biomass combustion varies between 20 and 40% [8]. The efficiency could be improved either by scaling up the system to over 100 MWe or co-firing with coal (<10 wt% by weight) [10].

2.2.2. Pyrolysis

Pyrolysis is a thermo-chemical process, in which biomass decomposes into fuel gas, bio-oil and solid char in the absence of oxygen. The selectivity leading to different types of products could be controlled by manipulating the operating conditions (temperature and residence time). Low temperatures (<500 °C) and long residence time favor the production of solid char

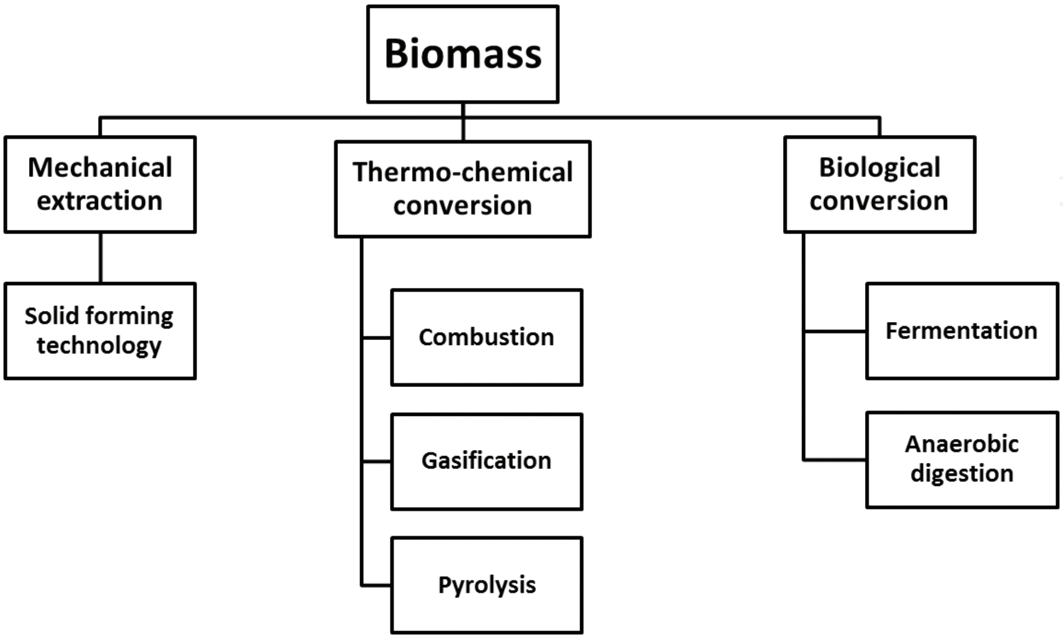

Figure 1. The main processes for the biomass conversion technologies [3].

(up to 35 wt% yield), while high temperatures (700–1100°C) and short reaction time favor the production of gases (up to 80 wt% yield) [11]. Bio-oil production is normally favored at 500°C, with very short retention time (<1 s) [12].

2.2.3. Fermentation

Fermentation is a bio-chemical process which is used for the production of about 80% of the world's ethanol [13]. The main process of fermentation involves using microorganisms to convert sugars into ethanol under a warm and wet environment. The sugar is typically obtained from the mechanical handling (crushing and mixing with water) of sugar-rich crops, such as sugar cane and sugar beet. However, the high cost of sugar-rich crops has diminished its proportion of utilization in fermentation. The starch-based biomass is also commonly used for ethanol production. However, it requires an extra step to convert starch into sugar by enzymatic reactions.

2.2.4. Anaerobic digestion

Anaerobic digestion involves using anaerobic microorganisms to convert biomass into biogas (CH_4 and CO_2 as the main gaseous products) by means of decomposition. Under the anaerobic environment, the organic material in biomass is decomposed into usable-sized molecules, such as sugar, as the first step. The sugar molecules is then converted into organic acids and further decomposed to CH_4 gas. This process has been proven as a commercially feasible technology and is widely applied in the rural areas of China.

3. Technologies of biomass gasification

Gasification process converts biomass, a low-energy density material, into a gaseous product (LHV at 4–11 MJ/N/m^3), which is a mixture of CO, H_2, CH_4 and CO_2 [10]. Gasification is a partial oxidation process and it is commonly operated at 800–900°C for biomass gasification [2]. In some cases, steam is also used as the gasification agents. The gaseous products from the gasifier can be utilized in gas engines or gas turbines for the generation of electricity. In terms of economics, it has also been proven that the performance of a biomass gasification plant with a combined cycle gas turbine (CCGT) is comparable to that of a conventional coal power plant [7], if not better.

3.1. Types of gasifiers

The gasifier, as the principle component of a gasification plant, actually provides a space for biomass and gasification agent being mixed to a certain extent, in some cases with catalysts or additives [14]. The different selection of gasifiers is actually responsible for keeping steady the production of syngas regarding the variations of biomass. Literature shows that gasifiers could be categorized into three main types: fixed bed gasifiers, fluidized gasifiers and the entrained flow gasifiers [15].

3.1.1. Fixed bed gasifier

Fixed bed gasifiers is the traditional approach applied for biomass gasification and generally operated around 1000°C. An alternative name for the fixed bed gasifier is "moving bed reactor". This is due to the movement of the biomass material in the main flow direction with very slow flowrate. The fixed bed gasifiers could be principally classified as updraft (countercurrent) and downdraft (co-current) due to the different airflow direction [14].

In an updraft gasifier (shown in **Figure 2**), the biomass material is fed from the top of the reactor, while the gasification agent enters from the bottom. The gasification agent flows through the bed of ash and biomass. The gas generated is exhausted through the top. For the reaction, the gasification agent meets the bottom char at first and achieves a complete combustion and raises temperature to c.a. 1000°C with production of H_2O and CO_2. This hot gas dries the incoming biomass near the top of the vessel and provides heat for pyrolysis of the descending biomass as well as percolates through the unreacted char bed to produce H_2 and CO [15]. In this gasification system, the product gas is withdrawn from the low temperature zone; thus, the product would be contaminated with significant amount of tars. If the product is used for further downstream applications like fuel in combustion engine electricity generator, a set of cleaning processes for tar removal is essential. However, the cleaning processes require intensive operation and establishment; therefore, the application of updraft gasification is not suitable for internal combustion engines [1].

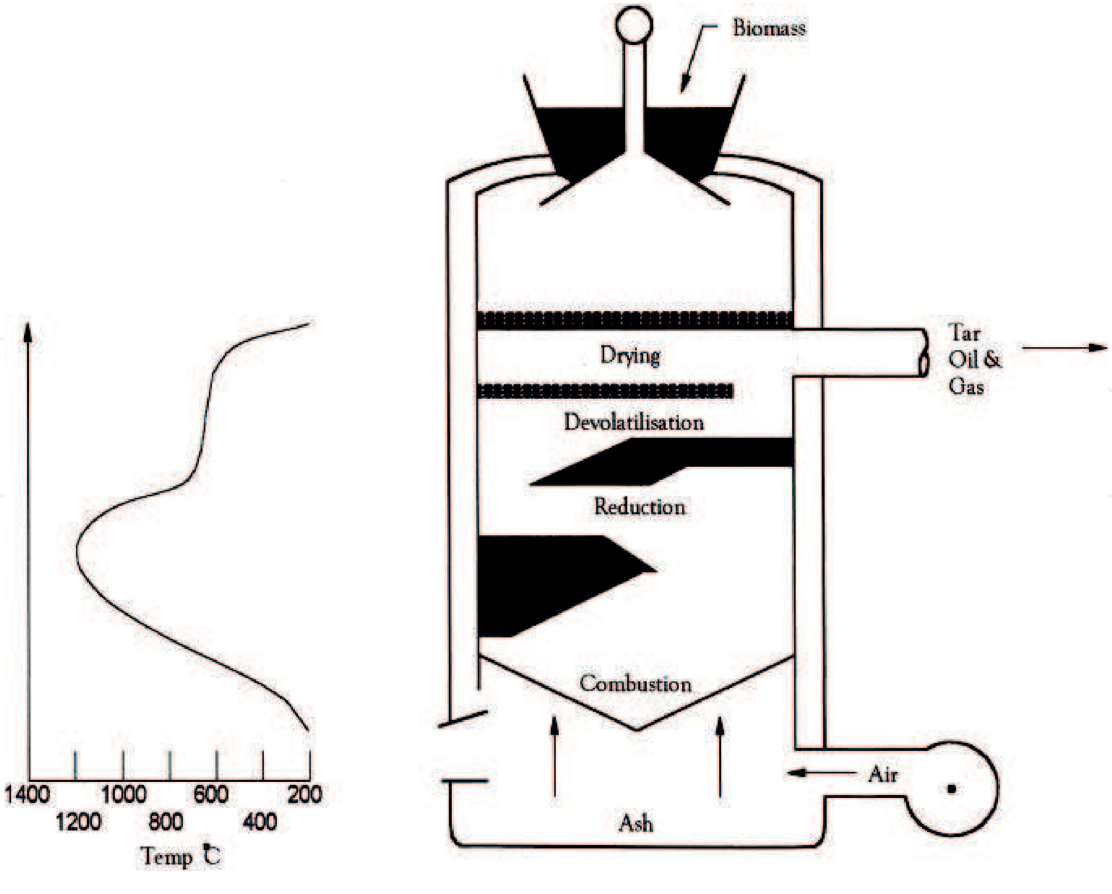

Figure 2. Schematic of updraft gasifier [16].

For the downdraft gasifier (shown in **Figure 3**), both biomass and gasification agent flow into the vessel from the top. At the "throated" area, where air or O_2 is fed into system with homogeneously distribution. The temperature could rise to around 1200–1400°C, which leads to both combustion and pyrolysis of the fuel. The produced hot gases will then be reduced to H_2 and CO as the main components after passing the hot char bed and will leave the gasifier unit at temperatures of about 900–1000°C. The tar content of the product gas is lower than that of the updraft gasifier, but the particulate content of the gas is higher [16]. Hence, the downdraft gasifier is suitable for downstream applications like internal combustion engines electricity generator. However, the product is withdrawn at a relatively high temperature; it needs to be cooled to acceptable range before further usage.

3.1.2. Fluidized gasifier

In the fluidized gasifier, the gasification agent enters the bed at a relatively fast rate from the bottom of the vessel and exits from the top. This kind of gasification features uniform temperature distribution in the bed zone. The consistency of temperature is obtained by the application of air-fluidized bed material, which ensured the intimate mixing of fuel, hot combustion gas and bed material. Currently, three main types of fluidized gasifiers are widely used [15], bubbling fluidized bed (BFB), circulating fluidized bed (CFB) and dual fluidized bed (DFB).

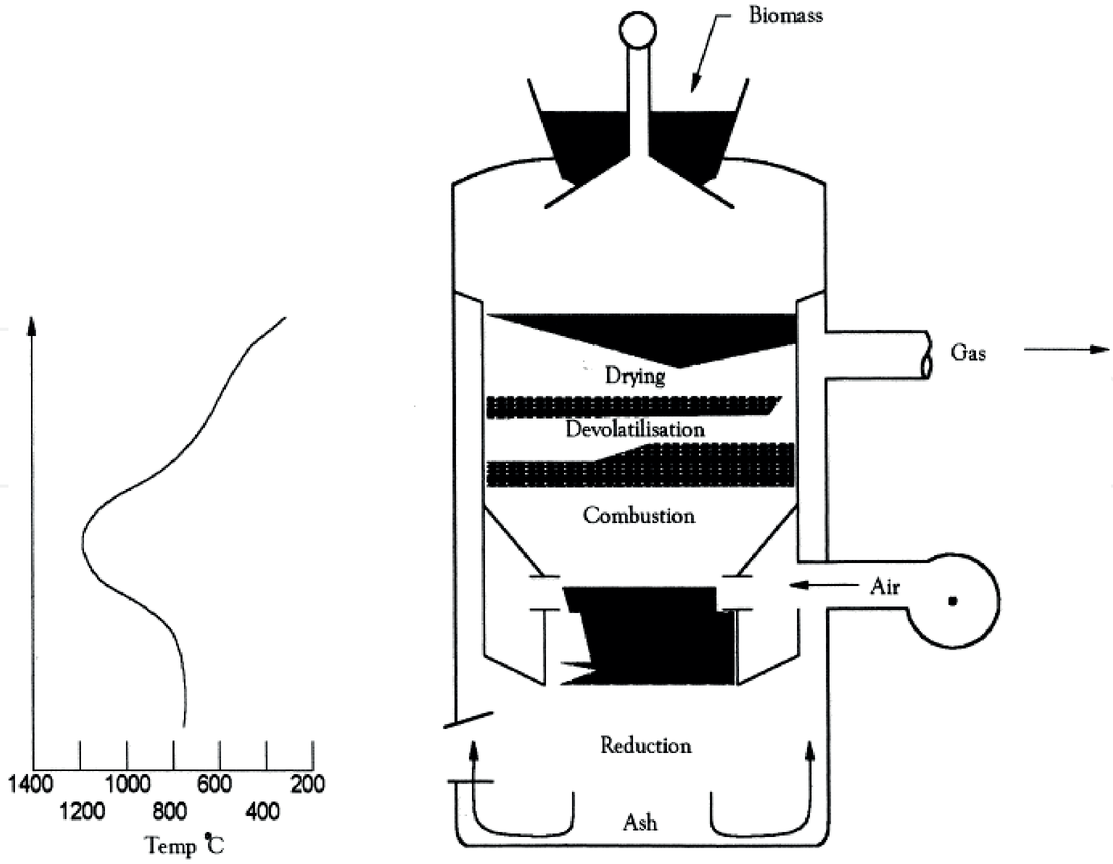

Figure 3. Schematic of downdraft gasifier [16].

BFB gasifier applies inlet from the bottom and moves the bed of fine-grained materials. The bed temperature is maintained at 700–900°C by manipulating the ratio of fed biomass and gasification agent [16]. The flowrate of gasification agent is set to be slightly greater than the minimum velocity of fluidization of the bed material. The biomass is decomposed into char and gas products with a low tar percentage.

The CFB gasifier consists of two principle units: the gasifier unit and the circulation unit, as shown in **Figure 4**. The bed material and char in this type of gasifier is circulated between the reaction chamber and the cyclone separator, where ash and hot gas could be separated. The bed material is fully fluidized and leaves from the first unit, and then it is sent back by the second unit. The solids are moving in the solid circulation loop in greater extent of fluidization with higher residence time. Moreover, its operation pressure is also relatively higher.

Dual fluidized bed (DFB) gasifiers consist of two separated fluidized beds which are used for pyrolysis process and combustion process [14]. The first bed is operated as a pyrolysis reactor and it is heated by the second reactor with hot circulated bed material. The second reactor provides heat by burning char provided from the first reactor. The bed material plays an important role as a heat transfer medium, which prevents the dilution of the hot gas product.

3.1.3. Entrained flow gasifier

Entrained flow gasifiers are generally classified into two types: top-fed gasifier and side-fed gasifier (shown in **Figure 5**), which is according to how and where the fuel and gasification agent is fed. This type of gasifier is suitable for integrated gasification combined cycle (IGCC) plants. It is extensively applied in large-scale gasification and is widely employed for coal, biomass and refinery residues. The gasification temperature of this kind of gasifier could reach 1400°C with a pressure range of 20–70 bar [14]. This high temperature could accelerate tar cracking and mitigate severe tar issue of biomass gasification. However, this kind of high

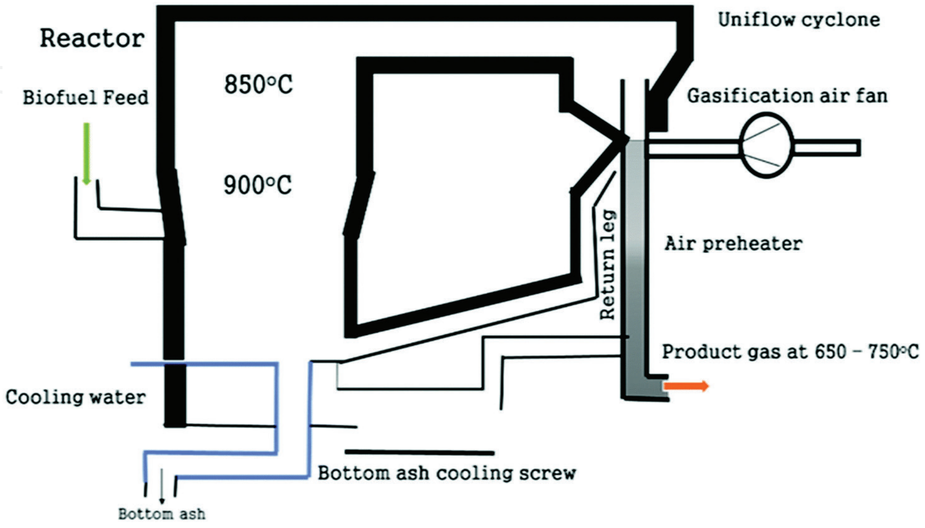

Figure 4. Schematic diagram of circulating fluidized bed gasifier (CFB) [17].

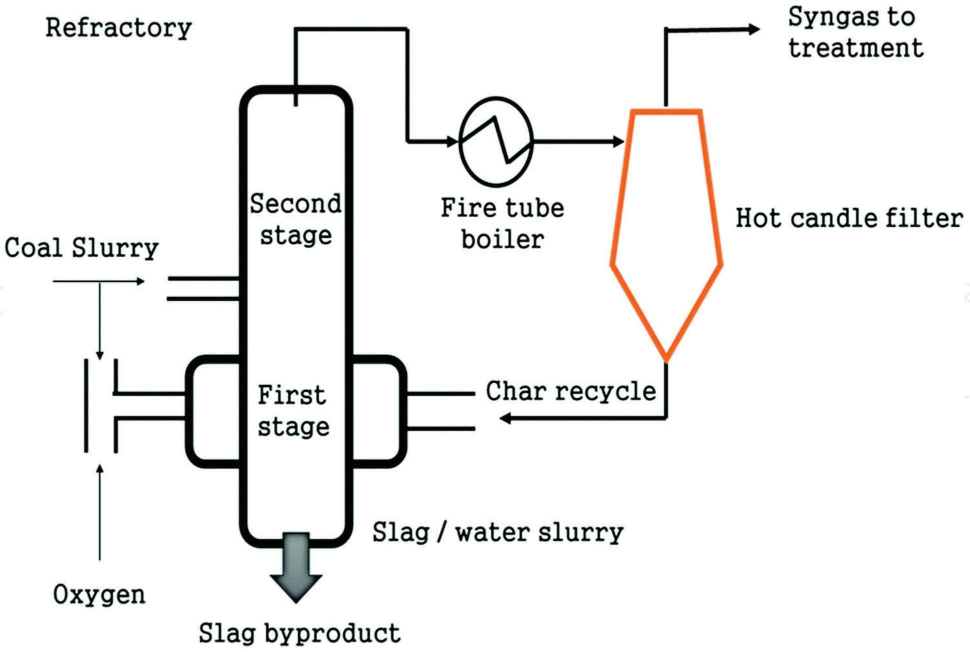

Figure 5. Schematic diagram of an entrained flow gasifier (side-fed) [17].

temperature gasification requires a finely fed biomass material (<0.1–0.4 mm), which makes this process unsuitable for most biomass materials (such as wood). Therefore, this process is not considered in detail.

3.2. Tar removal

Tar is a major inherent problem in biomass gasification; it can cause a lot of issues such as equipment blockages, lower system efficiency, poor quality gas output and increased maintenance. Tar consists of a group of very complicated mixtures with more than 200 components. Several key components include benzene, toluene, single-ring aromatic hydrocarbon, naphthalene and so on. The formation of tar was due to lower temperature of gasification. It was confirmed that increased temperature of gasification could reduce the content of tar in the outflow and it was believed that higher temperature can promote the cracking of tar [18]. Currently, there are a lot of methods that could be employed for tar minimization, and they can be divided into two categories depending on where the removal technology is applied.

Firstly, tar could be removed inside the gasifier by choosing an appropriate operation parameter or using a catalyst. Previous research indicates that both particle size and surface area-volume ratio of loading feedstock have a significant effect on tar yields [19, 20]. It showed that the gasification of pine saw dust only produced 0.4 wt% of tar at 700°C when the particle size was smaller than 75 micron. While if particle size increased to the range of 600–1000 micron, the tar yield would be higher than 10 wt% even at 900°C. From the view of thermal kinetics, the gasification of larger size of particles needs to overcome greater resistance of thermal conductivity; in other words, it needs more time to complete heat transfer and the devolatilization of biomass materials. On the other hand, small particle size also can contribute to a fast diffusion of the gasification agent and shorten time duration of the whole process. However, the small size of feedstock particle required much more energy input during the biomass pre-preparation process. In addition, it is also effective by applying an optimal design of gasification reactor. A collaborative project between Switzerland and India demonstrated that an open-top fixed bed would produce much less tar and particulates than a closed-top fixed bed [15]. The reason behind this is that the open-top fixed bed could introduce dual air from the top and nozzles actually increase the residence time for degrading tar.

Secondly, in many processes, tar is removed as a downstream step after gasification, including mechanical method, thermal cracking and catalysis. The details of some common technologies have been listed in **Table 1**. Wet gas cleaning method has been accepted at an early stage. Its equipment investment is relatively low and the operation is also easy to handle. But this technology would also create a lot of waste water and bring serious environmental issues. Therefore, dry gas cleaning method becomes more widespread via various types of filters, rotating particle separators and dry cyclones. Although the dry method avoids waste water issues, its efficiency of tar removal is not good enough if compared with wet method. On the other hand, the replacement, renewal or disposal of filter materials reduces the financial effectiveness of the entire gasification system. This similar situation could also be applied to thermal cracking method and higher operation temperature requires much more energy input.

In the recent two decades, catalytic cracking has attracted more and more attention and has already become the central branch of research. Catalytic cracking is more like a downstream catalytic reforming unit and could easily degrade comparative stable tar to a significant extent. The previous research indicated that the catalytic cracking unit could promote gas yield by 10: 20 vol% and increase the heating value by c.a. 15% [23]. Ni-based catalyst is applied most widely and especially preferred for hydrogen or syngas production. Nickel has a very good catalytic activity and a preferable price advantage. While the application of Ni catalysts needs to avoid extremely high heavy-tar content flue gas, which will form a serious carbon deposition over the catalyst surface and lead to a quick deactivation. The other transition metal-based catalysts, such as co, Fe and cu, also have similar issues. Thus, some applications used the two-stage catalytic reforming process: the first stage used dolomite to

Method	Technique used	Details/examples
Wet gas cleaning [21]	Usage of mechanical device or equipment	Electrostatic precipitator, wet cyclone, wet scrubber
Dry gas cleaning [21]	Usage of mechanical device or equipment	Cyclone, rotary partial separator, fabric filter, ceramic filter, activated carbon adsorber, sand filter
Thermal cracking [21, 22]	Application of high temperature with long residence time	Maximum tar destruction was found at 1250 ° C and 0.5 s
Catalytic cracking [21]	Usage of appropriate catalyst	Tar cracking catalysts are divided into five major groups, namely Ni-based, non-Ni-based, alkali metal-based, acid catalysts, basic catalysts and activated carbon-based catalysts

Table 1. Post-gasification tar removal methods [15].

reduce the concentration of tar to a certain level and then the second stage employed transition metal-based catalysts bed for near-completed removal of tar. But this kind of two-stage reforming process would increase operational cost clearly. In the research scale, some people applied noble metal catalysts and achieved highly catalytic activity as well as better carbon-resistant ability. However, high cost and low accessibility still restrain the wide utilization of noble metal-based catalysts before the technical breakthrough of catalyst regeneration. Alkali metal catalyst is an alternative with good catalytic performance and also exhibits outstanding coke resistance. It is due to this that alkali metal could suppress directly decomposition of hydrocarbon by avoiding quick adsorption of tar components. But alkali metal evaporates under high temperature gasification condition. In many practical process, biomass ash has been reused as an alkali catalyst because most biomass contains abundant alkali metal elements and it is believed that this type of natural catalyst with properties of low cost and disposability should attract special attention

In the future, the development of novel and economic catalysts is still a promising option for tar elimination. At this stage, the biggest barrier for the catalyst development is the unclear mechanism of complex tar reformation. Therefore, employing model tar components for the study of coke formation mechanism is still very important and will be an effective way out. For the catalyst synthesis, composite catalysts with different components should be considered. It is also favored that if the developed catalyst could be applied under a low temperature condition (400–600°C), it will minimize cost effectively in a practical operation by using waste heat. In addition, the practical application of the catalyst also requires solving many scale-up issues, such as variation of temperature and pressure, impurities, fly ash and catalyst collapse

4. Socio-environmental impact

Biomass gasification could exploit an abundant variety of waste materials as feedstock such as agricultural residues and food waste. It actually achieves resource recovery and mitigates CO_2 emission as an environmental benefit. However, power generation from biomass gasification poses several key hazards and socio-environmental impacts.

4.1. Health and safety hazard

One of the major risks is the potential emission of toxic producer gas and particulates. The production of CO, SO_x, NO_x and volatile organics involves incomplete combustion and oxidation of trace elements in feedstock [24]. As one of the most dangerous constituent, CO can permeate into human blood system and combine with hemoglobin to stop oxygen adsorption and distribution. Long-term exposure to CO causes asthma, lung inflammation, schizophrenia and cardiac defects. Toxic gases like SO_x, NO_x and volatile organics could also destruct inhalation, ingestion and dermal system of human [25]. Hence, the entire gasification process should prevent leakage and an efficient gas clean-up system is essential. In recent years, the hazard of particles emission ($PM_{2.5}$) attracts public attention increasingly, due to its carcinogenicity. $PM_{2.5}$ particles can adsorb many soluble organic compounds including alkanes, carboxylic acid and aromatic compounds, which will damage human organs like lung and liver [26]. For control of these particles' emission, an efficient gas clean-up system with conditioning unit is necessary, as well as avoiding insufficient combustion and gasification. In addition, ashes and condensate from biomass gasification also contribute to environmental problems if they are not disposed properly. Especially the toxic condensate with high content of tar is very difficult to deal with and has higher risk of hazards.

Besides the risk of health hazards and environment, gasification is also confronted with risk of fire and explosion. Because the gasification system is normally operated at relatively high temperature and pressure, it also produces flammable gas mixture with a great portion of hydrogen gas. However, explosion is not easy to be created even air leakage into the gasification system, which could raise a partial combustion. This will only lead to lower quality and higher temperature of producer gas [1], unless there is a large amount of air which enters with feedstock from the feeding system or massive leakage of flammable outlet gas occurs.

4.2. Social impact

The development of bioenergy will need a lot of land for energy-growing crops. This requirement will clash with other applications of farmland, like food and other cash crops. The competition with food agriculture must be intensive. The food shortage is still a big global issue nowadays. According to the data of World Hunger Education Service, the world's hungry population was 925 million in 2010. Besides this, the world population is still growing by rate of 1.2%. The natural disasters and climate change also affect agriculture. These three factors will decide that the demand of the farmland in the future will expand. Thus, transferring farmland for energy crop planting in a large scale would be difficult, especially in Europe.

4.3. Ethical issues

The bioethics report by Nuffield council points out that deployment of bioenergy should not violate the human right which is reflected in the Universal Declaration of Human Right (UDHR). In the UDHR, it states that every people can share and enjoy the protection of the moral and the any product from any scientific, literary or artistic which is owed by them. There are a lot of ethical issues referring bioenergy, like human rights, solidarity and sustainability. Biofuel production application will require land use, water supply and labor from local community. Destruction to the land and local ecosystem cannot be avoided. Also, land displaced for energy crops will not only bring food price increases; some local residents may face migration. All these could be regarded as the actions, which violate the human rights of citizens and non-citizens.

5. Conclusion

The commercialization of biomass gasification is still at the early stage of development and leaves a lot to be desired on the technology aspect. In particular, large-scale utilization of biomass still needs to overcome the challenge of biomass collection and transportation, due to its low energy density. However, in some small communities, with large amount of local biomass materials, using biomass to replace polluting fossil fuels is a competitive way for providing reliable and clean power and heat.

This chapter provides the current technique status and development condition in China. It concludes that the gasification of biomass waste with distributed power generation would be a potential market. The properties of biomass feedstock have been analyzed and both advantage and disadvantage of biomass utilization were pointed out. Consequently, highly dispersed property and the low volumetric of biomass limit its large-scale application. Apart from that, this chapter also detailed some common types of gasifiers, except some emerging technologies, for meeting special requirements such as supercritical water gasification (SCWG) for wet biomass and plasma gasification for toxic organic waste. The tar issue, one of the most baffling problems in biomass gasification, is introduced briefly as well as its removal technologies. In our view, the socio-environmental impact is not the primary factor for restriction of biomass gasification development, while an objective financial return can actually attract investors and accelerate commercialization; in the meantime, it will also contribute to other technical breakthroughs.

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Chapter 7

Biomass Gasification: A Review of Its Technology, Gas Cleaning Applications, and Total System Life Cycle Analysis

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.70727

Abstract

Gasification technology presents one option for energy-conversion technique from woody biomass contaminated by radionuclides released in March 2011 during the Fukushima Dai-ichi Nuclear Power Plant accident. The gasification process converts carbonaceous materials into combustible gases, carbon dioxide, and residues. Owing to their small-scale distributed configuration, woody biomass gasification plants are suitable for gasifying Japan's biomass and have been installed increasingly in Japan recently. This chapter reviews current trends of gasification and life cycle assessment (LCA) of total systems, including gas cleaning.

Keywords: biomass gasification, gas cleaning, desulphurisation, radioactive materials, life cycle assessment

1. Introduction

Lignin is a crosslinked macromolecular material based on a phenylpropanoid monomer structure. Vascular plant species such as fern-related plants, gymnosperms, and angiosperms have lignin structures. Woody plants such as softwoods and hardwoods are composed, respectively, of 25–35% and 20–25%. Recently, small-scale woody biomass power generation plants have been installed increasingly in Japan. Such plants are suitable for gasifying Japan's biomass because of their small-scale, distributed characteristics.

To utilise small-scale biomass more effectively, biomass plants must be installed near energy source and demand sites in order to shorten transport distances. This is especially effective for small-scale woody biomass plants. Here small scale is defined as a plant scale of at most

2 MWe. Power generation in such small-scale plants requires biomass gasification technology in order to obtain higher thermal efficiency. Gasification is a process that converts carbonaceous materials into carbon monoxide, hydrogen, carbon dioxide, and gaseous hydrocarbons (producer gas). Producer gas can be supplied as fuel to internal combustion engines and power generators. To maximise the efficiency of woody biomass conversion, producer gas should be utilised not only for power generation but also for thermal production from the producer gas' sensible heat. Cogeneration system for heat and power production is called combined heat and power (CHP).

Recently, many kinds of biomass gasification combined heat and power (BGCHP) systems have been developed (mainly in Europe). These micro/small-scale CHP systems can be connected and integrated to achieve an appropriate plant scale according to the biomass supply and heat and power demands. Further description of BGCHP is presented in section 2.4.

Woody biomass in Fukushima was contaminated by radionuclides released between 12 and 31 March 2011 due to the Fukushima Dai-ichi Nuclear Power Plant accident. To safely utilise the contaminated woody biomass in Fukushima as biomass gasification (BG) fuel, the radioactivity of products and by-products such as offgas and ashes in ash bins and on filters must be investigated.

This chapter reviews current trends of gasification and life cycle assessment (LCA) of total systems, including gas cleaning. Previously, there have been no reviews of small-scale gasification process for hydrogen production and CHP and no critical review of LCA of BG processes. Gas cleaning is one of the most important processes in BG systems for controlling contaminants in producer gases and preserving the catalysts of fuel cells and gas engines.

2. Gasification technology

A biomass gasifier is comprised of four reaction zones, i.e. drying, pyrolysis, combustion, and reduction. The produced gas (syngas) contains impurities to be cleaned utilising a bag filter, activated carbon, scrubber, etc. This chapter describes the fates of two contaminants, radionuclides and sulphur, during the gasification process. The radioactivity of caesium-137 (^{137}Cs) and caesium-134 (^{134}Cs) in fly ash over a bag filter was observed using a germanium semiconductor detector. The fate of sulphur was also reviewed because sulphur often triggers fuel cell catalyst poisoning and gas engine erosion. The LCA of a total system based on the energy profit ratio and environmental impact is then reviewed.

2.1. Biomass feedstock

Biomass feedstocks are classified based on several factors: moisture content, material, and form, as presented in **Table** 1. Biomass is broadly divided into three groups: dry, wet, and other. Dry biomass is classified as woody or herbaceous and wet biomass as sludge/excreta, common food, or other. Each classification has three sub-categories: waste, unutilised, and produced.

Moisture	Classification	Wastes	Unutilised	Produced
Dry	Woody	Construction wastes, Timber offcuts	Forest thinnings, Remaining forest timbers, Damaged trees	Short-rotation woody crops (eucalyptus, willow, etc.)
	Herbaceous		Crop residues (rice / wheat straw, rice husk)	Grasses (Napier grass, sorghum, Miscanthus etc.)
Wet	Sludge /Excreta	Sewage sludge, Livestock excreta		
	Common food	Food-processing wastes, Kitchen wastes		
Other	Other	Molasses, Waste food oil	Landfill gas	Cultivated maize, Cultivated sugar cane

Table 1. Classification of biomass feedstocks.

Among these, dry woody/herbaceous biomasses are used as feedstocks for BG plants in Japan. For instance, woody biomasses contain waste woods (construction wastes and timber offcuts) and unutilised woods (forest thinnings, remaining timbers, and damaged trees) composed of cedar, cypress, pine, etc. Short-rotation woody crops (eucalyptus, willow, etc.) are categorised as produced woods. Energy crops such as willow are expected to be cultivated in land fallow and used as biomass because non-food-producing farmlands have been recently abandoned in Japan [1].

For unutilised herbaceous biomass, crop residues such as rice/wheat straw and rice husks [2] are available, while for produced herbaceous biomass, grasses such as Napier grass, sorghum, and Miscanthus are usable. Above all, rice husks contain abundant silica. The ash by-product from gasifiers has potential use in nanomaterials [3].

2.2. Gasifier

There are various kinds of gasifiers (e.g., fixed-bed, fluidised, pressurised, etc.). This chapter describes the simplest fixed-bed gasifiers. Fixed-bed gasifiers have a long history and have established confidence through experience with small-scale biomass gasification reactors [4]. **Figure 1** schematically illustrates fixed-bed updraft and downdraft gasifiers. The flows of biomass and producer gases are counter-current for updraft and co-current for downdraft. The gasification reaction is comprised of four main reaction zones. Heat released during the combustion process is used for drying, pyrolysis, and reduction processes in the gasifier.

For both gasifier types, biomass fuels are supplied into each gasifier followed by a drying process. The dried biomass is then pyrolysed to release volatiles and gases. These products are combusted partially or completely using air fed with heat released from the combustion process. The gases, tars, and chars resulting after combustion are reduced in the reduction zone. The positional relationship of these processes is shown schematically in **Figure 2**.

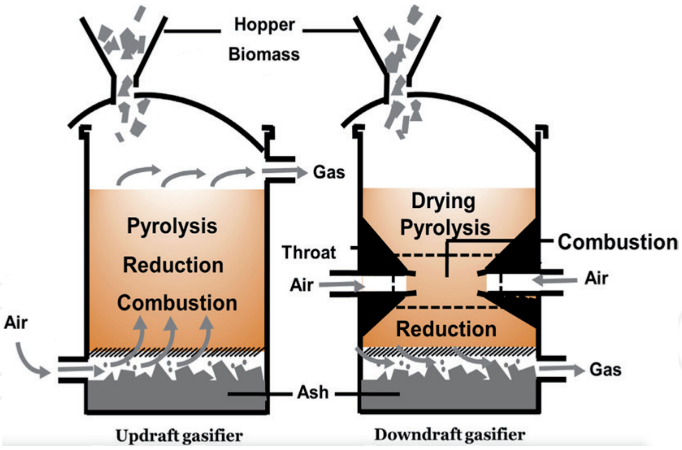

Figure 1. Schematic of updraft and downdraft fixed-bed gasifiers [5].

2.3. Gasification mechanisms

Gasification proceeds through many kinds of simultaneous or consecutive complex reactions. Reactions corresponding to each reaction zone are shown in this section. **Figure 3** represents several main reaction pathways in biomass gasification reactions. The reactions for each pathway (or reaction zone) are presented in **Table 2** based on the literature [7, 8].

2.3.1. Drying

Biomass moisture at ordinary temperatures becomes water vapour during the drying process at about 100–250 °C. The conversion occurs owing to heat transfer between hot gases from the oxidation and biomass in the drying zone [4]. First, the moisture on the biomass surface evaporates followed by inherent moisture evaporation. The vapour produced is used for reduction reactions in the reduction zone, including the water-gas reaction.

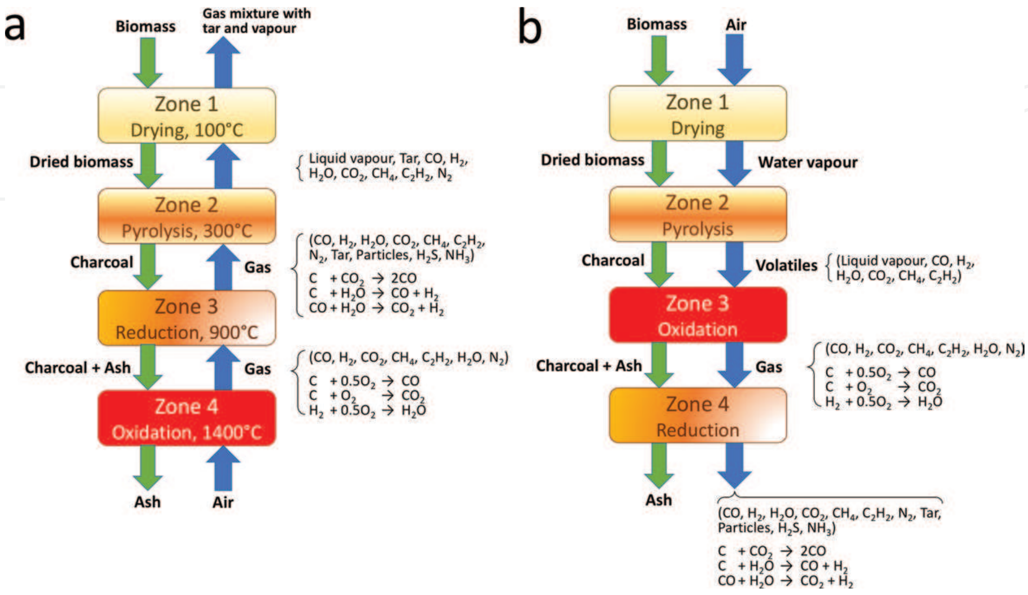

Figure 2. Conceptual diagram of multiple steps in fixed-bed (a) updraft and (b) downdraft gasifiers [6].

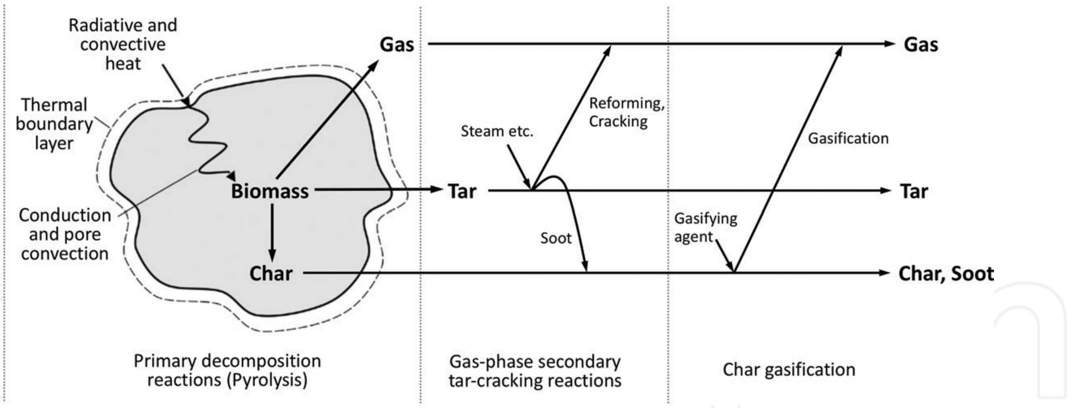

Figure 3. Biomass gasification pathway proposed based on Ref. [10, 11].

2.3.2. Pyrolysis

In the absence of oxygen, volatiles with weaker molecular bonds begin to be thermally decomposed at 200–240 °C; this continues up to 400 °C. The volatiles are vaporised to produce gases, tars, and chars. The chars are also pyrolysed with gas production and weight loss of about 30% [9]. Pyrolysis takes place owing to heat transfer from radiation, convection, and conduction to the biomass as shown in **Figure 3a**. The pyrolysis reactions are represented as Reaction (R1) in **Table 2**.

Name of reaction	Chemical reaction	$\Delta H^0_{r(298)}$ (kJ/mol)	$\Delta G^0_{r(298)}$ (kJ/mol)	No.
Pyrolysis	$C_xH_yO_z \rightarrow aCO_2 + bH_2O + cCH_4$ $+ dCO + eH_2 + fC_{2+} + \text{char} + \text{tar}$			(R1)
Partial oxidation	$C + 0.5\,O_2 \rightarrow CO$	−111		(R2)
Complete oxidation	$C + O_2 \rightarrow CO_2$	−394		(R3)
Steam-tar reforming	$C_nH_m + 2nH_2O \rightarrow (2n + m/2)\,H_2 + nCO_2$			(R4)
Hydrogenating gasification	$C + 2H_2 \leftrightarrow CH_4$	123.7	168.6	(R5)
Boudouard equilibrium	$C + CO_2 \leftrightarrow 2CO$	205.3	140.1	(R6)
Water-gas shift (WGS)	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41.47	−28.5	(R7)
Heterogeneous WGS	$C + H_2O \leftrightarrow CO + H_2$	130.4	89.8	(R8)
Steam reforming of methane	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	172.6	118.4	(R9)
Dry reforming of methane	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	−74.9	−50.3	(R10)
Ethylene	$2CO + 4H_2 \leftrightarrow C_2H_4 + 2H_2O$	−104.3	−111.6	(R11)
Ethane	$2CO + 5H_2 \leftrightarrow C_2H_6 + 2H_2O$	−172.7	−212.7	(R12)
Propane	$3CO + 7H_2 \leftrightarrow C_3H_8 + 3H_2O$	−165.1	−293.2	(R13)
Butane	$4CO + 9H_2 \leftrightarrow C_4H_{10} + 4H_2O$	−161.9	−376.7	(R14)
H_2S formation	$S + H_2 \rightleftarrows H_2S$			(R15)
H_2S-COS equilibrium	$H_2S + CO \rightleftarrows COS + H_2$			(R16)

Table 2. Chemical reactions occurring in biomass gasification (gasifying agent: steam).

2.3.3. Oxidation

Heat is released during the oxidation of gases and of gaseous volatiles and chars produced in pyrolysis under supplied air. The heat is used for drying, pyrolysis, and other endothermic reactions [4]. Partial oxidation (R2) and complete oxidation (R3) occur. Reaction temperatures are around 600–900 °C for partial oxidation and around 800–1400 °C for complete oxidation. Partial oxidation releases 111 kJ/mol of heat while complete oxidation releases 394 kJ/mol.

2.3.4. Reduction

During the reduction process, the char and tar produced from oxidation release gases at around 600–950 °C via several reactions. The typical reactions include the heterogeneous water-gas shift (HWGS: $C + H_2O \rightarrow H_2 + CO$) and water-gas shift reaction (WGS: $CO + H_2O \leftrightarrows CO_2 + H_2$). Via the endothermic HWGS reaction, char or tar reacts with water vapour (derived from biomass and air) to produce CO and H_2 at temperatures greater than 750 °C. The WGS reaction is an exothermic reversible reaction and has an equilibrium point for CO, H_2O, CO_2, and H_2 concentrations. The higher the reaction temperature, the greater the amount of gaseous products produced on the equation's right-hand side. Reduction is a totally endothermic reaction because the water-gas reaction is dominant.

2.4. Combined heat and power gasification

Gasification power generation systems are different in terms of gasifier type, gas cleaner for dust/tar/hydrogen sulphide removal (as described in sections 3.2 and 3.3), heat exchanger type, and power generator type (gas turbine, internal combustion engine, fuel cell, etc.). A BGCHP requires seven elemental processes: (i) pretreatment, (ii) storage, (iii) gasifier, (v) gas cleaner, (iv) gas cooler, (vi) gas engine, and (vii) power generator, as shown in **Figure 4**. BGCHP is a process that cogenerates heat and power from syngas produced in the gasifier. **Figure 4** shows a simplified schematic of BGCHP. Generally, biomass power generation from direct combustion has an efficiency of ca. 30% at most. However, via BGCHP, a total efficiency of ca. 85% is attained with thermal-load-following operation.

There are many kinds of small-scale gasifiers manufactured by European companies such as in Germany (e.g., Burkhardt [12], Spanner [13], Entrade [14], etc.), Finland (e.g., Volter [15]), and Sweden (e.g., Cortus Energy AG [16]).

2.5. Biohydrogen production via gasification

Biohydrogen via thermochemical conversion is obtained by gasifying woody biomass followed by a gas cleaning process. Biomass gasification typically yields producer gases such as H_2 (14–25%), CO (15–24%), CO_2 (12–15%), CH_4 (2.0–2.5%), H_2S (<100 ppmv), and COS (50 ppmv) [6]. For H_2 production, gas cleaning is required for gases other than H_2. Generally, CO is converted into H_2 and CO_2 with steam by a shift converter packed with nickel or nickel oxide catalysts.

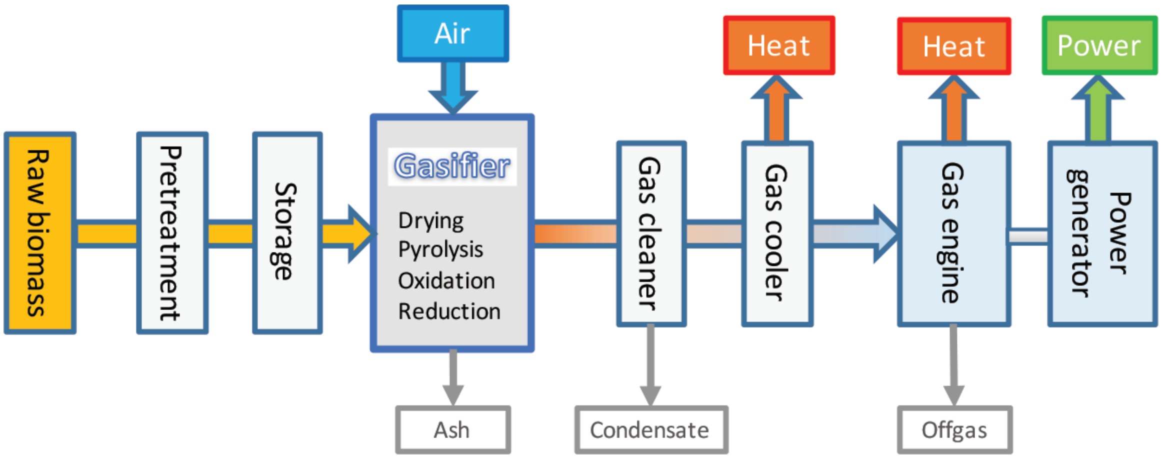

Figure 4. Flow diagram of power generation from biomass gasification.

3. Gas cleaning

3.1. Contaminants

Contaminants in syngas generally include particulate matter, condensable hydrocarbons (i.e. tars), sulphur compounds, nitrogen compounds, alkali metals (primarily potassium and sodium), hydrogen chloride (HCl), and radioactive nuclides. In this review, the sulphur compounds and radioactive nuclides in Fukushima, Japan are the focus.

Syngas ($CO + H_2$) has many uses ranging from heat and/or power applications (e.g., CHP) to many kinds of synthetic fuels and chemicals as shown in **Figure 5**. During production, each contaminant triggers process inefficiencies, including not only corrosion pipe blockages but also rapid and permanent deactivation of catalysts [17].

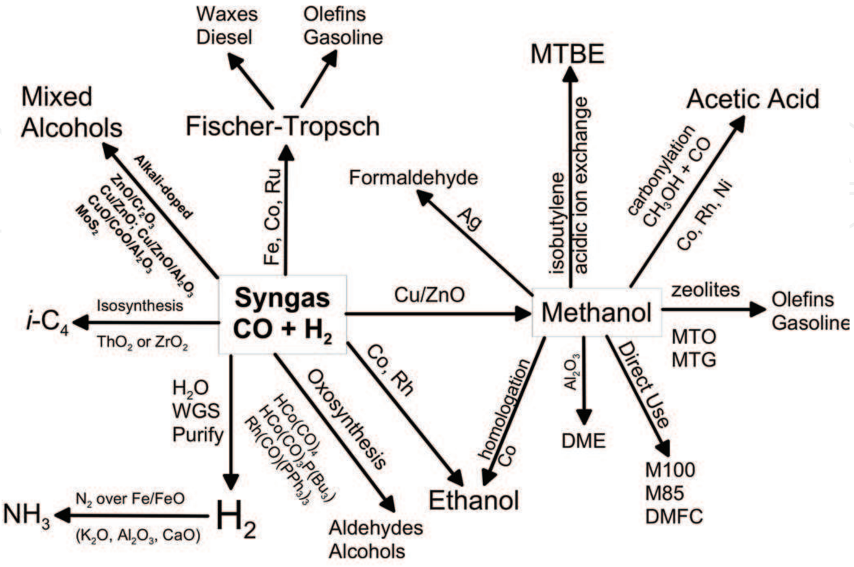

Figure 5. Different syngas transformation routes for synthesising fuels and other chemicals [18].

Contaminant levels depend on feedstock impurities and the syngas generation method used. The level of cleaning required may also be influenced substantially by end-use technology and/or emission standards [17]. **Table 3** shows the syngas cleaning requirements for some typical end-use applications.

3.2. Sulphur

There are several gas cleaning technologies: absorption, adsorption, conversion, and biological transformation. Wiheeb et al. has described the adsorption process of H_2S. **Table 4** presents a summary of the characteristics of sulphur removal technologies [19]. In gasification processes, absorption and adsorption are employed well as gas/bag filter and scrubber processes, respectively.

3.2.1. Fate of sulphur during gas cleaning over adsorbents

The fate of sulphur during the gasification of lignin slurry was investigated by Koido et al. [20]. In their study, hydrogen sulphide removal from bio-synthesis gas over a nickel oxide catalyst supported by calcium aluminate ($NiO/CaAl_2O_4$) was investigated at high temperatures. They investigated the sulphur balance of the process at different operating temperatures (T = 750–950 °C), moisture contents of the lignin slurry (MC = 73–90 wt%), and catalyst loadings (CL = 0.00–0.61 g-catalyst/g-feedstock). The sulphur balance was 0.79, 0.04, 0.003, and 0.378 mmol/g-lignin for the gas, char, water-soluble fraction, and $NiO/CaAl_2O_4$ catalyst surface, respectively.

3.3. Radionuclides

3.3.1. Introduction

Radionuclides including ^{134}Cs and ^{137}Cs were released into the environment after the Fukushima Dai-ichi Nuclear Power Plant accident in March 2011. After the accident, decontamination was

Contaminants	**Applications**			
	Methanol synthesis (mg m^{-3})	**FT synthesis (μL L^{-1})**	**Gas turbine (μL^{-1})**	**IC engine (mg m^{-3})**
Particulate (soot, dust, char, ash)	<0.02	Not-detectable	<0.03 (PM_5)	< 50 (PM_{10})
Tars (condensable)	–[a]	<0.01[b]	—	—
Tars (heteroatoms, BTX)	<0.1	<1	—	<100
Alkalis	—	<0.01	<0.024	—
Nitrogen (NH_3, HCN)	<0.01	<0.02	<50	—
Sulphur (H_2S,COS)	<1	<0.01	<20	—
Halides (primarily HCl)	<0.1	<0.01	1	—

[a] Data are not available in the original literature.

[b] All values are at STP unless explicitly specified.

Table 3. Syngas cleaning requirements for some typical end-use applications [17].

Classification [19]	Technology [19]	Characteristics [19]	Reference
Absorption (wet desulphurisation)	Conventional absorption process	• Absorption has been used in petroleum and gas industries to remove H_2S and CO_2 from sour natural gas and refinery gas. • The removal is called gas sweetening, which involves transferring of H_2S from a gaseous phase (feed) into a liquid phase (solvent). • The conventional process has higher sulphur removal but requires strict pH control of chemical concentrations and wastewater treatment, which could cause corrosion problems.	Taheri et al., [21]
	Membrane reactor	• Membranes can be used to purify biogas. • Membranes are not usually used for selective removal of H_2S, but rather to upgrade biogas to natural gas standards.	Dolejš et al., [22]
Adsorption (dry desulphurisation)	Carbonaceous adsorbents	• Activated carbon has a high specific surface area of more than 1000 m^2/g. • The surface area, pore volume, and surface chemistry promote numerous catalytic reactions.	Kazmierczak-Razna et al., [23]
	Metal oxide adsorbents	• The removal of H_2S at high temperature has received much attention owing to its potential in reducing H_2S concentration to 10 ppm. • Metal oxide: FeO, Cu_2O, MnO, ZnO CoO, NiO and MoO, alkaline earths (CaO, SrO, and BaO), and alkalis (Li_2O, K_2O and Na_2O). • The process has higher thermal efficiency through sensible heat utilisation and easy treatment of wastewater but requires either catalyst exchange or regeneration.	Abdoulmoumine et al., [24]
Conversion	Claus process	• The Claus process is used in oil and natural gas refining facilities and removes H_2S by oxidising it to elemental sulphur. • Removal efficiency is about 95% using two reactors and 98% using four reactors.	Ibrahim et al., [25]
	Selective catalytic oxidation	• The selective catalytic oxidation of H_2S into elemental sulphur is one of the treatment methods employed for the removal of H_2S from Claus process tail gas. • The catalytic oxidation of H_2S can be performed above or below the sulphur dew point (180 °C).	Tasdemir et al., [26]
	Liquid redox sulphur recovery	• Liquid-phase oxidation systems convert H_2S into elemental sulphur through redox reactions by electron transfer from sources such as vanadium or iron reagents.	Kim et al., [27]
Biological transformation	Biological methods	• Microorganisms have been used for the removal of H_2S from biogas. • Ideal microorganisms would have the ability to transform H_2S to elemental sulphur.	Tóth et al., [28]

Table 4. Characteristics of each sulphur removal technology [20].

implemented in resident areas, and was completed over all residential area surfaces at the end of March 2017 [29, 30]. However, for utilisation of Fukushima's forest resources, which are contaminated by radioactive nuclides, utilisation of woody biomass as fuel for bioenergy production from gasification (such as heat, power, hydrogen, etc.) in the near future is a possible option. For this purpose, the mass balance of radionuclides must be revealed.

In particular, ^{137}Cs is almost distributed in argilliferous soils and fallen leaves in Fukushima. Of all the local ^{137}Cs in 2015, 87% was distributed in soil with 10% in fallen leaves in Japanese cedar forests, while 87% was distributed in soils with 11% in fallen leaves in *Quercus serrata* forests [31]. Moreover, 3% of ^{137}Cs was in Japanese cedar timbers (bark: 0.5%; boards: 0.4%; branches: 0.7%; and leaves: 0.6%), while 2% of ^{137}Cs was found in *Quercus serrata* timber (bark: 0.7%; boards: 0.2%; branches: 0.5%; and leaves: 0.1%) [31].

The radioactivity of gasification pellet fuel, products, and by-products was measured to clarify the fate of ^{134}Cs and ^{137}Cs from Fukushima's woody biomass during the biomass gasification process.

3.3.2. Material and methods

The measured samples were woody pellet fuel, gasification residue in ash bins (main ash), soot on ash filters (fly ash), and exhaust gas, which are produced from woody BGCHP systems (E3 unit, Entrade Energy) at the Spa Resort Abukuma in Nishigo village, Fukushima. The woody pellets are comprised of a mixture of Japanese cedar and *Quercus serrata* obtained from the Yamizo Mountains. Using these pellets, the radioactivity of products/by-products for each BGCHP process was observed. The exhaust gas was filtered by means of a high-volume air sampler (Shibata Scientific Technology Ltd., HV-500RD) for 30 min at suction flow rate of 500 L/min.

A germanium semiconductor detector (CANBERRA GC4020) was used to detect the radioactivity arising from radionuclides such as ^{134}Cs and ^{137}Cs. To minimise measurement errors, each measurement was taken over 3 h for the pellet fuels, the gasification residues, and the soot on filters, while 12 h for the filter of high-volume air sampler. Each radioactivity concentration was calculated by dividing the measured radioactivity by the sample mass/volume. The solid samples were placed into a vessel (100 mL) and measured.

3.3.3. Results and discussion

For ^{137}Cs, the radioactivity levels of solid samples were 20.6 Bq/kg (standard error, SE: 1.01 Bq/kg) for the woody pellets, 1333 Bq/kg (SE = 10.4 Bq/kg) for residue, and 5432 Bq/kg for soot from bag filters as presented in **Table 5**. The offgas radioactivity was not detectable when the limit of detection (LOD) was 0.002 Bq/m^3. All of the by-products were smaller than the criterion. For ^{134}Cs, the solid sample radioactivity levels were less than 4.10 Bq/kg for the woody pellets, 207 Bq/kg (SE = 7.58 Bq/kg) for residue, and 849 Bq/kg for soot from bag filters as presented in **Table 5**. The offgas radioactivity was not detectable. All of the by-products were smaller than the criterion. In this study, the biomass gasification plant was capable of keeping the radioactive nuclides (in the residue and the filters) within the plant. However, radionuclides should be monitored periodically.

Sample	^{137}Cs			^{134}Cs			Sample amount
	Mean	SE[a]	LOD[b]	Mean	SE[a]	LOD[b]	
Woody pellet (Bq/kg)	20.6	1.01	3.50	< 4.10	na	3.55	70.5 g
Residue (Bq/kg)	1333	10.4	15.0	207	7.58	15.4	39.6 g
Bag filter (Bq/kg)	5432	na	43.0	849	na	46.8	11.6 g
Offgas (Bq/m^3)	nd	na	0.002	nd	na	0.003	14.9 m^3

[a] SE = standard error.
[b] LOD = limit of detection.
na = not available.
nd = not detectable.

Table 5. Radioactivity levels in the E3 biomass gasification process.

4. Life cycle assessment of the biomass gasification process

Life cycle assessment (LCA) is a methodology that examines products and services "from cradle to grave" with a view to understanding system-wide environmental impacts. A cradle-to-grave LCA study of a product considers all life cycle stages from extraction or primary production of materials and fuels ('cradle') through production and use of the product to its final disposal ('grave'). The framework has been standardised by the International Organisation as ISO 14,044:2006 [32].

Recent studies concerning biomass gasification are summarised in **Table 6**. Recent LCA studies concerning biomass gasification are categorised into four groups: (i) biomass-based hydrogen (bio-H_2) production [33–38], (ii) biomass gasification combined heat and power (CHP) [39–44], (iii) other energy systems [45–48], and (iv) dynamic LCA [49]. This chapter covers the review of the LCA studies about biomass gasification.

4.1. Biomass gasification for hydrogen production

To evaluate the environmental performance of H_2 production via indirect gasification of short-rotation poplar, a LCA was implemented using process simulation for normal BG processes [33] and for BG with CO_2 capture by pressure swing adsorption [34]. From a life-cycle perspective, H_2 from poplar gasification generally arose as a good alternative to conventional, fossil-derived H_2 produced via steam methane reforming.

Moreno and Dufour [35] examined the environmental feasibility of four Spanish lignocellulosic wastes (vine and almond pruning, and forest wastes coming from pine and eucalyptus plantation) for the production of H_2 through gasification via LCA methodology using global warming potential, acidification, eutrophication and the gross energy necessary for the production of 1 Nm^3 of hydrogen as impact categories.

Kalinci et al. [36] performed LCA for stages from biomass production to the use of the produced hydrogen in proton exchange membrane fuel cell vehicles. Two different gasification

Study	Methodology				Economic impact	Environmental impact category												
	Location	FU	System boundary	Products		EC	AC	EP	GWP	HT	LU	OD	PO	RC	WC	ET	PM	IR
Susmozas et al. [33]		1 kg of H_2 produced from the plant with 99.9 vol% purity	Cradle-to-gate	Bio-H_2 from BG with CCS		X	X	X	X		X	X	X					
Susmozas et al. [34]	EU	1 kg of H_2 produced from the plant with 99.9 vol% purity	Cradle-to-gate	Bio-H_2 from indirect BG with CO_2 capture		X	X	X	X		X	X	X					
Moreno and Dufour [35]			Cradle-to-gate	H_2, CO_2, other emissions, wastes		X	X	X	X									
Kalinci et al. [36]			Cradle-to-gate	Bio-H_2	X				X									
Iribarren et al. [37]		1 m^3 stp of purified H_2	Cradle-to-gate	Bio-H_2		X	X	X	X		X	X	X					
El-Emam, et al. [38]		1 TJ of produced energy	Cradle-to-gate	Bio-H_2					X									
Elsner et al. [39]	Poland		Cradle-to-gate	CHP	X													
Adams and McManus [40]	UK	1 MJ (or kWh) of energy produced	Cradle-to-gate	Small-scale BG CHP		X			X	X				X	X	X	X	
Patuzzi et al. [41]	South-Tyrol, Italy	Thermal efficiencies	Cradle-to-gate	Small-scale BG CHP		X												
Oreggioni et al. [42]	EU		Cradle-to-gate	Small-scale BG CHP			X			X				X			X	
Klavina et al. [43]	Latvia	1 kg of untreated forest residue woodchips	Cradle-to-gate	Small-scale BG CHP		X	X	X	X		X	X				X		X
Kimming et al. [44]	EU	1 y supply of heat and power to a modern village of 150 households	Cradle-to-gate	Small-scale BG CHP		X	X		X		X							

Study	Methodology				Economic impact	Environmental impact category												
	Location	FU	System boundary	Products		EC	AC	EP	GWP	HT	LU	OD	PO	RC	WC	ET	PM	IR
Sreejith et al. [45]	State of Kerala in India	1 MJ energy content in the gaseous fuel	Cradle-to-gate	Producer gas generated from coconut shell gasification					X			X		X				
Parvez et al. [46]			Cradle-to-gate	Heat and syngas produced from gasification		X			X									
Kalina [47]	Poland	Cold/hot gas efficiency	Cradle-to-gate	Integrated BG dual fuel combined cycle power plant	X	X												
Wang et al. [48]	Harbin, China	1 y operation	Cradle-to-gate	Building cooling heating and power	X	X			X					X				
Yang and Chen [49]	China	1 MJ of primary energy produced in a BG plant (dynamic LCA)	Cradle-to-grave	Producer gases (CO_2, H_2, CO and CH_4) from BG	X				X									

Abbreviation: CCS: carbon dioxide capture; na: not available; CHP: combined heat and power; BG: biomass gasification; EC: energy consumption; AC: acidification; EP: eutrophication; GWP: global warming potential; HT: human toxicity; LU: land use; OD: ozone depletion; PO: photochemical oxidation; RC: resource consumption; WC: water consumption; ET: ecotoxicity; PM: particulate matter; IR: ionising radiation.

Table 6. Recent life cycle assessment studies on biomass gasification.

systems, a downdraft gasifier and a circulating fluidised bed gasifier (CFBG), are considered and analysed for H_2 production using actual data taken from the literature. Functional unit was 1 MJ/s H_2 production. Then, the costs of GHG emissions reduction are calculated.

Iribarren et al. [37] assessed environmental and thermodynamic performance of H_2 production via BG through a LCA and an exergetic analysis. The case study involves poplar gasification in a low-pressure char indirect gasifier, catalytic tar destruction, cold wet gas cleaning, syngas conversion and hydrogen purification. The system boundary covers from poplar cultivation to H_2 purification.

El-Emam et al. [38] focused on efficiency and environmental impact assessments of steam biomass gasification and gasification-solid oxide fuel cell (SOFC) integrated system for power and H_2 production. The environmental assessment is performed based on the carbon dioxide produced from the system with respect to the generated useful products.

4.2. Biomass gasification for CHP

Experimental and numerical analyses of a CHP installation (75 kWe of electrical power) was investigated by Elsner et al. [39], which is equipped with a biomass downdraft gasifier, gas purification system, and gas piston engine. The economic analysis was performed taking into account policies and regulations in the Polish energy market sector. They revealed that it is more profitable to consume the generated power and heat for its self-consumption rather than selling it on the market.

Using the techniques of LCA and net energy analysis, the study by Adams and McManus [40] quantified the energy, resource, and emission flows, to assess the net energy produced and potential environmental effects of BG using wood waste. The paper conducted a case study that uses waste wood from a factory for use in an entrained flow gasification CHP plant. Overall, small-scale biomass gasification is an attractive technology if the high capital costs and operational difficulties can be overcome, and a consistent feedstock source is available.

Patuzzi et al. [41] did an investigation resulting in an overview of the actual state-of-the-art of small-scale biomass gasification technology in Italy in terms of energy efficiency of the plants, effectiveness of the adopted solutions and characteristics of the products and by-products. In the study by Oreggioni et al. [42], a combined heat and power via BG, CHP with pre-combustion adsorptive carbon capture unit, and CHP with post combustion absorptive carbon capture unit were environmentally assessed.

Klavina, et al. [43] performed environmental performance analysis of biochar from woodchip pyrolysis, and woodchip CHP through midpoint category impact comparison using LCA. Kimming et al. [44] conducted a simplified LCA over four scenarios for supply of the entire demand of power and heat of a rural village. Three of the scenarios are based on utilisation of biomass in 100 kW_e CHP systems and the fourth is based on fossil fuel in a large-scale plant.

4.3. Biomass gasification for other energy systems

Sreejith et al. [45] investigated the suitability of coconut shell-derived producer gas as a substitute for coal gas from an environmental perspective using LCA. Thermochemical gasification in an air-fluidised bed with steam injection is the gaseous fuel production process. The study indicates that coconut shell-derived producer gas life cycle is capable of saving 18.3% of emissions for global warming potential, 64.1% for ozone depletion potential, and 71.5% for nonrenewable energy consumption. The analysis of energy and exergy consumptions is 62.9% for producer gas life cycle, while it is only 2.8% for coal gas life cycle.

In the study of Parvez et al. [46], air, steam, and CO_2-enhanced gasification of rice straw was simulated using Aspen Plus™ and compared in terms of their energy, exergy, and environmental impacts. The maximum exergy efficiency occurred in 800–900 °C. For CO_2-enhanced gasification, exergy efficiency was found to be more sensitive to temperature than CO_2/Biomass ratios. In addition, the preliminary environmental analysis showed that CO_2-enhanced gasification resulted in significant environmental benefits compared with steam gasification.

Kalina [47] presents theoretical study of the concept of a small-scale combined cycle system composed of natural gas fired micro turbine and Organic Rankine Cycle, integrated with thermal gasification of biomass. The main issues addressed in the paper are configuration of the ORC technology and allocation of generated electricity between natural gas and biomass. Energy and exergy allocation keys are demonstrated. An initial cash flow calculations are presented in order to assess financial performance of the plant.

Wang et al. [48] proposed a combined methodology of optimisation method and life cycle inventory for the biomass gasification based building cooling, heating, and power (BCHP) system. The system boundary of life cycle models includes biomass planting, biomass collection-storage-transportation, BCHP plant construction and operation, and BCHP plant demolition and recycle. Economic cost, energy consumption and CO_2 emission in the whole service-life were obtained. Then, the optimisation model for the biomass BCHP system including variables, objective function and solution method are presented.

Prior to large-scale crop-residue gasification application, the lifetime environmental performance should be investigated to plan sustainable strategies. As traditional static LCA does not include temporal information for dynamic processes, Yang and Chen [49] proposed a dynamic life cycle assessment approach, which improves the static LCA approach by considering time-varying factors, e.g., greenhouse gas characterization factors and energy intensity. Results show that the crop residue gasification project has high net global warming mitigation benefit and a short global warming impact mitigation period, indicating its prominent potential in alleviating global warming impact.

5. Conclusions

After the nuclear power plant accident in Fukushima, nearby forests were contaminated by the released radionuclides. Gasification technology can gasify the contaminated woody biomass and produce syngas and ash. Current trends in biomass gasification technologies and the subsequent gas cleaning process including desulphurisation and separation of radioactive substances were reviewed.

Life cycle assessment of the total gasification system is receiving increasing attention. It analyses the energy profit ratio and environmental impacts of a process of interest (e.g. greenhouse gas emission, acidification potential, photochemical oxidation, eutrophication potential, land competition, etc.).

The radioactivity of the syngas produced was quite low, and that of ash was high (within acceptable levels), implying that the gasification technology can be utilised as an option for energy conversion of contaminated woody biomass in Fukushima.

Acknowledgements

The author thanks all those involved in preparing this chapter, including Mr. Tachihara and Dr. Moritz for providing plant data. The authors acknowledge financial aid from Fukushima prefecture for overseas collaboration on renewable energy research and development.

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Journal of Energy Chemistry 25 (2016) 10–25

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Review

Biomass gasification technology: The state of the art overview

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ARTICLE INFO

Article history:
Received 20 May 2015
Revised 22 September 2015
Accepted 25 September 2015
Available online 28 November 2015

Keywords:
Gasification
Biomass
Syngas
Gasification technology
Biofuel
Power and heat generation

ABSTRACT

In the last decades the interest in the biomass gasification process has increased due to the growing attention to the use of sustainable energy. Biomass is a renewable energy source and represents a valid alternative to fossil fuels. Gasification is the thermochemical conversion of an organic material into a valuable gaseous product, called syngas, and a solid product, called char. The biomass gasification represents an efficient process for the production of power and heat and the production of hydrogen and second-generation biofuels. This paper deals with the state of the art biomass gasification technologies, evaluating advantages and disadvantages, the potential use of the syngas and the application of the biomass gasification. Syngas cleaning though fundamental to evaluate any gasification technology is not included in this paper since; in the authors' opinion, a dedicated review is necessary.

1. The biomass gasification process

The biomass gasification process consists in the conversion of a solid/liquid organic compound in a gas/vapor phase and a solid phase. The gas phase, usually called "syngas", has a high heating power and can be used for power generation or biofuel production. The solid phase, called "char", includes the organic unconverted fraction and the inert material present in the treated biomass. This conversion represents a partial oxidation of the carbon in the feeding material and is generally carried out in the presence of a gasifying carrier, such as air, oxygen, steam or carbon dioxide. Biomass gasification is considered as a way to increase the use of biomass for energy production allowing widespread biomass utilization. The development of biomass gasification processes is pushed up by the growing awareness of the possible effects of fossil fuels on the climate and by the continuous increase in oil prices.

The syngas produced is a gas mixture of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2) as well as light hydrocarbons, such as ethane and propane, and heavier hydrocarbons, such as tars, that condense at temperatures between 250 and 300 °C. Undesirable gases, such as sulphidric (H_2S) and chloridric acid (HCl), or inert gases, such as nitrogen (N_2), can also be present in the syngas. Their presence depends on the biomass treated and on the operational conditions of the gasification process. The lowest heating value (LHV) of the syngas ranges from 4 to 13 MJ/Nm^3, depending on the feedstock, the gasification technology and the operational conditions [1–3].

The char produced is a mixture of unconverted organic fraction, largely carbon, and ash. The amount of unconverted organic fraction mainly depends on the gasification technology and the operational conditions. On the other hand, the amount of ash depends on the biomass treated. The LHV of the char ranges from 25 to 30 MJ/kg [4], depending on the amount of unconverted organic fraction.

The principal reactions of the gasification are endothermic and the necessary energy for their occurrence is, generally, granted by the oxidation of part of the biomass, through an allo-thermal or an auto-thermal phase. In the auto-thermal process, the gasifier is internally heated through partial combustion, while in the allo-thermal process the energy required for the gasification is supplied externally [5,6]. Considering the auto-thermal system, gasification can be seen as a sequence of several stages. A simplified schematic representation of the gasification is reported in Fig. 1. The main steps of the gasification process are:

(1) Oxidation (exothermic stage).
(2) Drying (endothermic stage).
(3) Pyrolysis (endothermic stage).
(4) Reduction (endothermic stage).

An additional step, consisting in tar decomposition, can be also included in order to account for the formation of light hydrocarbons due to the decomposition of large tar molecules.

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http://dx.doi.org/10.1016/j.jechem.2015.11.005
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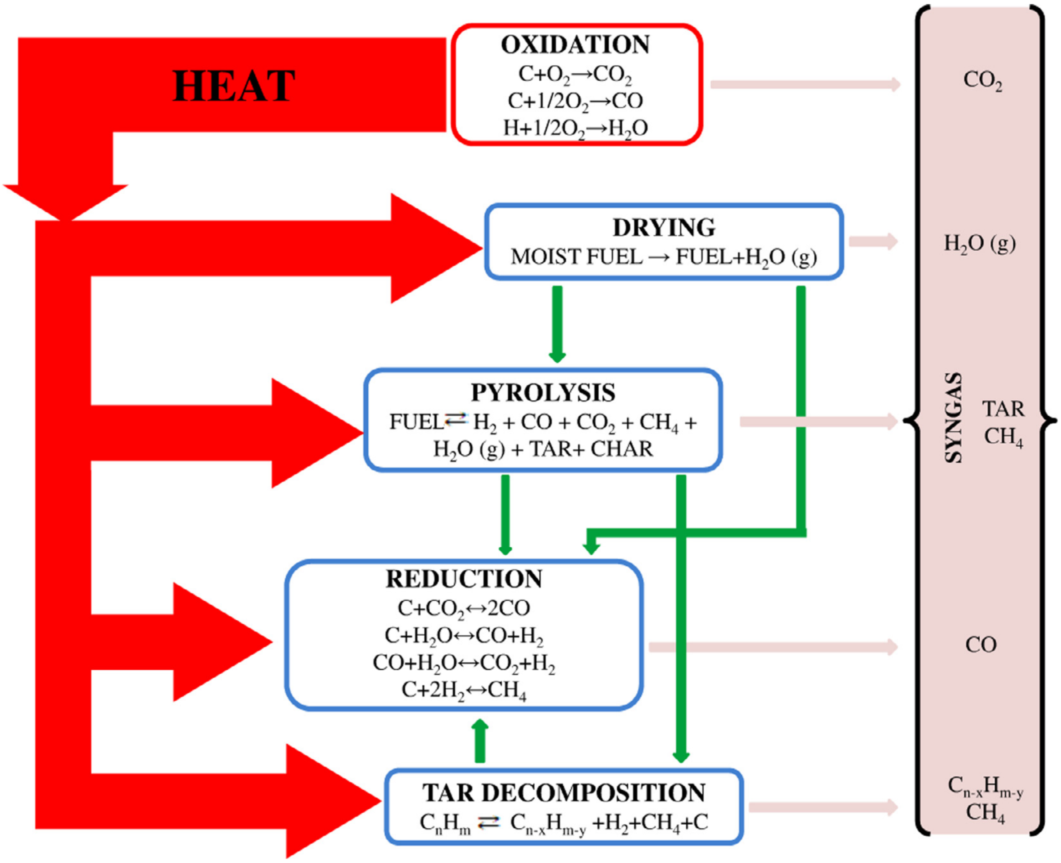

Fig. 1. Main stages of the gasification process.

1.1. Oxidation

The oxidation of part of the biomass is necessary to obtain the thermal energy required for the endothermic processes, to maintain the operative temperature at the required value. The oxidation is carried out in conditions of lack of oxygen with respect to the stoichiometric ratio in order to oxidize only part of the fuel. Despite the partial oxidation involving all carbonaceous species (tars included), it is possible to simplify the system considering that only char and the hydrogen contained in the syngas participate in the partial oxidation reactions. The main reactions that take place during the oxidation phase are the following:

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -394\,\mathrm{kJ/mol} \quad \text{Char combustion} \tag{1}$$

$$C + 1/2O_2 \rightarrow CO \quad \Delta H = -111\,\mathrm{kJ/mol} \quad \text{Partial oxidation} \tag{2}$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad \Delta H = -242\,\mathrm{kJ/mol} \quad \text{Hydrogen combustion} \tag{3}$$

The main product of this step is the thermal energy necessary for the whole process, while the combustion product is a gas mixture of CO, CO_2 and water. In this mixture nitrogen can be present if the biomass oxidation is performed with air, otherwise nitrogen is practically absent if only oxygen is used.

1.2. Drying

Drying consists in the evaporation of the moisture contained in the feedstock. The amount of heat required in this stage is proportional to the feedstock moisture content. Generally, the heat required derives from the other stages of the process. Drying can be considered complete when a biomass temperature of 150 °C is achieved, as discussed by Hamelinck and co-workers [187].

1.3. Pyrolysis

This phase consists in the thermochemical decomposition of the matrix carbonaceous materials; in particular, the cracking of chemical bonds takes place with the formation of molecules with a lower molecular weight. By pyrolysis it is possible to obtain different fractions: a solid, a liquid/condensed and a gaseous fraction [7–10].

The solid fraction, which can range from 5–10 wt% for fluidized bed gasifiers to 20–25 wt% for fixed bed gasifiers [7–10], has a high carbon content and is characterized by a high heating value. This fraction includes the inert materials contained in the biomass in the form of ashes and a high carbon content fraction, called “char”.

The liquid fraction, usually called "tars", varies according to the gasifier type, such as lower than 1 wt% for downdraft gasifiers, 1–5 wt% for bubbling bed gasifiers, 10–20 wt% for updraft gasifiers and is constituted by complex organic substances, condensable at relatively low temperatures [10,47,188,189].

The gaseous fraction is typically 70–90 wt% of the fed material [10,188] and is a mixture of gases that are incondensable at ambient temperature. The gaseous fraction is called "pyrolysis gas" and consists mainly of hydrogen, carbon monoxide, carbon dioxide and light hydrocarbons such as methane and other C_2, C_3 hydrocarbons; minor constituents are acid or inert gases.

The pyrolysis reactions take place with a temperature in the range 250–700 °C. They are endothermic and, as in the drying step, the heat required comes from the oxidation stage of the process.

Table 1. Gasifiable biomass [13].

Supply sector	Type	Example
Forestry	Dedicated forestry	Short rotation plantations (e.g., willow, poplar, eucalyptus)
	Forestry by-products	Wood blocks, wood chips from thinnings
Agriculture	Dry lignocellulosic energy crops	Herbaceous crops (e.g., miscanthus, reed canary grass, giant reed)
	Oil, sugar and starch energy crops	Oil seeds for methylesters (e.g., rape seed, sunflower)
		Sugar crops for ethanol (e.g., sugar cane, sweet sorghum)
		Starch crops for ethanol (e.g., maize, wheat)
	Agricultural residues	Straw, pruning of vineyards and fruit trees
	Livestock waste	Wet and dry manure
Industry	Industrial residues	Industrial waste wood, sawdust from sawmills
		Fibrous vegetable waste from paper industries
Waste	Dry lignocellulosics	Residues from parks and gardens (e.g., prunings, grass)
	Contaminated waste	Gemolition wood
		Organic fraction of municipal solid waste
		Biodegradable landfilled waste, landfill gas
		Sewage sludge

The pyrolysis process can be schematized with the following overall reaction [11]:

$$\text{Biomass} \rightleftarrows H_2 + CO + CO_2 + CH_4 + H_2O(g) + \text{Tar} + \text{Char} \quad (\text{Endothermic}) \tag{4}$$

When the feedstock is made of biomass, since cellulose is its main component (typically 50% of the weight), in this reaction the biomass can be indicated with the chemical formula of cellulose [12]: $C_6H_{10}O_6$.

Several complex phenomena are involved in the pyrolysis process. They include heat transfer, product diffusion from biomass pores towards gas phase bulk and reactions in series. At low temperatures the kinetic of the reactions may be the limiting step, while at higher temperatures the limiting step may become the heat transfer or the product diffusion. For cellulose, the pyrolysis reactions occur between 600 and 700 °C.

1.4. Reduction

The reduction step involves all the products of the preceding stages of pyrolysis and oxidation; the gas mixture and the char react with each other resulting in the formation of the final syngas. The main reactions occurring in the reduction step are:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = 172\ \text{kJ/mole} \quad \text{Boudouard reaction} \tag{5}$$

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = 131\ \text{kJ/mole} \quad \text{Reforming of the char} \tag{6}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mole} \quad \text{Water gas shift reaction} \tag{7}$$

$$C + 2H_2 \leftrightarrow CH_4 \quad \Delta H = -75\ \text{kJ/mole} \quad \text{Methanation} \tag{8}$$

Reactions (5 and 6) are endothermic, while Reactions (7 and 8) are exothermic; however, the contribution of both Boudouard Reaction (5) and char reforming (6) makes the reduction step globally endothermic, and then the whole step requires energy from the oxidation reactions. Reactions (5–8) are chemical equilibrium reactions and therefore products and reactants can coexist and maintain their concentration ratios as defined by the laws of thermodynamic equilibrium. In general, it can be stated that the endothermic Reactions (5 and 6) are favored (condition of equilibrium shifted toward the formation of products) when temperature increases, while Reactions (7 and 8) are favored at low temperatures. The temperature at which the reduction step is carried out has a fundamental role in determining the composition of the syngas, and therefore its characteristics (lower heating value, presence of tar). High temperatures increase the oxidation of char (reducing the solid residue of the process) and reduce the formation of tar. On the other hand they increase the risk of ash sintering and reduce the energy content of the syngas.

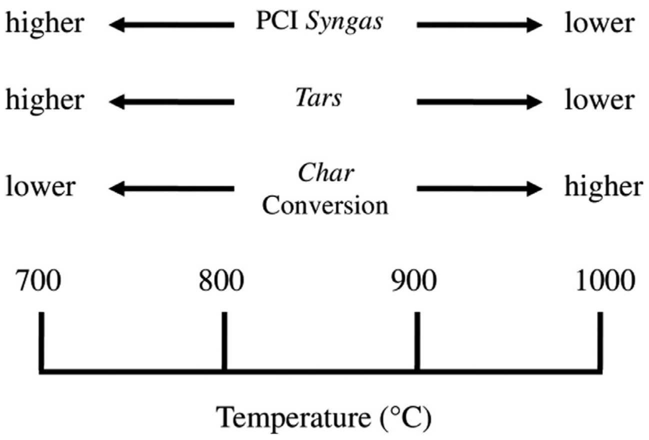

Fig. 2. Influence of temperature process on the syngas characteristics.

The reduction temperature is a key parameter of the overall process, determining the characteristics of the solid residue and those of the syngas. These effects are summarized in Fig. 2.

The influence of temperature on the entire gasification process has led to the development of multiple technological solutions, each one characterized by a different syngas composition and a different amount of solid residue.

The typical temperature range in which gasification processes have been developed at full scale is 800–1100 °C, while in the processes that use oxygen for the gasification step, the process temperatures are in the range 500–1600 °C.

2. Gasifiable biomass and their pre-treatments

The 2009/28/EC European Directive defines biomass as “the biodegradable fraction of products, waste and residues of biological origin from agriculture (including vegetal and animal substances), forestry and related industries, including fisheries and the aquaculture, as well as the biodegradable fraction of industrial and municipal wastes”. Examples of gasifiable biomass are shown in Table 1 [13] and they are composed of cellulose, hemicellulose, lignin and proteins [14,15]. Cellulose and hemicellulose are made of saccharides that bond to form long polymeric chains, which are the fibers of the biomass; lignin (a phenolic polymer) acts as the glue of the fibers, and therefore, has a key role in ensuring the structural protein stiffness. The proteins are mainly present in herbaceous species.

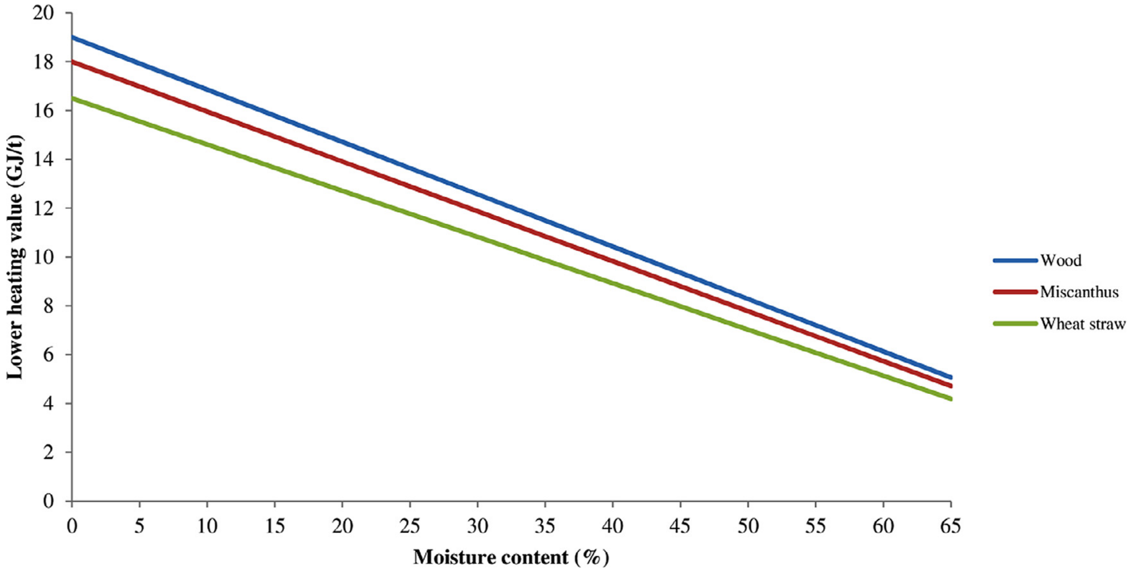

Fig. 3. Influence of temperature process on the syngas characteristics.

Table 2. Composition of hardwood, softwood and straw (wt% on dry basis) [13,193,194]

Biomass type	Cellulose	Hemi-cellulose	Lignin
Hardwood	42–48	27–38	16–25
Softwood	40–45	24–29	26–33
Straws	36–40	21–45	15–20

Table 2 reports the composition of some woody biomasses [13].

The knowledge of biomass physical-chemical properties is fundamental for its use as sustainable resource for energy production. Biomasses diversify for various parameters such as moisture, chemical composition, ashes and inorganic substance content. The elements mainly present, in decreasing order of abundance are: carbon, oxygen, hydrogen, nitrogen, calcium, potassium, silicon, magnesium, aluminum, sulphur, iron, potassium, chloride, sodium and manganese [201].

Syngas composition is not largely affected by biomass type, however if straw is used as feedstock an increase of hydrogen content can be observed while the lower heating value (LHV) of the produced gas degreases. Using softwood as feedstock, the highest LHV can be found [188,190].

The highest and the lowest char contents can be found for softwood biomass and straw biomass, respectively, otherwise the higher dust content can be observed for straw. The higher tar content can be found for hardwood biomass [188,190–192].

The moisture content is one of the most important parameters and critically affects the energy balance of the biomass gasification process. Fig. 3 shows the trend of the Lower Heating Value (LHV) as a function of the moisture content in some types of biomasses [16] while Table 3 reports the typical LHV values for the main fuels, as a comparison term.

3. Biomass gasification products

The biomass gasification end products may be distinct in a solid phase and a gas/vapor phase. The solid phase, ash, consists in the inert materials present in the feedstock and the un-reacted char. The char in the ashes is a very low percentage of the total ash amount, generally lower than 1 wt%, the transformation of the carbon matrix in gas being the objective of the overall process [17,18].

The gas/vapor phase, syngas, may be divided in a gas phase and a condensable phase. The gas phase is a gas mixture that contains the gases that are incondensable at ambient temperature, CO, H_2, CO_2, light hydrocarbons, CH_4 and some C_2–C_3. If air is used in the oxidization step as a gasifying carrier, then inert N_2 is present in the gas phase. Minor components are NH_3 and inorganic acid gases (H_2S and HCl and some minor gaseous compounds [182–184] (RIF)). The amounts of minor components depend on the biomass composition. The amount of syngas may range in 1–3 Nm^3/kg on a dry basis, with a LHV spanning over 4–15 MJ/Nm^3. These values may be highly affected by the gasification technology chosen and the operating variables [19,20]. Particular considerations are required for the condensable phase, tar, since it is made of several organic compounds that, once condensed, may be considered as bituminous oil. The European board for standardization [21] has defined tar as: "all the organic compounds that are present in the syngas excluded the gaseous hydrocarbons from C_1 to C_6" and has defined the main procedure

Table 3. Lower calorific value of the main fuels [16].

Fuel	LHV (MJ/kg)	Bulk density (kg/m^3)	Energy density by volume (MJ/Nm^3)
Wood chips (30% MC)	12.5	250	3100
Log wood (stacked-air dry: 20% MC)	14.7	350–500	5200–7400
Wood (solid-oven dry)	19	400–600	7600–11,400
Wood pellets	17	650	11,000
Miscanthus (bale-25% MC)	13	140–180	1800–2300
House coal	27-31	850	23,000–26,000
Anthracite	33	1,100	36,300
Heating oil	42.5	845	36,000
Natural gas (NTP)	38.1	0.9	35,200
LPG	46.3	510	23,600

Table 4. Tar type classification [28].

Tar type	Type name	Peculiarity	Characteristic compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC	Determined by subtracting the GC-detectable tar fraction from total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms, highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2-3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4-7 rings)	Larger than 3-ring, these components condense at high-temperature at low concentration	Fluoranthene, pyrene, chrysene, perylene, coronene

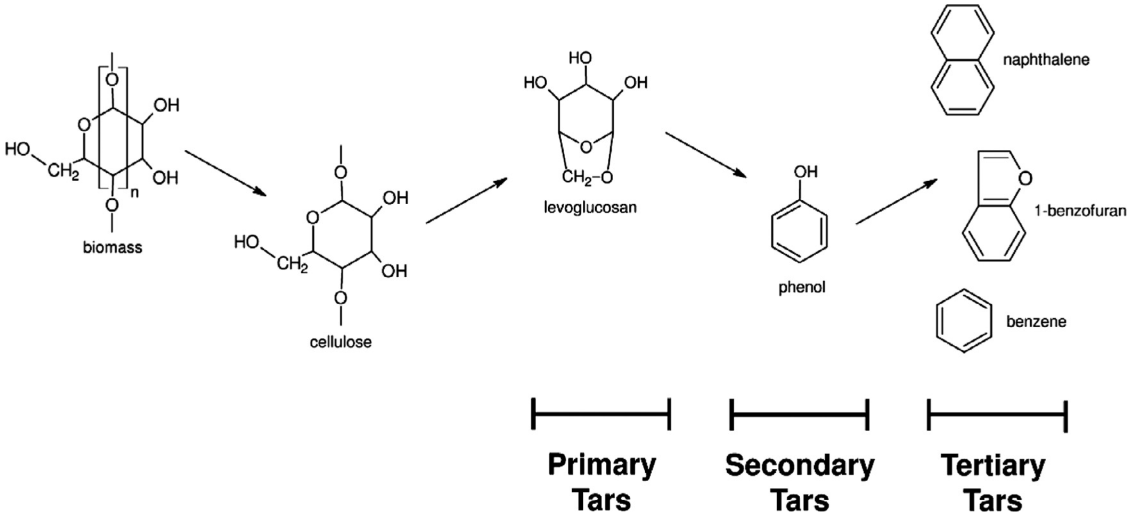

Fig. 4. Simplified mechanism of tar formation [29].

for their analysis. A large number of scientific papers have been devoted to tar characterization [22–24,185] and to tar formation [25–27].

Tars are a complex mixture of condensable hydrocarbons whose composition depends on the biomass feedstock, the gasification technology used and on the operating parameters chosen. Various research groups give different definitions of tars but there is general consensus [28] on dividing them into five classes, as reported in Table 4, according to their molecular weight.

Tar compounds belonging to class 1 are not known, they have a very high molecular weight and cannot be detected by gas chromatography. Tar compounds grouped into class 2 include oxygenated condensable compounds that are highly water-soluble. Tar compounds grouped in the classes 3–5 are aromatic compounds with an increasing number of aromatic rings; class 3 includes single ring compounds, while PAH compounds are included in the classes 4 and 5. In any case tar composition and classification are a major issue in gasification process. The European Commission defined a standardized protocol to collect and to measure the tars produced by biomass gasification [21].

In a gasification process, the tars are formed in a series of complex reactions, which are highly dependent on the reaction conditions. Tars stem from the pyrolysis step and are subject to recombination and decomposition (Fig. 1). The reaction paths are complex and not completely understood; they include a large number of reactions in series or parallel to one another. A possible simplified mechanism of tar formation [29] is shown in Fig. 4, which considers tars as the end products of three main macro-phenomena and classifies primary, secondary and tertiary tars.

Primary tars arise directly during the pyrolysis step and mainly depend on the biomass gasified. In particular cellulose and hemicellulose, which are made of a lot of oxygen atoms, determine primary tars containing oxygenated organic compounds (alcohols, carbon acid, ketones, aldehydes, etc.). On the other hand the pyrolysis of lignin gives rise mainly to aromatic compounds, mostly bi- or tri-functional substituted phenols (cresol, xylenol, etc.). In the oxidation step, the increase in temperature, above 500°C, and the presence of an oxidant (oxygen, air or steam), may allow for the transformation of primary tars, which begin to rearrange (via dehydration, decarboxylation, and decarbonylation reactions) forming more gas and a series of molecules known as secondary tars. Secondary tars are alkylated mono- and di-aromatics including hetero-aromatics like pyridine, furan, dioxin, and thiophene [30]. A further increase in temperature, over 800 °C, may lead to the formation of tertiary tars. Tertiary tars are also known as recombination or high-temperature tars. Tertiary tars are mainly made of aromatic and polynuclear aromatic hydrocarbons (PAH), e.g., benzene, naphthalene, phenanthrene, pyrene, and benzopyrene. Compounds in tertiary tars are not present in the biomass gasified and they are the results of the decomposition and recombination of secondary tars in the reducing environment of the syngas. Tertiary tars and primary tars do not coexist, and tertiary tars appear when primary tars are completely converted into secondary tars [29].

A schematic representation of tar types as a function of temperature is reported in Fig. 5.

The formation of tertiary tars and their decomposition in smaller compounds is a complex scientific problem on which several research groups are working to define the reaction path and to develop a kinetic model that describes the experimental results. However, the results obtained are often conflicting and unable to describe neither the large variety of compounds in the tars nor their dependence on the process conditions [31–46]. The general approach is to treat the

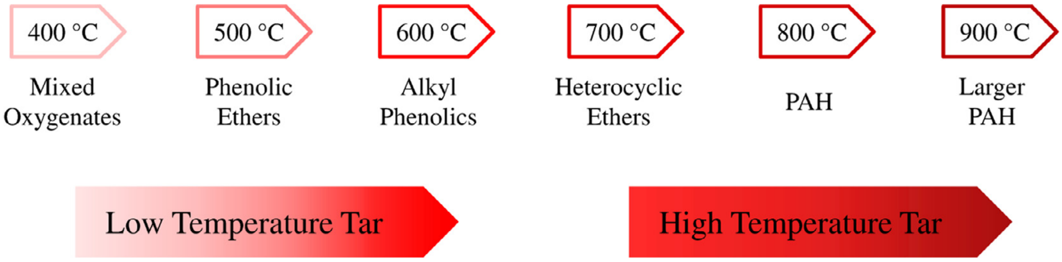

Fig. 5. Tar types as function of temperature [29].

tar compounds as a certain number of lumped classes and to define a reaction path for a single compound, which is considered as representative of the total amount of the classes. A lot of papers can be found in the scientific literature [42], in which this approach is used to overcome the difficulty in describing the large number of reactions involving the numerous compounds found in the tar mixture. However, to the best of our knowledge, at this moment any defined reaction path for tar formation and decomposition does not exist. Discrepancies among authors [42,43] exist even for the description of the formation of the simplest PHA compounds: naphtalene, considered as representative of two ring aromatic compounds.

The simplest way to describe tar decomposition/recombination is the following reaction:

$$\alpha C_nH_m \rightarrow \beta C_{n-x}H_{m-y} + \delta H_2 \quad \text{(Endothermic)} \quad \text{Tarcracking} \tag{9}$$

$$C_nH_m \rightarrow nC + (x/2)\,H_2 \quad \text{(Endothermic)} \quad \text{Carbon formation} \tag{10}$$

$$C_nH_m + nH_2O \rightarrow (n + x/2)\,H_2 + nCO \quad \text{(Endothermic)} \quad \text{Steam reforming} \tag{11}$$

$$C_nH_m + nCO_2 \rightarrow (x/2)\,H_2 + 2nCO \quad \text{(Endothermic)} \quad \text{Dry reforming} \tag{12}$$

where, C_nH_m represents a generic tar while $C_{n-x}H_{m-y}$ are representative of hydrocarbons with a weight lower than that of tars.

The presence of tars in the syngas may be considered, as stated by Reed already in 1997 [47], as the Achilles' heel of biomass gasification affecting the final use of the syngas itself: energy production and/or chemical utilization. Tars removal or their conversion is the great technical challenge to overcome and develop a successful application of biomass-derived gas. Different approaches are being followed by researchers [41,48,49,195]:

- End of pipe tar syngas clean-up process;
- In bed thermal tar cracking;
- In bed catalytic tar reforming.

4. Biomass-pre-treatment

The pre-treatment of biomass has the primary objective to ensure that the gasification process is conducted using a feedstock material that is homogeneous by size and composition. Other pre-treatments aim at reducing the initial moisture content that, in general, must not exceed 25–30 wt%; among these the main pre-treatments, besides drying, are torrefaction and hydrothermal upgrading (HTU).

4.1. Torrefaction

Torrefaction is a thermochemical process which is carried out at a temperature between 200 and 300 °C in the absence of oxygen. At these temperatures some chemical reactions take place; the biomass loses both the rigid fibrous structure and the moisture content, with a consequent increase in the energy content. In many cases the torrefaction process is performed with a system of pelletization to increase the bulk density of the material [50–52].

The roasted pellets have an amount of energy per unit volume of 14,000–18,500 MJ/Nm^3, which is significantly greater than the pellets produced by conventional material, such as wood-pellets, which are between 8,000 and 11,000 MJ/Nm^3 [51]. This type of pre-treatment consists of a combination of torrefaction and pelletization and was introduced by the Energy Research Centre of the Netherlands (ECN).

4.2. Hydro thermal upgrading (HTU)

The HTU consists in the production of an oil, like crude oil, named "bio-crude" oil, by the decomposition of biomass in water. The pre-treatment is conducted, essentially, in two stages. The first one consists in treating the biomass with water at temperatures of 200–250 °C and a pressure of about 30 bars. The second one is an increase both in temperature and pressure in a period of time variable from 5 to 10 min, in which the conversion of the biomass takes place by bringing the water at pressures of 120–180 bar and temperatures of 300–350 °C [53,54]. Bio-crude is a mixture of different hydrocarbons, with a LHV between 30 and 36 MJ/kg that can be employed as a co-fuel in the coal power plants or in the chemical industry to produce chemicals or synthetic fuels with diesel-like properties [54]. The combination of gasification and biomass hydro thermal upgrading could be an optimal treatment strategy although further studies and R&D on HTU are required [55,56].

5. Gasification technologies

The reactors used on an industrial scale to gasify a pre-treated biomass, usually called gasifiers, essentially differ from one another for:

1. Mode of contact between the feed material and the gasifying agent.
2. Mode and rate of heat transfer.
3. Residence time of the fed material into the reaction zone.

Different technological solutions can be implemented in order to obtain different plant configurations; in particular, the mode of contact of the biomass with the gasification agent may be in counter-current, or co-current, or cross flow, and the heat can be transferred from the outside or directly in the reactor using a combustion agent; the residence time can be in the order of hours (static gasifiers, rotary kiln) or min (fluidized bed gasifiers).

The main reactors used in the biomass gasification process are:

1. Entrained flow reactor.
2. Fixed bed.
3. Fluidized bed.
4. Rotary kiln reactor.
5. Plasma reactor.

A brief description of the different reactors is reported below in order to highlight the main advantages and disadvantages.

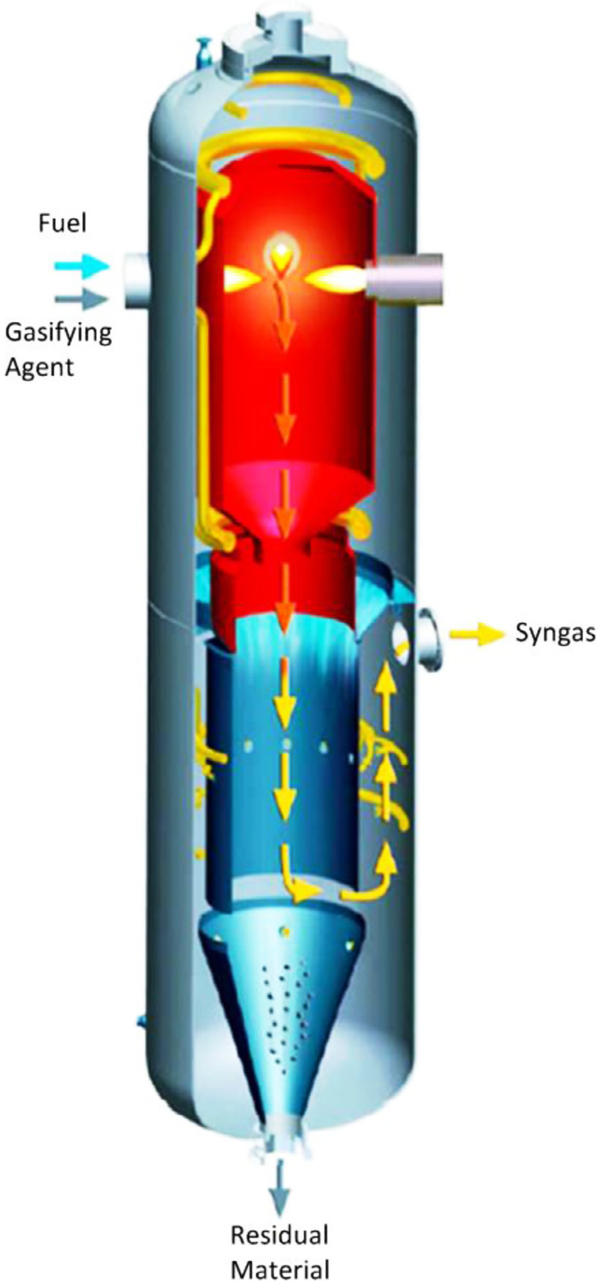

Fig. 6. Entrained flow reactor.

5.1. Entrained flow reactor

In an entrained flow reactor the feed fine fuel (0.1–1 mm particles) and the gasifying agent are injected in co-current (Fig. 6). The gasifier operates at high temperatures (1300–1500 °C) and pressures (25–30 bar) and water slurries or dry feeds can be used as raw material. A pneumatic feeding is usually used to inject pressurized powder solid fuels into the gasifier, while slurries are atomized and subsequently fed as pulverized solid fuel. Entrained flow reactors can be divided in slagging and non-slagging: in the former the ash leaves the reactor as a liquid slag, and in the latter slag is not produced (1% is the maximum allowable ash content). Usually a torrefaction-based pre-treatment is required to reduce the bulk density and moisture content, when biomass fine particles are used as feedstock [52,56–58].

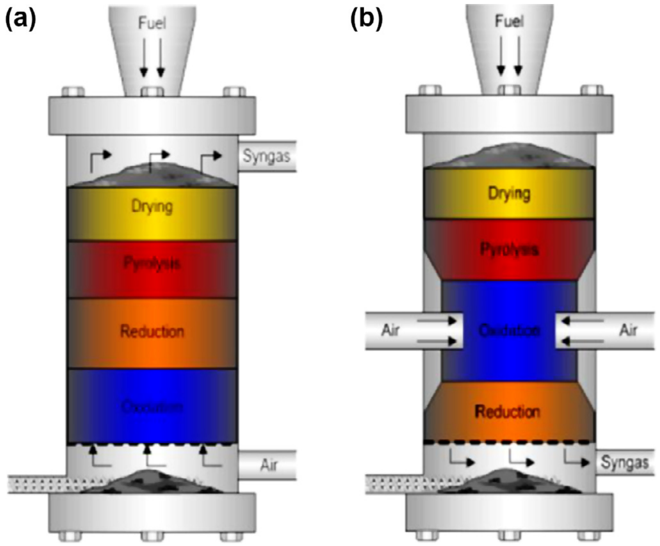

Fig. 7. Fixed bed reactor: (a) updraft, (b) downdraft.

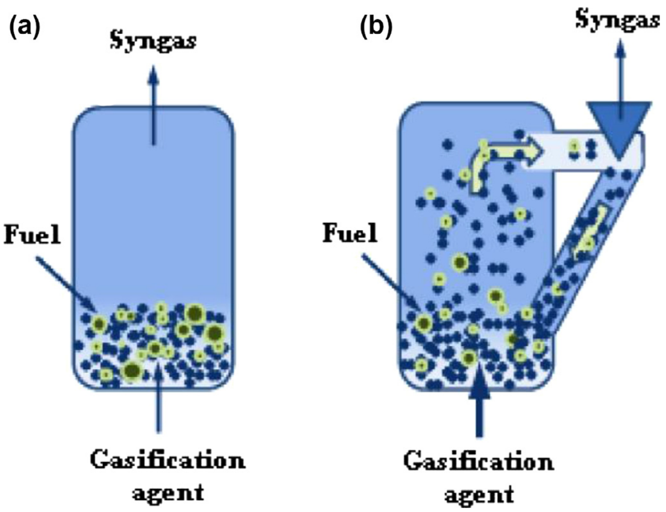

Fig. 8. Fluidized bed reactor: (a) bubbling, (b) circulating.

Using biomass powder as fuel during entrained flow gasification may give an extra cost due to its low bulk density, which might be reduced by an initial torrefaction process [59].

Table 5 shows the main advantages and disadvantages of these types of reactors [60–62].

5.2. Fixed bed reactor

The main technological solutions based on the fixed-bed reactor are the updraft and the downdraft reactor (Fig. 7a and b). In the updraft reactor the solid moves downwards with respect to the gasification agent and then the syngas produced moves upward (countercurrent); while in the downdraft reactor, both the solid and the gas are moved downward (co-current).

Table 6 shows the main advantages and disadvantages of these types of reactors, as reported in the scientific literature [61–65,196].

5.3. Fluidized bed reactor

The bubbling fluidized bed reactor (Fig. 8a) is made of a bed of inert granular material (sand) held in a condition of fluidization where the gasification agent is fuelled bottom-up from the bed through a

Table 5. Advantages and disadvantages of the entrained flow reactor.

Reactor type	Advantage	Disadvantage
Entrained flow reactor	-Fuel flexibility -Uniform temperature -High carbon conversion -There are not problems of scale-up -Good ability to control the parameters process -Short reactor residence time. -Very low tar concentration. -High Temperature slagging operation (vitrified slag).	-Large oxidant requirements -High level of sensible heat in product gas -Heat recovery is required to improve efficiency -Low cold gas efficiency -Requires the reduction of size and preparation supply -Short life of system components, including gasifier vessel refractory -High plant cost -High maintenance cost

Table 6. Advantages and disadvantages of fixed bed reactors.

Reactor type	Advantage	Disadvantage
		-High content of tar in the syngas
	-High thermal efficiency	-Energy content of tar> 20%
	-Good contact between the solid material and the oxidizing agent	-Low production of CO and H_2. -requires a subsequent treatment of the tar cracking
	-Can handle materials of different sizes	-Limited flexibility to load and process (the treated material should have properties homogeneous)
Fixed bed “Updraft”	-Can handle materials with high humidity	-Reduced starting difficulties and temperature control
	-Reduced entrainment both of dust and that of Ashes	-Need for installation of mobile grates to avoid the formation of preferential paths in the fixed bed
	-Simple construction	-According to catalysts, they may be not usable since syngas energy may be lower than that necessary for the activation, requiring external energy supply -Poisoning deactivation of catalysts may be possible
	-Robust technology	-Low specific capacity
	-There are no problems of scale-up	-Need for uniform sizes in input (pellets no larger than 100 mm)
		-Training of sintered slag on the grid
Fixed bed “Downdraft”	- High carbon conversion	-Requires materials with a low moisture content
	-Low production of tar	-Limited flexibility to load and process (the treated material must have the same characteristics)
	-Limited entrainment of ash and dust	-Low coefficient of heat transfer
	-High solid residence time	-Difficulty starting and controlling the temperature
	-Simple construction	-Poisoning deactivation of catalysts may be possible
	-Reliable technology	-Limited possibility of scale-up (the dimensions of the reactor are limited by problems of temperature control)

distribution grid, with a velocity between 1 and 3 m/s. In these conditions, the bed of inert solid behaves like a liquid, and is continuously stirred by the presence of gas bubbles whose mobility ensures uniform conditions both of exchange of matter and heat between the solid and the gas. The extent of the grid region can significantly affect the mass and heat transfer between the gasification agent and the bed solids [66]. The various phases of the gasification process occur within the bed, although a part of the gasification reactions can be completed in the freeboard, i.e., the upper part of the reactor that is not reached by the fluidized bed, where only the gas phase is present. In recirculating bed reactors (Fig. 8b), the gasification process is divided into two stages; in the first, generally consisting of a bubbling fluidized bed, the reactions of combustion generating the heat necessary for gasification occur, and in the second there is a high-speed gas (5–10 m/s) to allow the dragging of the solid, where the reactions of pyrolysis and gasification take place. At the outlet of the reactor a cyclone is also present; it allows for the separation of the solid, which is, generally, re-circulated to the bubbling fluidized bed. At present, the fluidized bed is the most promising technology in biomass gasification as much as for tar conversion: it has high mixing capabilities, with a high mass and heat transfer rate, which secures constant temperatures all over the gasifier, and moreover catalysts can be used as part of the gasifier bed, affecting tar reforming [197–200]. Furthermore Puadian and co-workers [67] demonstrated that the biomass injection point is extremely important, as these benefits are enhanced when the biomass is fed deep inside the fluidized bed; this results in the greatest product gas yield, due to the increased exposure to the catalytically active bed environment.

Fluidized bed reactors have advantages and disadvantages depending on the various technological solutions: bubbling fluidized bed or dragged bed. Table 7 shows the main advantages and disadvantages of these types of reactors, as reported in the scientific literatures [3,58,62,68].

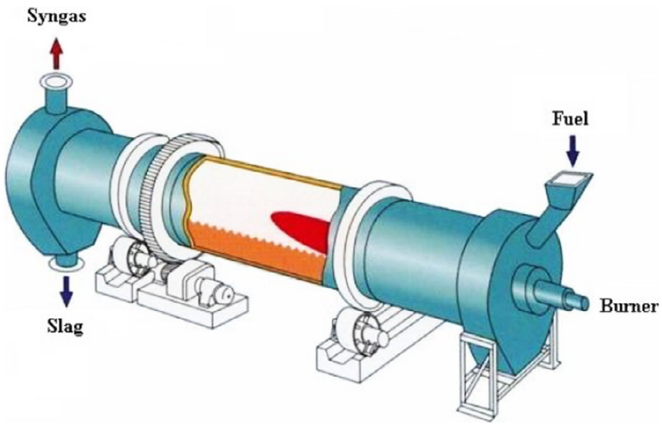

Fig. 9. Rotary kiln reactor.

5.4. *Rotary kiln reactor*

Rotary kilns (Fig. 9) consist in a slightly tilted (1%–3%) cylindrical chamber that slowly rotates around its own axis. The gas–solid contact takes place due to the rotation of the drum that, by continuously stirring, exposes the new solid surfaces to the gasification agent. The conditions for the exchange of matter and heat between the solid and the gas are not very effective, and then, the residence time (reaction volumes) is higher than those with the other gasification technologies. The efficiency of solid-gas contact may be improved with the

Table 7. Advantages and disadvantages of fluidized bed reactors.

Reactor type	Advantage	Disadvantage
Bubbling fluidized bed	-High mixing and gas-solid contact -High carbon conversion -High thermal loads -Good temperature control (temperature distribution along the reactor) -Can handle materials with different characteristics -Good flexibility both of load and process -Suitable for highly reactive fuels such as biomass and municipal waste pre-treated -Low level of tar in the syngas -Ease of start-up, shutdown and control -Possibility to use catalysts, even on a large scale (thanks to the good temperature control) -No moving parts -Good ability to scale-up	-Loss of carbon in the ashes -Dragging of dust and ashes -Pre-treatment need with heterogeneous materials -Need to have a relatively low process temperature to avoid phenomena of de fluidization of the bed (temperature lower than the softening point of the solid residues) -Restrictions on the size -High investment costs and maintenance costs
Circulating fluidized bed	-Lower tar production -High conversions -Flexible load -Reduced residence times -Good ability to scale-up	-Possibility of casting the ashes -Loss of carbon in the ashes -Requires the reduction of size and preparation supply (the solid material must be finely pulverized, with dimensions lower than 100 mm) -Restricted solid-gas contact - Need for special materials -Technology complex and difficult to control. -Security issues -High start-up costs and investment costs

Table 8. Advantages and disadvantages of the rotary kiln reactors.

Reactor tyoe	Advantage	Disadvantage
Rotary kiln	-Low sensitivity to changes in composition, humidity and size of the fed -Maximum loading flexibility -High conversion -Suitable for waste that can melt -There are problems of scale-up -Simplicity of construction and high reliability of operation -Reduced investment costs	-Significant difficulty in starting and temperature controlling -Presence of movement part and their problems with leakage and wear -Consumption of refractory quite high -Low capacity of heat exchange -High content of dust and tar -Low efficiency heat -Limited flexibility process -High maintenance costs

installation of barriers inside the drum that increase the handling of the solid material and improve the contact with the gaseous stream.

The most used configuration is the one in countercurrent: the matrix to be gasified is fed into the top of the reactor and the oxidizing agent in the bottom of the reactor. Table 8 shows the main advantages and disadvantages of these reactors, as reported in the scientific literatures [69–71].

5.5. *Plasma technology*

The plasma is an ionized gas stream at high temperature (up to 10,000 °C) obtained from the application of an electric discharge, typically indicated as "arc". The device on which the electrodes are installed is called "flashlight"; the electrodes used are usually in copper, but it is also possible to use carbon electrodes (Fig. 10).

The plasma process consists in an atomic degradation of the matter; consequently if it is applied to the treatment of an organic matrix (waste/biomass) and in the presence of an oxidizing agent (air/oxygen/steam), the energy flow, supplied from the plasma, determines the rise in temperature necessary for the reactions that make up the gasification process, while in the absence of an oxidizing agent the plasma process is similar to the pyrolysis at higher temperature.

The use of plasma technologies for the thermal treatment of organic matrices can occur in two patterns:

(1) Direct application to the solid to be treated, in adequate size, when the main goal is the thermal destruction. The application of the plasma process directly to the matrix allows for the control of the temperature of the process independently from any fluctuations in the quality of the solid and of the gasification agent, accepting a wide variation in the flow rate, moisture content, size and elemental composition of the material to be treated.

(2) Application to the gas produced by a gasification upstream process, when the main objective is to maximize the production of a synthesis gas with a high content of light components, removing the tar initially present (the plasma process has a function of clean syngas without altering the energy content).

Table 9 shows the main advantages and disadvantages of this type of reactor, as reported in the scientific literature [72].

5.6. *Gasification technology comparison*

The main “bottlenecks” of the biomass gasification technology can be summarized in: feed material, syngas quality and development status. An entrained flow reactor requires specific features of the feed fuel, in terms of particle size (0.1–1 mm), moisture content (< 15 wt%) and a constant composition, while biomass feedstock with light or without pre-treatment can be supplied to a plasma gasifier and a rotary kiln reactor. Fluidized and fixed bed reactors are more flexible than an entrained flow reactor operating with larger particle sizes (20–100 mm) and a wider range of moisture contents (5%–55%), however a feedstock with low ash melting temperatures should be used. In terms of syngas quality, the best gasifier is the plasma reactor; entrained flow gasifiers also ensure a very low tar content with a better

Table 9. Advantages and disadvantages of plasma reactors.

Reactor type	Advantage	Disadvantage
Plasma reactor	-Production of vitrified completely inert and non-leachable slag, which include heavy metals -The waste products, being non-leachable, can be recovered and used directly as a building material -Reduced flow rate of the syngas -Content extremely limited polluting compounds in syngas -Extremely short reaction times -There are not problems of scale-up	-Presence of nanoparticles in the syngas -Presence of moving parts with their maintenance problems -Consumption of refractory -Non continuous process -Heat Schock for the start-up and shout-down -Necessity of auxiliary fuel for obtain an homogeneous temperature inside the reactor -Frequent changing of the electrodes -Safety problems -Solidification of molten material in the ducts -High plant, operational and exercise costs

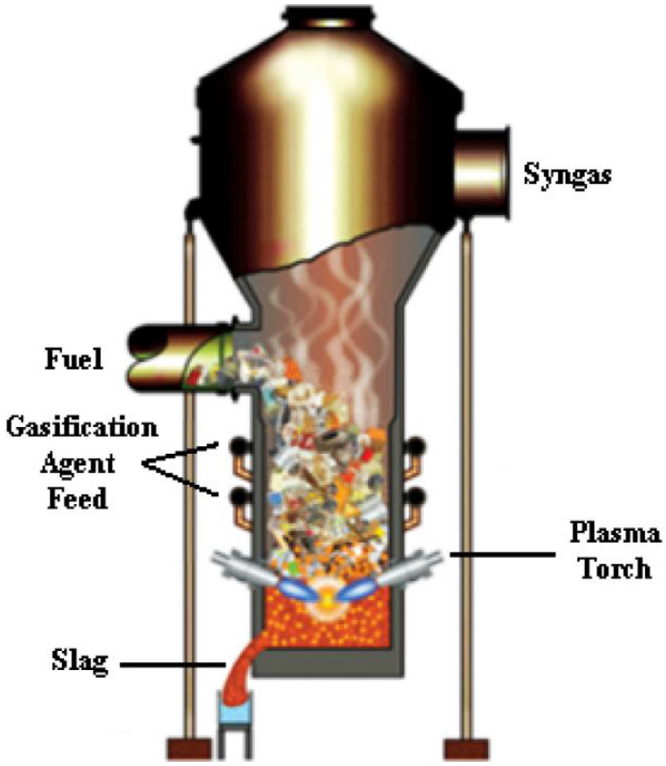

Fig. 10. Plasma reactor.

quality syngas than a fluidized and fixed bed reactor. In turn the syngas from a fluidized bed gasifier has a better quality than the syngas produced by a fixed bed reactor. The syngas from a rotary kiln reactor has the worst quality [73]. Entrained flow gasifiers are very promising in terms of commercialization, showing a great potential for scale-up and, consequently, low capital costs, thanks to economies of scale; fluidized bed gasifiers are a consolidated technology for biomass gasification, with good established heat and power applications; plasma gasifiers are used for power production, but they are mainly focused on municipal waste, with a little experience with biomass. Fixed bed and rotary kiln gasifiers are not widespread because of the low syngas quality.

It is not possible to carry out a real gasification technology cost analysis because the data available in the literature refer to gasifiers with various plant scales, development phases and technical concepts, however some general considerations are possible [73,74]: entrained flow gasifiers have high efficiency versus high pre-treatment costs (if decentralized) and moderate capital and maintenance costs; fixed bed gasifiers have moderate efficiency and limited capital and maintenance costs; fluidized bed gasifiers show both high efficiency and high capital and maintenance costs; rotary kiln gasifiers are characterized by good efficiency, low capital costs and high maintenance costs; plasma gasifiers show low efficiency versus high capital and maintenance costs.

6. End use of thermochemical biomass conversion products

Roskilly et al. [75] define biofuels as any type of combustible substance derived from biomass conversion. Biofuels have raised a great interest over the past ten years due to the growing attention to climate change and to renewable energy sources. The use of biofuels for energy conversion allows reducing greenhouse gas emissions, thanks to the CO_2 neutral conversion, and fossil fuel dependence [76–78]. For these reasons, the industrial production of bioethanol and biodiesel has greatly increased in the last decade [79] with 100 billion of liters and 60 billion of liters, in 2010, respectively [80,81]. These production levels have been reached by first generation biofuels, mainly bio-ethanol and bio-oil whose production technologies can be considered as mature; on the contrary, first generation biofuels that use food products to produce fuels (e.g. ethanol from corn) have problems of sustainability and security of feedstock. The production of second-generation bio-fuels, that use no-food biomass such as indigenous wood, grass species, forestry residues and municipal solid waste (MSW) is not fully developed as a technology and further improvements are required.

The gasification process and other biomass conversion technologies such as pyrolysis, and combustion, can provide several primary products, charcoal, liquid, fuel gas and heat that can be processed for obtaining secondary products as electricity, gasoline, diesel, methanol, chemicals and ammonia [82]. A schematic representation of the thermochemical processing and products is shown in Fig. 11. This figure, starting from the version proposed by Bridgwater [82] has been updated to include novel processes and products.

Primary products can be directly used as combustible substances in power plants for heat and power production (CHP); primary products, after a more or less advanced purification step, may be used in facilities with high energy efficiency such as gas turbines [83], internal combustion engines [75], solid oxide fuel cells (SOFC), molten carbonate fuel cells (MCFC) [84].

Secondary products include the electricity and the heat obtained using the primary products and chemical compounds such as gasoline, diesel, methanol, and some chemicals that can be used as fuels for energy conversion or as reagents in chemical processes.

A brief description of the different uses of primary and secondary gasification processes/products is given in the following.

6.1. Electricity and heat production

6.1.1. Steam cycle

The combustion of syngas or cracking oil in a boiler is a simple use of the thermochemical primary products as fuels in a conventional

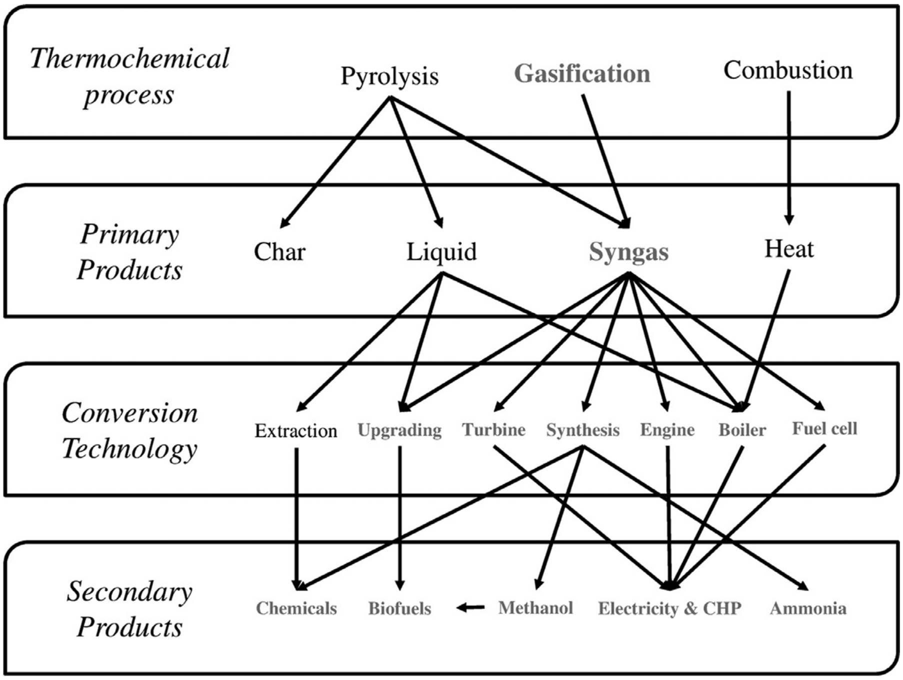

Fig. 11. Thermochemical biomass processing and products.

steam cycle [85,186]; using these fuels does not increase the impact on the environment [86]. A lot of power plant applications are fuelled by syngas or by cracking oil without any particular problem, however the overall electricity energy efficiency is low and varies from 15% up to 35% in plants with a boiler energy size higher than 150 MWth [87,88]. Higher energy efficiency may be reached if cogeneration units for heat re-use are applied.

6.1.2. *Co-combustion*

The primary products obtained by the thermochemical conversion of biomass may be added to conventional fuels (coal, heavy oil or biomass) in power plants for co-combustion processes [90]. This use does not imply any technical problem and the overall electrical efficiency of these plants (about 35%) [89] is not affected if fuel replacement by biomass primary products is limited to 5–15 wt% [90,91].

6.1.3. *Combustion in gas turbines*

Fuel combustion in gas turbines (GT) may reach a higher electrical conversion efficiency, up to 40%, than conventional steam cycles, even in low size plants (<50 MWth) [87,88,92–94]. However, in order to avoid the rapid deterioration of the blades of the turbines because of the high temperature of the flue gas, an accurate cleaning (Tars = 10 mg/Nm^3, Particulate = 2.4 mg/Nm^3, Metals = 0.025–0.1 ppmw, H_2S = 20 ppmv) and a calorific value greater than 4 MJ/Nm^3 are required [95,96].

The energy conversion in the gas turbine may be increased by adding an additional energy recovery system (steam cycle–Integrated Gasification Combined Cycle–IGCC) that allows for an overall energy efficiency in the range 30%–60% [87,88]. Furthermore, the gas turbine may be coupled to tri-generative systems or to heat re-use in order to improve the energy use in terms of fuel utilization, which can reach 70%–90% [97].

6.1.4. *Combustion in internal combustion engines*

The syngas produced by biomass thermochemical conversion may be fed to internal combustion engines (ICE) obtaining an overall electrical energy conversion in the range 35%–45% [88]. However, a high calorific value (>4 MJ/Nm^3) and a low pollutant contents (Tars = 100 mg/Nm^3, Particulate = 50 mg/Nm^3, Metals = 0.025–0.1 ppmw, H_2S = 20 ppmv) are required [95,96,98–100]. In particular, comparing syngas characteristics for GT and ICE it is possible to highlight that gas turbines need a higher purity syngas in terms of tar and particulate contents.

The main problem is that in the current market, the engines are designed for gasoline and diesel, and therefore a modification of the injection system is necessary [101,102]. In internal combustion engines the syngas can be also used for co-combustion, mixed with biogas derived from the anaerobic digestion of organic waste [103].

6.1.5. *High temperature fuel cells*

High temperature fuel cells are electrochemical systems for electricity production via chemical energy conversion [104]. The key advantage of these systems is that an electric conversion efficiency greater than 40% can be easily obtained [105]; moreover high temperature fuel cells can be fed with a mixture of H_2 and CH_4 or directly by syngas. The syngas usage in high temperature fuel cells, without any combustion processes, has a lower impact on the environment.

Molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) are the main fuel cells technologies that can be fed with syngas. The great advantage is the flexibility of the fuel that can be made of carbon monoxide or carbon dioxide in addition to hydrogen and methane. In MCFC a nickel catalyst is required for the reforming reaction and the H_2S content in the gas must be lower than 10 ppmv to avoid catalyst poisoning deactivation. SOFC can only tolerate 1 ppmv of H_2S. For both technologies tars and particulate have to be removed. Furthermore, the high temperature, in the range 700–1000 °C, promotes a higher energy recovery than in MCFC [106].

In any case, both molten carbonate fuel cells and solid oxide fuel cells can be fuelled by syngas, after a cleaning phase [106], and to the best of our knowledge no one other technology have reached full scale application.

6.2. *Secondary products*

The use of biofuels for energy conversion allows reducing greenhouse gas emissions, thanks to the CO_2 neutral conversion, and fossil fuel dependence [77,78].

Gaseous and liquid biofuels can be easily used instead of fossil fuels (transport, energy, heat and chemical production). Thermal treatments directly produce gaseous and/or liquid biofuels. The latter can also be produced through conversion processes starting from syngas.

Gaseous biofuels are mainly methane and hydrogen, the others (CO and light hydrocarbon) being generally in a negligible amount [75,107]. The main liquid biofuels are gasoline and diesel; they are obtained by the direct thermal conversion of biomass and ethanol and of methanol and dimethylether after syngas conversion [108–110].

The industrial production of liquid biofuels (bioethanol and biodiesel) has greatly increased in the last decade [79]. In particular, from 2001 to 2010, the world bioethanol production tripled reaching about 100 billion of liters in 2010 [80,81]; at the same time the world biodiesel production increased by an order of magnitude, reaching about 60 billion liters in 2010 [80,111].

6.2.1. *Secondary liquid bio-fuels*

Ethanol can be produced from biomass-derived syngas through two processes: syngas fermentation and syngas thermochemical catalyst conversion [112–114].

Syngas fermentation is led by acetogenic bacteria. This process presents a greater flexibility in terms of biomass type and is more cost effective [112,114]. Acetogens are anaerobic bacteria able to transform CO and/or CO_2 and H_2 into acetyl-CoA through the reductive acetyl-CoA pathway [115]. The well-kwon acetyl-CoA pathway was first characterized by Ljungdahl and Wood [116]; for this reason it is also known as the Wood-Ljungdahl pathway. CO_2 fixation consists of a methyl branch (also called “Eastern”) and a carbonyl branch (also called “Western”). Six electrons reduce one molecule of CO_2 to a methyl group in the methyl branch, while another CO_2 molecule is reduced to CO in the carbonyl branch; the combination of the methyl group with CO and the enzyme acetyl-CoA synthase results in acetyl-CoA. The reduction of CO_2 is catalyzed by the enzyme CO dehydrogenase [117]. Ethanol can be produced through two systems: directly from acetyl-CoA in a two-step reaction via acetaldehyde, or via acetate and subsequent reduction to acetaldehyde [112].

Syngas thermochemical catalyst conversion into bioethanol can be obtained using several catalysts. Rhodium-based catalysts are ideal catalysts for their C^{2+} alcohols high selectivity but because of their cost researchers focus on more affordable substitutes, such as copper-based catalysts [118–122]. If copper-based catalysts are used, promoters are required to minimize the undesired reactions and maximize the ethanol production. Alkali, transition metals and their oxides are common promoters [121]. The main reaction occurring in long chain hydrocarbons synthesis follows the general scheme [123,124]:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{OH} + (n{-}1)\mathrm{H_2O} \tag{13}$$

where, n is an integer ranging from 1 to 8 (for ethanol $n = 2$).

Temperature is a fundamental parameter to control alcohol productivity. High production of C_2–C_3 alcohols can be achieved in the interval 833–858 °C; this temperature range minimizes the formation of unwanted by products [125].

The methanol production is carried out via catalyst conversion, in particular copper- or nichel-allumina-based catalysts [83,126–129].

The main processes to produce biodiesel from syngas are based on the Fischer–Tropsch (FT) synthesis [130–133]. The well-assessed FT process, when applied to a biomass syngas, can be defined as the indirect liquefaction of the biomasses in the presence of a catalyst [134]. Indeed, the syngas obtained by steam/air biomass gasification is cleaned and then fed to the Fischer–Tropsch reactor where the reaction between H_2 and CO occurs to produce hydrocarbons of varying molecular weight. According to Schulz [135], the main reaction occurring in the FT process follows the scheme:

$$(2n + 1)\,\mathrm{H_2} + n\mathrm{CO} \rightarrow \mathrm{C}_n\mathrm{H}(2n + 2) + n\mathrm{H_2O} \tag{14}$$

where, n is an integer. Methane (for $n = 1$ in reaction (14)) is considered as an unwanted compound.

The most significant parameter for Fischer–Tropsch synthesis is the H_2/CO ratio, for which the optimal value required by the process is ~2 (or higher) [136]. In the syngas produced by biomass gasification, the characteristic H_2/CO ratio is ~1 (or lower). Typically, the water gas shift reaction is favored by an increase in the H_2/CO ratio. Among the catalysts adopted in the FT synthesis, iron has a higher water-gas-shift activity than the others, therefore an iron-based catalyst is the most appropriate to obtain a H_2/CO ratio useful for biomass gasification syngas [135,137–139]. Cobalt-based catalysts are more active than iron, but their water-gas-shift activity is lower [135].

FT synthesis is characterized by a process temperature in the range of 693–893 °C and an operative pressure in the range of 1–30 atm. Increasing temperature and pressure lead to a higher conversion rate but high temperatures favor methane production. The formation of methane is minimized by working at temperature of about 693–753 °C. The methane produced by the synthesis and the methane contained in the biomass syngas can be converted into H_2 through catalytic dehydrogenation, with the advantage that CO_2 emissions are reduced if FT synthesis and catalytic dehydrogenation are coupled [140].

Several research centers are studying new catalysts like carbon nanotubes containing acidic functional groups and zeolites to produce biodiesel from syngas via FT synthesis [141,142].

Bio-dimethylether is obtained from methanol via catalytic dehydration using catalysts based on silica-alumina [83,129,143,144]. DME is also produced directly from syngas using bifunctional catalysts such as copper-ZSM-5 zeolite [145–147] or hybrid copper-allumina based catalysts [148]. Several research centers showed that it is possible to obtain an increasing of DME production with lanthanum oxide [149] or niobium–allumina [150]. An innovative, one-step process for DME production is based on the “reactive dividing-wall column” where it is possible to combine the unit of reactive distillation with the “dividing-wall column” technology in one single process [151–153].

At atmospheric pressure Bio-DME has a gaseous state, but due to its high capacity to liquefy at low pressure, as liquefied petroleum gas (LPG), it is used as a liquid biofuel [154,155].

According to Park and Lee [154] the engine performance improves with bio-dimethylether combustion thanks to its higher cetane number than biodiesel. Moreover HC and CO emissions are lower than in biodiesel combustion. An exhaust gas recirculation can be adopted to reduce the NO_x emission from DME combustion.

Laksmono and co-workers [131] studied thermal cracking and catalytic cracking as methods to exploit the tars from biomass gasification as fuels for internal combustion engines. They found that using thermal cracking, biodiesel production was around 75 wt% of feed at a temperature of about 953 °C; using catalytic cracking in the presence of zeolite, magnesium oxide, and aluminum oxide catalysts biodiesel production was 62–75 wt%, 55–66 wt%, 67–71 wt%, respectively.

6.2.2. *Gaseous products*

The biomethane production from biomass thermochemical conversion begins by syngas production. The syngas is compressed and fed to the catalytic methanation stage, where the exothermal reactions due to catalyst systems, such as nickel-allumina catalyst occur [156–162]. Biomethane can also be produced by a membrane technology, using a multistage configuration process, in which the syngas is compressed and fed to some polymer permeation modules in series [163,164].

The great advantage of the production of biomethane is the possibility to plug it directly into the natural gas grid, upgraded to natural gas quality [163]. By 2020 the German government intends to increase the biomethane injection in the pipeline system to 6 billion m^3/y [165]. Moreover biomethane can be used as transport biofuel

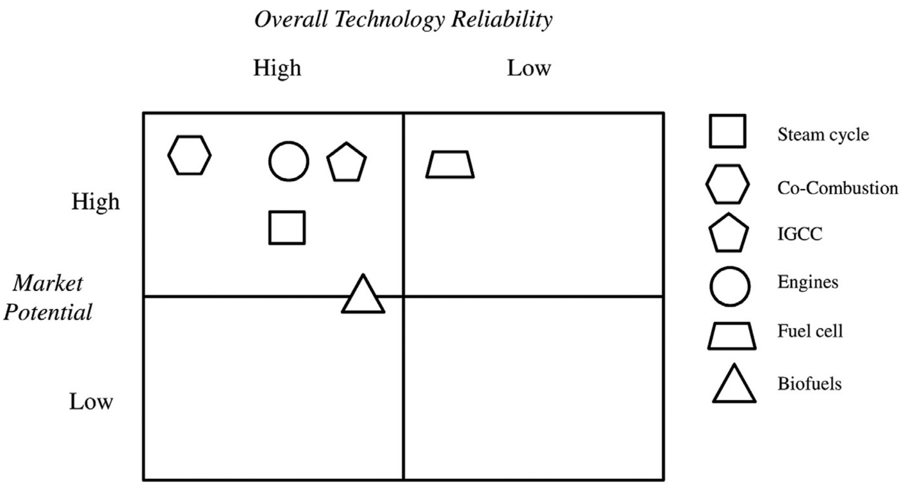

Fig. 12. Status of applications for market potential and technology reliability derived from Maniatis [172].

Table 10. European biomass gasification plants [173].

Site gasification plant	Input	Product	Output	Technology
Skive, Denmark	Lignocellulosics; wood pellets	Heat; power	11 MWth; 5,5 MWel	CHP conversion
Harboøre, Denmark	Lignocellulosics; wood chips	Heat; power	3,5 MWth; 1 MWel	CHP conversion
Barrit, Denmark	Lignocellulosics; wood chips	Heat; power	140 kWth; 35 kWel	CHP conversion
Kgs. Lyngby, Denmark	Lignocellulosics; wood chips	Heat; power	140 kWth; 35 kWel	CHP conversion
Cumbria, United Kingdom	Lignocellulosics	–	1 MWel	CHP conversion
Mossborough, United Kingdom	Lignocellulosics; wood chips	–	250 kWel	CHP conversion
Neunkirchen, Austria	Lignocellulosics; waste wood, clean wood, biomass	Heat; power	620 kWth; 300 kWel;	CHP conversion
Güssing, Austria	Lignocellulosics; wood chips	Heat; power	4.5 MWth; 2.0 MWel	CHP conversion
Oberwart, Austria	Lignocellulosics; wood chips	Heat; power	1–6 MWth; 2.7 MWel	CHP conversion
Neumarkt, Austria	Cleanwood, biomass	Heat; power	580 kWth; 240 kWel	CHP conversion
Sulzbach-Laufen, Germany	Other; wastewood, biomass	Heat; power	280 kWth; 130 kWel	CHP conversion
Neufahrn bei Freising, Germany	Lignocellulosics; waste wood, clean wood	Heat; power	250 kWth; 110 kWel	CHP conversion
Langballig, Germany	Lignocellulosics; wood chips	Heat; power	280 kWth; 70 kWel	CHP conversion
Carlow, Ireland	Lignocellulosics; wood chips	Heat; power	140 kWth; 35 kWel	CHP conversion
Wila, Switzerland	Lignocellulosics; dried chips from waste wood	Heat; power	425 kWth; 350 kWel;	CHP conversion
Stans, Switzerland	Lignocellulosics; dried chips from demolition wood	Heat; power	1.2 MWth; 138 kWel	CHP conversion
Geertruidenberg, Netherlands	Wastewood; demolitionwood	Heat; power; gas for coal-fired boiler	30 MWel	Co-firingconversion
Buggenum, Netherlands	Biomass /biomasscoalblends	Power	280 MWth	Co-firingconversion
Lahti, Finland	Lignocellulosics; wood chips, wood waste, plastic waste	Fuel gas	40–90 MWth	Co-firingconversion
Värö, Sweden	Lignocellulosics; bark	Heat	35 MWth	Co-firingconversion
Varkaus, Finland	Other; wood fibre, plastic, aluminium	FT-liquids; heat; aluminium	14 t/d; 50 MWth	Synthesisconversion
Groningen, Netherlands	Other; from biodiesel and oleochemicals	Methanol	200 000 t/a	Synthesisconversion

for gas-operated cars or for electric cars [166–168]. For example, in the Swedish city of Västerås biomethane has been adopted as vehicle fuel in the local public transport system [169].

The typical path to produce hydrogen from syngas is the catalyzed Water-Gas Shift Reaction [170]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (15)$$

Two kinds of catalyst can be used: high temperature and low temperature shift catalysts.

Chromium-supported iron-based catalysts are the main high temperature shift catalysts. They must operate at a temperature in the range 350–400 °C to achieve a CO outlet concentration in the range 2–4 vol%, in a single adiabatic fixed bed [171].

Using a dual fixed bed system, CO conversion can be improved. If copper-based catalysts are used in the second bed, the CO outlet concentration can reach the range 0.1–0.3. Copper-based catalysts are the main low temperature shift catalysts. They must be operated at a temperature of about 200 °C [171].

Hydrogen can be used as the chemical basis for ammonia production or as a fuel for fuel cells. A schematic representation of the market potential and the technological reliability of the products of biomass gasification is shown in Fig. 12; this figure, starting from the version proposed by Maniatis [172], has been updated to include novel processes.

7. Status of the European biomass gasification plants

In the last decades, the presence of the gasification process in the European market has increased. In Europe there are 22 gasification plants and 7 companies have the know-how for their construction [173]. Sixteen are power generation or combined heat and power generation plants, four are co-combustion plants and two plants are dedicated to the production of chemicals, as show in Table 10.

Table 11. Italian biomass gasification plants [174].

Site gasification plant	Input	Output (kWe)
Rossano calabro (CS)	Olive pomace	4,200
Belluno (BL)	Wood chips	1000
Parma (PA)	Kenaf	1000
Vistarino (PV)	Wood chips	1000
Gadesco pieve delmona (CR)	Biomass chopped/biomass chips	960
Alessandria (AL)[a]	Biomass forestry	640
Vigevano (PV)	Wood chips	500
Caluso (TO)	Agriculture waste, biomass forestry, food industry waste	400
Oltrepo pavese (PV)	Wood chips	320
Castel san pietro (BO)	Pruning wastes, corns stocks, wood chips	250
Orzinuovi (BS)	Biomass forestry	250
Verbania (VB)[a]	Biomass forestry	250

[a] Experimental plant.

Table 12. Biomass gasification plants in Europe with an operation time greater than 7000 h/y [176–180].

Site	Thermal output (MW)	Running (h/y)
Harboore (Denmark)[a]	20	8000
Gussing (Austria)[b]	8	7000–8000
Skive (Denmark)[c]	20	7500[f]
Lahti (Finland)[d]	40	7000
Buggenum (the Netherlands)[e]	600	7500

[a,b,c] Biomass gasification plant.
[d,e] Co-combustion plant fuelled with carbon and biomass.
[f] Cumulative hours in the 2008–2009 biennium.

In Italy several gasification plants exist, they have low capacity and are power generation plants, as show in Table 11 [174].

The biomass gasification plants operating in Europe produce electricity in combined heat and power (CHP) configuration; these plants often do not produce more than 1 MWe. On the other hand, larger plants are often co-combustion plants and only few biomass gasification plants are able to produce biofuels such as methanol or others biofuels via Fischer Tropsch process [175].

In several cases there is no information about the yearly running time for these plants, and, when this information is available it is discouraging. The biomass gasification plants with long running times per year are reported in the Table 12. The data in this table show that about 700 MW are running for biomass gasification in Europe; these plants have an operation time greater than 7000 h/y [176–180].

Although this paper is focused on biomass gasification, according to the authors it can be useful to present a short overview of the waste gasification plants (Table 13) in Europe at present. It is possible to see that in several cases the gasification stage is a pre-stage for the successive complete combustion. In this way the combustion stage, burning the syngas, is cleaner and more efficient than the direct combustion of wastes and it is possible to use a reduced excess air. Only few gasification plants, SchwarzePumpe, Rudersdorf, Freiburg, Lahiti, Greve and Norrsundet are pure-gasifier which produces syngas usable in combustion devices for the power production such as the internal combustion engines, using biomass as co-feeding material [181].

8. Conclusions

Gasification technology can be a good solution for energy production from renewable sources, but in order to eliminate the causes that hinder its development on a large scale other efforts are necessary. Several technological problems exist, first of all the compatibility between the engines and syngas. The optimal operation of engines coupled with gasification plants requires a high quality standard fuel, but due to the high concentration of pollutants, such as tar, ammonia and sulphidric/chloridric acids, the syngas quality is often not sufficient. Furthermore, gasification companies provide little information about the cleaning section of plants and the engine is not guaranteed for a long period of time. Moreover, economic profitability strongly depends on the biomass market price, even if gasification plants often obtain considerable financial incentives from governments.

A Best Practics in biomass gasification process is the heat recovery of power production flue gas. To achieve the highest energetic efficiency heat and power production systems (CHP) or tri-generative processes are combined with electrical, heat and cool production (CCHP).

Syngas is not only an energetic carrier for power production but also an intermediate product for liquid and gaseous biofuel production. Liquid biofuels, such as biodiesel and bioethanol, can be stored and used as transport fuels; gaseous biofuels, such as biomethane, can be injected directly in the natural gas distribution grid. A high overall efficiency of biomass power production–Organic Rankine Cycle or heat, cool and power production–is the key for the success of such a plant.

Due to the high syngas purity, required to save the catalyst in the biofuel synthesis, only few pilot or industrial plants for the production of liquid or gaseous biofuels from syngas are functioning at present.

Table 13. Waste gasification plant running in Europe [181].

Site	Input	Technology
Averoy, Norway	MSW	Gasificat. + combustion
Hurum, Norway	MSW and industrial waste	Gasificat. + combustion
Sarpsborg, Norway	MSW and industrial waste	Gasificat. + combustion
Forus, Norway	MSW	Gasificat. + combustion
Karlsruhe, Germany	MSW and commercial waste	Pyrolysis + gasification
Minden, Germany	MSW and commercial waste	Gasificat. + combustion
SchwarzePumpe, Germany	plastics, RDF, wood, sewage, sludge, lubricants,coal RDF	Gasification
Rudersdorf, Germany	plastics, RDF, wood, sewage, sludge, lubricants,coal RDF	Gasification
Freiberg, Germany	sewage sludge + MSW	Pyrolysis and entrained flow gasification
Lathi, Finland	biomass fuels (up to 40% RDF)	Circulating fluidized-bed boiler with gasification
Greve-in-Chianti, Italy	pelletised RDF	Gasification
Norrsundet, Sweden	MSW and industrial waste	Gasification

In several gasification plants, in order to increase the cleaning efficiency, syngas depuration is performed at atmospheric conditions, with consequent losses in terms of gasification process efficiency and power production, especially when the gasifiers are coupled with high energetic conversion devices that require syngas at high temperature, such as high temperature fuel cells or gas turbines.

Biomass gasification has some advantages over traditional combustion processes, in terms of heat and power production and environmental protection:

- Combustion of syngas is cleaner and more efficient respect to the direct combustion of biomass and it is possible to reduce excess air and heat loss into the exhaust gases.
- Combustion in the homogeneous phase allows greater continuity of the process and easier control.
- Volumetric flow rate of the produced fuel gas is much reduced compared to that of the effluent gas of a direct combustion process, resulting in lower costs of the cleaning process.
- Even if the syngas produced is burned on site, there is the possibility of removal of certain impurities after the gasification stage and before the syngas combustion.
- Allows to have more restrictive environmental limits than at the 2000/76/EC European law for the incineration of waste, in fact it is possible to reduce the production of organic micropollutants such as dioxins and furans as well as NO_x and SO_x.

The gasification process is a valid alternative to traditional thermochemical processes for power generation, and also a process for the production of a chemical intermediate usable to produce other compounds, such as biofuels and green chemicals, such as methanol and DME. Therefore more research is required in order increase the overall efficiency of gasification processes. A new approach, capable to valorize all gasification products–chemicals fuels and heat–is required to allow the diffusion of such a process in the international market.

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