

Review

Fluidized Bed Gasification as a Mature And Reliable Technology for the Production of Bio-Syngas and Applied in the Production of Liquid Transportation Fuels—A Review

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Abstract: Biomass is one of the renewable and potentially sustainable energy sources and has many possible applications varying from heat generation to the production of advanced secondary energy carriers. The latter option would allow mobile services like the transportation sector to reduce its dependency on the fossil fuel supply. This article reviews the state-of-the-art of the fluidization technology applied for the gasification of biomass aimed at the production of gas for subsequent synthesis of the liquid energy carriers via, e.g., the Fischer-Tropsch process. It discusses the advantages of the gasification technology over combustion, considers the size of the conversion plant in view of the local biomass availability, assesses the pros and cons of different gasifier types in view of the application of the product gas. Subsequently the article focuses on the fluidized bed technology to discuss the main process parameters and their influence on the product composition and the operability of the gasifier. Finally a synthesis process (FT) is introduced shortly to illustrate the necessary gas cleaning steps in view of the purity requirements for the FT feed gas.

Keywords: biomass; gasification; fluidized bed; BTL; transportation fuels

1. Biomass: An Introduction

1.1. History of Biomass Use for Energy Generation

Biomass is the oldest fuel known by mankind and has been used for thousands of years for cooking and heating purposes. Fossil fuels were also known, for example coal was used by the Chinese probably as early as 1000 B.C., and by the Romans prior to A.D. 400 [1], however the first biblical references that indicate its use are approximately from the 13th century onwards [2]. The use of coal was also initially limited as compared to biomass. However, since the beginning of the Industrial Revolution in the 18th century, the demand for energy started to increase. This was initially due to industry and later also to households. Biomass could not compete with the “convenient” and seemingly inexhaustible fossil fuels that also had significantly higher energy density than biomass. At the end of the 19th century, due to the introduction of the automobile, petroleum gained wider use as a fuel. However, crisis situations worldwide exposed the first weakness of fossil fuels, namely their strictly distributed availability. After World War I and especially during World War II, shortage in petroleum supplies led to the re-introduction of biomass use as an energy source. However, in contrast to previously mentioned applications of biomass, the process did not involve combustion (complete oxidation) but production of a secondary (gaseous) energy carrier via the gasification (partial oxidation) route. The German term “Holzgas” (woodgas) is still a widely recognized term for the vehicle fuel produced in that way. Figure 1 shows the practical implementation of such a system. Next to this woodgas technology, a synthesis process of diesel-like fuel, invented by F. Fischer and H. Tropsch successfully yielded substitute vehicle fuel, which ultimately covered 90% of German consumption at that time [3]. Although the Fischer-Tropsch process was based on (brown) coal, it initiated the interest in solid-to-liquid fuel technologies, also applicable for biomass.

Figure 1. A WWII car with woodgas generator [4].



After World War II development in this area was abandoned due to lack of strategic impetus and abundant availability of cheap fossil fuel. However, some countries (e.g., Sweden) continued to work on producer gas technology and included it in their strategic emergency plans [5]. Today’s interest in biomass (and other renewable energy sources) and its related research and development, for the most part, dates from the 1973 oil crisis. The developing political situation made clear that the concentration

of major fossil fuel resources in certain (often politically unstable) areas of the world threatened the energy security of the depending countries. Decreased supply and demand which is still increasing has led to an excessive rise in energy prices—this being the second weakness of fossil fuels. Around that time a third weakness was also exposed, which was the negative environmental impact of the emissions related to the rapid consumption of carbonaceous resources stored under the Earth's crust. Phenomena like acid rain, smog, global warming, air pollution, *etc.* forced not only the improvements of existing conversion technologies in terms of efficiency and residue (exhaust) clean-up, but also the search for alternative, renewable and environmentally neutral sources of energy. Biomass is one of such sustainable energy sources.

For some applications the production of secondary (gaseous or liquid) fuels has remained the best option. Consequently high efforts, both financially and intellectually, are currently being put into the revival, expansion and improvement of the work initiated by Fischer and Tropsch, now coupled with biomass gasification.

1.2. Definition and the Availability of Biomass

Currently the mostly exploited renewable energy resource is hydropower. From the estimated 62 EJ of hydropower available on a yearly basis (2005 data [6]), nearly 26 EJ (42%) is being used. Looking at the availability of modern biomass (thereby including agricultural wastes and crops grown for energy purposes), which in 2005 was estimated at 250 EJ [6] per year only 9 EJ (3.6%) has actually been used for energy generation. Biomass has been mentioned to be the fourth largest energy resource in the world, after geothermal, solar and wind energy, currently contributing to about 15% of the world's total primary energy consumption, while fossil fuels contribute to about 81% [6]. The total estimated biomass resources amount to about 2900 EJ per year (of which 1700 EJ are from forests, 850 EJ from grasslands and 350 EJ from agricultural areas). However, only 270 EJ [7] (250 EJ in [6], see also Table 1) could be considered available on a sustainable basis and at competitive prices. The management of biomass resources and delivery of the energy, either in the original form (raw biomass) or as secondary fuel, to the end user are the key aspects that will decide whether a certain batch of biomass can be considered as being sustainable or not.

There are several definitions of biomass. The European Commission (EC) states, that biomass “shall mean the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste” [8]. However, in general terms it can be described as “plant materials and animal waste used especially as a source of fuel” [9]. The renewability and sustainability aspects of biomass originate from the fact that the carbon dioxide from the atmosphere is stored by the plants during the photosynthesis process, and released again during biomass conversion to generate usable energy. In between those two processes the plant material is either harvested and it enters the conversion process directly or as a waste stream from e.g., agriculture or forestry, or alternatively it enters the food chain (this is why animal waste is also considered as being biomass). Figure 2 shows the carbon cycle, together with photosynthesis and the main biomass conversion technologies. This figure clearly illustrates that biomass is a CO₂ neutral energy source (so no net CO₂ emission in the atmosphere). However it should be mentioned that this cycle shows the ideal situation and that the input of minerals/fertilizers whilst

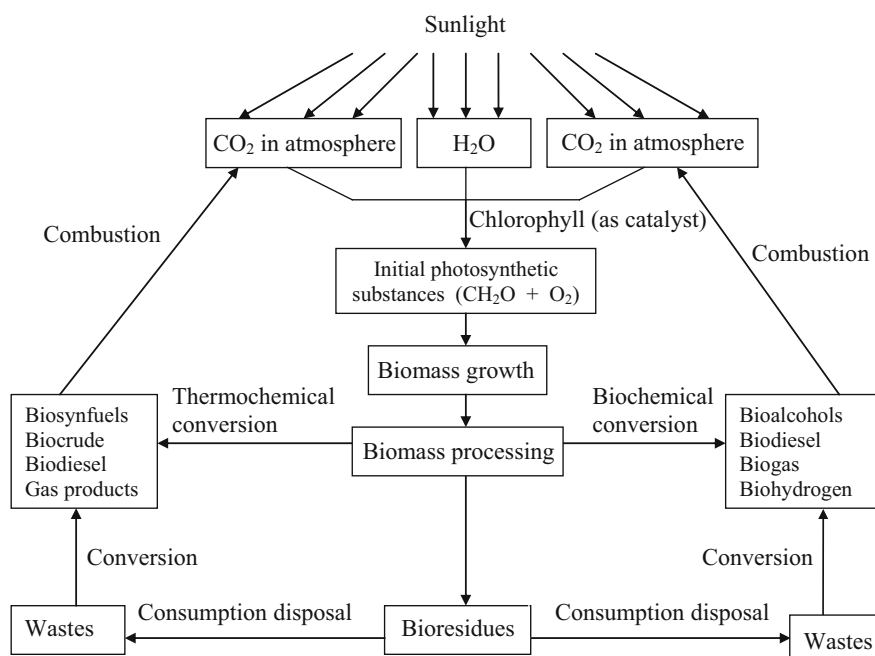
plants are growing, and emissions during biological degradation (CH_4 that has a significantly higher greenhouse gas potential than CO_2), transportation, drying and storage of biomass have not been taken into account. Therefore, the use of biomass can also have an adverse effect on the environment and care should be taken to minimize these negative effects in order to remain on the sustainability path. Life Cycle Analysis (LCA) can be a helpful assessment tool in this process (see, e.g., [10]).

Table 1. Energy demand and availability of main renewable resources on annual basis (adapted from [6]).

Renewable Resource	Estimated Availability [EJ]	Rate of Use (2005) [EJ]
Hydro	62	25.8
Wind	600	0.95
Biomass	250	46 ^a
Geothermal	5000	2
Solar (PV)	1600	0.2
Total	7512	75.0
Current Demand	490	

^a including 37 EJ of traditional biomass use (heating and cooking).

Figure 2. Carbon cycle, photosynthesis and main steps in biomass technologies [11].



1.3. Types and Properties of Raw Biomass

From the definition given above it is quite evident that biomass may vary significantly in its physical and chemical properties. A typical composition of biomass comprises of cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, inorganics (ash), and other compounds. As a result of different origins and variety of compositions, the classification of biomass

is not an easy task. Many classification attempts can be found in literature. Demirbas [11] gives the following categorization:

1. Forest products: wood, logging residues, trees, shrubs and wood residues, sawdust, bark, *etc.*;
2. Bio-renewable residues: agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes;
3. Energy crops: short rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops;
4. Aquatic plants: algae, water weed, water hyacinth, reed and rushes;
5. Food crops: grains, oil crops;
6. Sugar crops: sugar cane, sugar beets, molasses, sorghum;
7. Landfill;
8. Industrial organic wastes;
9. Algae, kelps, lichens and mosses.

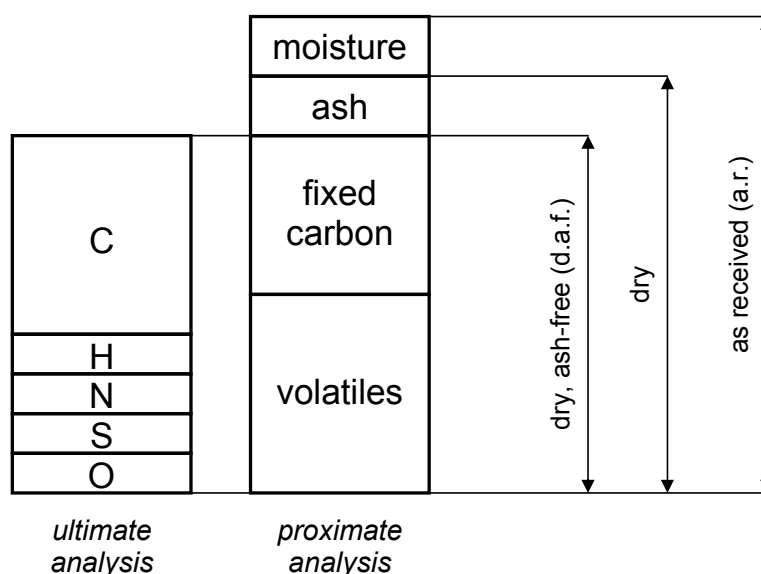
When considered as a primary energy carrier, each category will have its specific benefits and problems, depending on the conversion technique. The main issues are:

- The amount of ash. Ash refers to the inorganic part of a solid fuel. In analytical chemistry it refers to the remaining solid matter after complete oxidation of the combustible fraction, mostly consisting of metal oxides. A high amount of ash will lower the energy content of the fuel and may cause handling problems during and after the conversion process (solid residues);
- The composition and the structure of ash. The interaction of ash with the remaining species in the process will depend on its composition. Often ash will show an inert behavior, not leading to any chemical interaction with the process. Some metal oxides, like CaO, MgO, Fe_xO_y may act as catalysts for some chemical reactions during and after the conversion process (see Section 3.2.—bed materials and additives part). This can be beneficial (faster conversion of species) or problematic (smouldering of disposed off ashes). In addition it is well known, that the presence of alkali metals in the ash, promoted by the presence of chlorine, will lead to the formation of low-melting, “sticky” compounds that are likely to cause problems, in particular during high temperature conversion processes. Furthermore, the presence of heavy trace metals (e.g., lead, mercury) may cause environmental and health problems irrespective of the conversion process applied. The structure of the ash may have negative influence on the volatile release and the burn-out of a fuel particle, leading to higher emissions or lower conversion efficiencies (e.g., the case of pepper plant residue, PPR [12,13]);
- The moisture content of raw biomass. Moisture, naturally present in raw biomass—just like ash—will lower the energy content of the fuel. However, for some conversion processes the presence of moisture is desired or even essential. The “classical” thermal conversion processes in particular, however, will not accept biomass of which the moisture content is too high (typically maximum 30%_{wt} [14]; Demirbas [11] quotes 10%_{wt} moisture, which in practice would not be realistic, as drying below 10%_{wt} moisture is expensive [15]; Hofbauer [16] indicates test runs

with wood chips containing 20–30%_{wt} moisture; the website of IEA Bioenergy Task 32 [17] reports commercial biomass gasifiers operating on fuels with 20–50%_{wt} moisture, e.g., in Lahti). Therefore often some kind of drying process will be applied upstream. Additionally, high moisture content of raw biomass will significantly increase the transportation costs, unless the biomass is transported as a slurry using pipelines.

From the above it is clear that the diversity of biomass will make the development of one universal conversion process very difficult. In Section 1.5. the most common biomass conversion processes will be introduced and their suitability to convert certain categories of biomass will be indicated. Figure 3 shows the main components of any organic fuel. It is obvious, that the calorific value is governed by the fraction of carbon (C), hydrogen (H) and sulphur (S), while moisture and ash basically act as “dilutants”. The proximate analysis indicates the amount of volatile matter and fixed carbon in the fuel, which together with the oxygen (O) content gives an indication of the reactivity of a fuel. Highest rank coals consist of over 90% fixed carbon [18], making them not very reactive. Biomass, on the other hand, is mostly composed of volatile matter and a significant amount of oxygen (>20%_{wt}), which makes it much more reactive than coal. Table 2 shows the main composition of some representatives of different classes of biomass; an extensive overview can be found elsewhere [19–21].

Figure 3. General composition and main chemical elements in typical solid organic fuels.



In addition to the very diverse composition and presence of potentially problematic constituents, as explained above, there are further aspects which do not make raw biomass very convenient to use, and for some applications it may not even be directly suitable. These are that:

- Biomass is a solid and therefore can only be distributed as any other bulk material (except for slurries, but their very high water content needs to be considered);
- Biomass has a relatively low volumetric energy density (typically $9 \pm 5 \text{ MJ m}^{-3}$, compared to $38 \pm 5 \text{ MJ m}^{-3}$, both on LHV-basis, for natural gas), which makes transport over long distances inefficient. Furthermore the energy density of biomass strongly depends on the appearance and densification methods applied (pelletized or “loose”);

- Conversion of a solid fuel is more complicated from a technical point of view than conversion of a gas or a liquid. In particular issues like pretreatment (size reduction), reactor feeding, ash removal (dedusting), *etc.* form main hurdles and make the processes more complicated compared to homogeneous gas processes or liquid/gas processes.

Table 2. Main compositions of different kinds of biomass; coal listed for comparison [19].

Biomass	C	H	O	N	S	Cl	Ash	Moisture
pine	52.1	6.36	41.0	0.07	0.05	0.01	0.37	
oak	49.9	5.98	42.6	0.21	0.05	0.01	1.29	
barley straw	42.9	5.53	45.5	0.56	0.25	0.35	4.95	
hay	45.5	6.1	39.2	1.14	0.16	0.31	5.70	
miscanthus	47.5	6.2	40.7	0.73	0.15	0.22	3.90	
algae (micro) ^a	52.7	7.22	28.9	8.01	0.49	0.18	2.5	
black liquor ^b	35.5	3.15	0.79	0.27	5.30	0.08	57.5	9.61
MSW	47.6	6	32.9	1.2	0.3		12	
sewage sludge	32.6	4.5	18.9	4.38	1.69	0.12	37.50	85.0
coal (bitum.)	75	4	14		2		5	

^a retrieved from [20]; ^b adapted from [22].

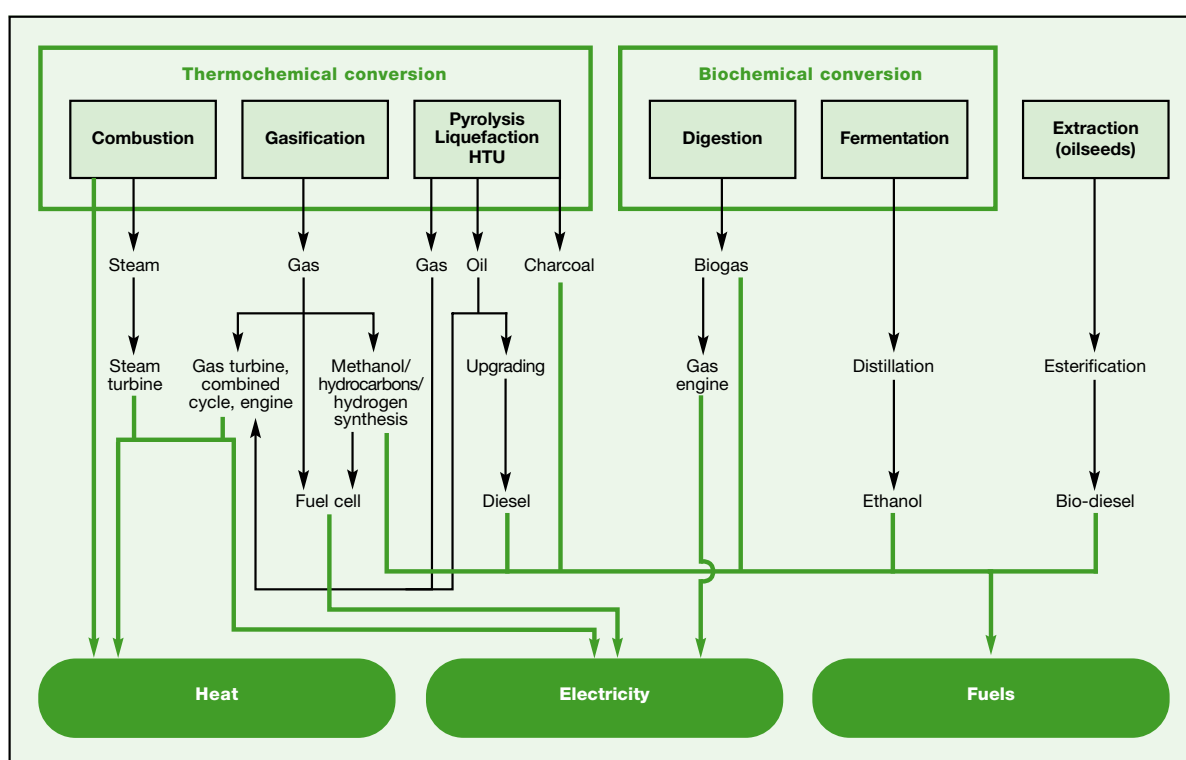
The (industrial) applications where raw biomass can be directly converted into the final product are basically limited to (co-)combustion. Over the last decades, many different technologies have been proposed to convert solid biomass into a more convenient secondary energy carrier. Figure 4 shows the currently known and investigated biomass conversion routes. It shows the three main groups of conversion technologies: mechanical extraction, biochemical conversion and thermochemical conversion. It also shows that there are many possible pathways that essentially lead to three products: electricity, heat and fuels (secondary energy carriers). Most of the conversion routes presented in Figure 4 are well-known chemical processes, but the difficulty is that those processes have not (extensively) dealt with biomass as a feedstock yet. The research and practical experience obtained from small pilot projects have shown that the use of biomass as feedstock can cause unexpected problems that have to be solved before a certain conversion route will be mature for industrial introduction. Except the technological advancement and maturity, the choice of the conversion route will strongly depend on the scale on which the process will be applied. The order of the magnitude of the scale of the three process categories mentioned above, expressed in terms of fuel thermal power input are as follows:

- Mechanical extraction: 500–50,000 tonnes product (oil) annually. Assuming a total biomass-to-oil efficiency of 42% and the heating value of biomass of 16 MJ kg⁻¹ it is approximately an equivalent of 0.6–60 MW_{th} ([23], pp. 143–172);
- Biochemical conversion: up to 400 MW_{th} [24], or even >800 MW_{th} [25] for 1st generation ethanol production;
- Thermochemical conversion: 1–1000 MW_{th} [19].

The above list shows that although the thermochemical conversion route gives the biggest scale-up possibilities, the biochemical conversion and the mechanical extraction can also be performed at

significant scale. However, at present there is a serious concern related to the first two processes when applied to the production of secondary energy carriers, namely they compete directly with the food and fibre production (except possibly the ethanol production from sugar cane) [26]. Using ligno-cellulosic residue streams and energy crops (the 2nd generation biofuels), that issue can be overcome. Nonetheless, both the mechanical extraction and biochemical conversion produce a solid waste stream that can only be utilized using a thermochemical conversion process. Currently the concept of a “biorefinery” is also receiving substantial attention; here each constituent of biomass is extracted or utilized using a dedicated process. Such a concept can include biochemical and thermochemical conversion side-by-side. However, this topic falls outside the scope of this work.

Figure 4. Main biomass conversion routes [29].



1.4. Optimal Scale of the Biomass Conversion Plant

Notwithstanding having different conversion processes available in a broad capacity range, the optimal size of the plant will still need to match the available biomass resources. Power plants fired on fossil fuels easily reach hundreds of megawatts of electrical output (often meaning more than 1 GW thermal output). This is justified by the economy of scale and the relatively low transportation costs of fossil fuels due to their high specific energy content and often concentrated deposits. In contrast, biomass is often distributed over a large area. In order to maintain the sustainability aspect of biomass use and minimize the energy consumption and emissions related to transporting biomass to the processing site, the size (in terms of fuel throughput) of the plant needs to match the local biomass resources. To illustrate this, a simple comparison of the raw biomass resources and their demand was undertaken for three different regions of France, one of the largest countries within the European Union. In that comparison the annual primary energy consumption *per capita* was retrieved from three different

sources and averaged. Then the availability of biomass within the radius of 100 km from three different French cities was calculated using BIORAISE, a tool for biomass resources assessment in Southern Europe [27]. With the known average population density in France (100.9 people per km² [28]), the match between the supply and demand can be assessed. The input and the results of that comparison are presented in Table 3. The assumed heating value of biomass was 16 MJ kg⁻¹, which is typical for relatively dry biomass; this value has been used throughout the comparison as the biomass resources are reported in “oven-dry tonnes” (o.d.t.). The primary energy requirement per capita is estimated from the following sources:

- 140 GJ, commercial & non-commercial, 1995 data for Western Europe [29];
- 4.5–6 toe (189–252 GJ, average 221 GJ), 2004 data for Western Europe [6];
- 6.5 kW (205 GJ per year), data for industrialized countries [30].

The average of the above will return 188.5 GJ per capita per year of primary energy demand. That figure and the average population density are used to calculate the demand for raw biomass within a 100 km radius; for the French case this amounts to approximately 37 Mtonnes per year. From Table 3 it is clear that the current biomass *potential* covers 12%–29% of the demand, whilst the *available* biomass would satisfy only 9%–18% of the demand. These figures may seem discouraging at first glance and they might be quoted by people that are sceptical about the use of biomass as an energy resource. However, already in Section 1.2. it was indicated that the world’s total biomass resource available on a sustainable basis and at competitive prices (250–270 EJ per year) would only be enough to cover approximately 50% of the primary energy needs (490 EJ per year). Therefore it is clear that to match the supply with the demand other renewable energy sources must also be used. In addition, it is unavoidable (but perhaps for many difficult to accept) that demand should also be reduced, meaning a global reduction of energy consumption. It should also be kept in mind, that the 188.5 GJ per capita represents the *total* primary energy requirement. Assuming that demand is equally split between the generation of electricity, spacial heating and cooking, transportation and industry (also accounted for in the total figure), then the biomass resources would be sufficient to cover one of the areas of partial demand. For example, the production of secondary fuels from biomass could cover the energy demand of the transportation sector; solar and wind energy assisted by small, decentralized (or even domestic) CHP units could contribute to the supply of heat and power. The industry should benefit from the synergetic effects of the existence of biomass conversion plants, such that their individual energy requirements could be partially covered by the “waste streams” from the biomass plant (e.g., steam, low-temperature heat). It is thus clear that the final solution of the “energy issue” is to be a complex mixture of technology development, system studies, legislation, as well as information and education.

Table 3. Availability of biomass in three different regions in France.

Region	Coordinates ^a		Biomass		Costs			
	x	y	Potential o.d.t	Availability o.d.t.	Collection k€	Transport k€	Total € tonne ⁻¹ ct GJ ⁻¹	
Bordeaux	3512775	2435650	4,675,295	3,265,897	89,463	76,678	50.87	0.32
Nancy	4039916	2848642	5,858,141	3,794,951	108,898	74,213	48.25	0.30
Paris	3761197	2889300	10,942,994	6,757,463	120,784	134,547	37.79	0.24
Est. average demand per region			37,344,995 o.d.t.					

^a BIORAISE input.

At this point it can be concluded that the size of a biomass conversion system should be chosen with care, and that probably more distributed units of smaller size may fit better to the fuel availability pattern. For Europe the suggested maximum size of a biomass processing plant was 30–80 MW_e in the short to medium term [31].

If the biomass is intended to be used in a process producing secondary energy carriers, and in particular liquid fuels for the transportation sector, then there is an obvious benefit from the economy of scale and therefore medium or large-size conversion plants come into consideration. From the list given at the end of Section 1.3., at present only the thermochemical conversion route allows scale-up possibilities into the tens or hundreds of megawatts scale. As the focus of this paper is on the production of liquid biofuels, henceforth this work deals with the thermochemical conversion of biomass.

1.5. Biomass Conversion Routes

Table 4 shows an overview of the main characteristics of the three thermochemical fuel conversion processes, as listed in Figure 4. The most well-known and applied process is combustion. The product of that process is a hot, inert gas. As storage is not a viable option, heat is usually transferred to another medium that often undergoes a thermodynamic cycle to deliver net work. A typical example of such an application is a power plant employing a steam cycle or an Organic Rankine Cycle to produce electricity. In fact, the functioning of the most countries relies on the electricity generated in a steam cycle, and its sudden absence has severe consequences (e.g., as during blackouts in New York City in 1965 and 1977). However, the combustion process and the electricity production route are not free from drawbacks. To begin with, electricity is a very convenient energy carrier, but its application is so far limited to stationary applications (disregarding small personal portable devices and the rail roads, which require dedicated infrastructure). Considering the problems faced in the development of electric passenger cars related to the operational range of the vehicle, it is clear that heavy road transport will not run on electricity until significant improvements will be made in the field of electricity storage capacity. At this stage processes like pyrolysis or gasification come into consideration (see Table 4), as both yield a combustible product in a liquid and/or gaseous state. The pyrolysis process can even be tuned to produce high fractions of liquids (pyrolytic oils); unfortunately their chemical composition is highly variable and can not be controlled easily. Furthermore high content of oxygenated compounds and the acidity of the oil make it reactive and degradable, causing problems with storage [31,32].

Table 4. Main characteristics of the three thermochemical fuel conversion processes.

	Combustion	Gasification	Pyrolysis
Main products	heat, flue gas	combustible gas, heat	oil, (combustible) gas & char
Energy balance	exothermal	autothermal	allothermal
Carbon conversion	>99%	80–95%	≈75% (oil yield)
Main product constituents (raw gas)	CO ₂ , H ₂ O, N ₂	CO, H ₂ , CH ₄ , CO ₂ , H ₂ O, N ₂ ^a , tar ^b	oil, tar vapor, CO, H ₂ , CH ₄ , CO ₂ , H ₂ O, char
Oxygen stoichiometry (λ)	>1, typically 1.3 for solid fuels	0 < λ < 1 typically 0.2 < λ < 0.4	0
Chemical reactivity of the main product	inert	combustible, but stable	combustible, reactive
Physical appearance	gas	gas	solid, liquid & gas
Heating value [MJ kg ⁻¹]	0	typically 5–20	16–19 (HHV)

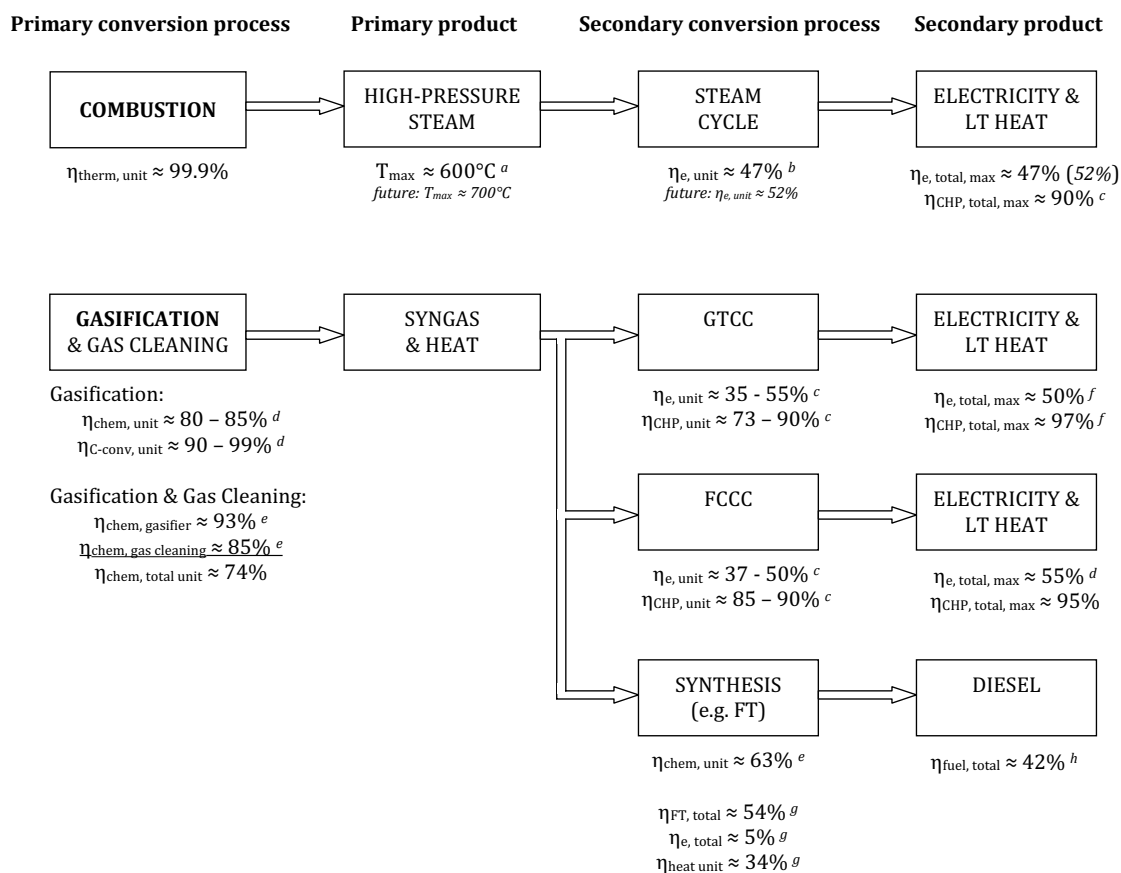
^a in case of air-blown gasification; ^b amount strongly depending on the gasification process.

1.5.1. Motivation to Apply Gasification as Biomass Conversion Step

In contrast to pyrolysis, the raw product of the gasification process, usually called “product gas” or “producer gas” consists of stable chemical species; the term “syngas” usually does not apply to the raw gas, as most gasification systems do not produce gas of such quality (syngas: a mixture of H₂, CO, CO₂ and H₂O) and the gas needs to be upgraded to be called “(bio-)syngas”. Therefore (biomass) gasification produces a more versatile secondary energy carrier, which is suitable to use in more downstream processes, than solely the generation of electricity, as in the case of combustion. This also opens a new path for the application of solid renewables, as the production of liquid fuels from biomass via the syngas route could allow the transportation sector to benefit from the renewable energy resources. In addition to the aforementioned benefit, also in the process of producing electrical energy, gasification is favorable above combustion in terms of the conversion efficiency. Figure 5 shows the main steps involved in the conversion process and their respective energy conversion efficiencies. A biomass boiler with a steam cycle operating at supercritical steam conditions will at present yield a maximal electrical efficiency of approximately 47%. This is expected to increase to 52% in the future, when new materials become available, allowing further increase of the live steam temperature. On the other hand, a gasifier-gas cleaning combination with a gas turbine combined cycle (GTCC) can reach an electric efficiency of approximately 50%, while an even higher value (approximately 55%) can be achieved when a fuel cell combined cycle (FCCC) is employed. The combined heat & power (CHP) efficiencies exceed 90% for all the three cases mentioned above. Last biomass conversion route presented in Figure 5 utilizes the syngas to produce a liquid energy carrier using a synthesis step instead of combusting it in a gas turbine or a fuel cell. It is clear that gasification not only shows a higher overall fuel-to-electricity conversion efficiency, but also extends the combined heat and power (CHP) principle with the possibility of producing secondary fuels or chemicals. The secondary fuels production route shows significantly lower total efficiency (42%) compared to the electricity production routes. However,

as already indicated earlier, heavy road transport will not run on electricity on a short term, therefore synthetic liquid energy carriers from biomass are a viable option to provide fuels based on renewables to this important part of the economy.

Figure 5. Comparison of the solid fuel combustion and gasification processes in terms of overall conversion efficiency. Notes: ^a supercritical steam conditions; ^b values greater than approximately 40% apply to supercritical steam conditions [33], typical values of 35% and 39% are reported for subcritical steam conditions by respectively [6] and [34]; ^c from [6], page 284; ^d from [22]; ^e from [35]; ^f from [31]; ^g from [35], based on the chemical efficiency of the gasification process of 93%. Subscripts: *therm*—thermal; *unit*—of the single process unit (block); *CHP*—Combined Heat & Power; *chem*—in terms of the chemical energy in the product; *C-conv*—in terms of the carbon conversion; *e*— electrical; *FT*—Fischer-Tropsch process; *fuel*— in terms of the chemical energy in the produced fuel.



The gasification of biomass has already been developed far enough to come into consideration as one of the contributors to the sustainable energy “well” during and after the energy transition. Nevertheless there are still some issues to be addressed before the successful large-scale commercial introduction of biomass gasification. These issues, depending on the type of the gasifier, are related to:

1. Technology scale-up;
2. Size distribution of raw biomass;

3. Operability of the gasifier with fuels containing large amounts of ash, especially if the fraction of alkali, chlorine and sulfur is high [36];
4. The formation of condensable higher hydrocarbons (tar);
5. Cleaning and upgrading of the gas for dedicated downstream application.

The section below gives an overview of the available thermochemical gasification technologies, and discusses their characteristics in view of the issues mentioned above. Together with the requirements imposed on the gas quality for the synthesis of liquid secondary fuels, the current choice of the most appropriate gasification system is evaluated.

2. Thermochemical Gasification of Biomass

2.1. Overview of gasification processes

A wide range of reactors for thermochemical gasification of biomass is under investigation at different commercial companies and research institutes. The aspects that play a role in the decision of employing a certain reactor design for biomass gasification are:

- Scale of operation;
- Feedstock flexibility (size and composition);
- Sensitivity to the amount of ash and its composition;
- Tar yield.

Scale of operation will most likely be the primary criterion. Small, decentralized systems will benefit from a simple, easy to control and maintain, and cheap reactor. On the other hand, a Biomass-to-Liquid (BTL) plant, for example, or maybe even a biorefinery where the gasifier is only one of the units-of-operation will benefit from the larger scale of the reactor in terms of its thermal efficiency and the economy-of-scale.

The feed flexibility is also a point of attention. Biomass is very fibrous and will consequently be difficult to cut or pulverize. Therefore it is not desirable to reduce the biomass in size too much because of the adverse effect on the energy efficiency of the whole process. Additionally, raw biomass is not dry, but contains a varying amount of moisture. Taking the above into consideration the gasification reactor should be able to cope with the changes in fuel supply characteristics, both physical and chemical.

As already mentioned in Section 1.3., in addition to the moisture and volatile fraction, each type of biomass also contains an amount of inorganic matter, usually referred to as ash. The main ash-related issues have already been highlighted. While ash-related issues may lead to difficulties in gasifier operation and unscheduled maintenance stops, the downstream equipment may be affected in a negative way by the tar produced in the gasifier. “Tar” is an umbrella term for various kinds of larger hydrocarbons produced during gasification. A clear and often used definition of tar is given in [37]: “A generic (unspecific) term for the entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar”. A similar, clear definition of tar found in literature [38] states that “tar” are “all organic compounds with a molecular weight larger than benzene (excluding soot and char)”. Tar formation is a well-known problem in gasification processes [38–41].

Although the main issues related to tar are condensation problems in the equipment downstream the gasifier that operates at lower temperatures (typically below 500 °C), tar also significantly contributes to the heating value of the product gas. Therefore its physical “removal” from the gas will reduce the net carbon conversion efficiency of the process, and in fact a “conversion” route should be preferred, where tar is broken into smaller molecules (e.g., CO and H₂). In any case, the exact extent of the “tar problem” depends on the downstream application of the product gas. For combustion applications the tolerance for tar is higher (even up to several grams per m_n³, whereas for fuel cell applications, synthesis of chemicals, *etc.*, it is essential to minimize the concentration of tar produced during gasification, not only to prevent the fouling of the downstream equipment, but also to make the chemical energy stored in the tar molecules available to the conversion process.

Since the first (controlled) attempts do perform thermochemical gasification of biomass a number of reactor designs have evolved as being suitable for that process. These reactors are:

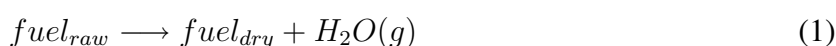
- Fixed beds (sometimes referred to as “moving beds”): updraft, downdraft, crossdraft;
- Fluidized beds: bubbling, circulating, dual;
- Entrained flow reactors.

Although each of these reactors is capable of carrying out the gasification process, each of them is also a compromise between the quality of the produced gas, conversion efficiency, suitability for handling of the feedstock with varying physical and chemical properties, the complexity of the design, complexity of the operation, and the investment costs. The main characteristics of the reactors listed above are described below; also some attention is given to novel, innovative technologies that are currently under consideration. First, however, in the next section the fuel conversion in a gasifier will be explained for better understanding of the advantages and disadvantages of each gasification system.

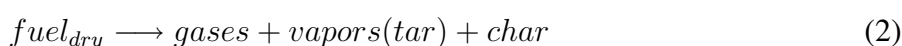
2.2. Conversion Steps inside the Gasifier

When a solid (organic) fuel undergoes a process of thermochemical conversion it passes through a number of conversion steps. These steps are listed below and are illustrated by the prevailing physical and chemical reactions.

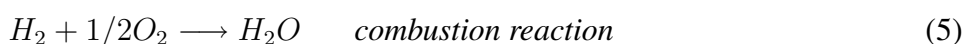
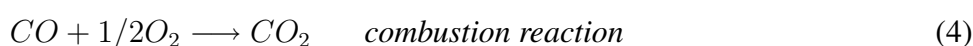
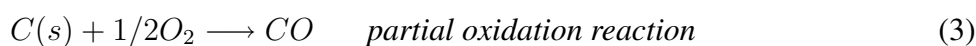
- Drying: evaporation of the fuel moisture;



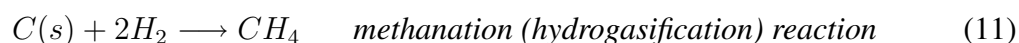
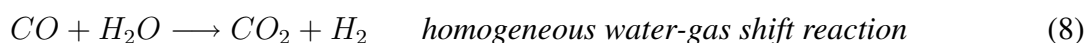
- Pyrolysis (devolatilization): the volatile fraction of fuel constituents (see Figure 3) is released into the gas phase; the remaining solid is called char, *i.e.*, fixed carbon and ash;



- Oxidation: the products of the pyrolysis step react with an externally supplied oxidant. The most common oxidant is the O₂ molecule itself, either from the (enriched) air or in the pure form, but also steam and CO₂ can act as oxidants;



- Gasification/reforming: this step will proceed only when there is (local) depletion of oxygen, therefore it does not apply to combustion processes with sufficient excess air. Opposite to the oxidation reactions, most gasification and reforming reactions are *endothermic* (the water-gas shift reaction, Equation 8, being an exception), therefore it is necessary to provide the required amount of heat to maintain the desired gasification temperature. In the “direct gasification” concept this is achieved by supplying more oxygen so the heat of combustion of the oxidation reactions will balance the heat required by the reduction reactions (plus the heat losses of the gasifier). In the “indirect gasification” concept, the heat from outside the gasification reactor is usually transferred by a circulating heat carrier.



As shown in Figure 6, in a Fixed Bed reactor (discussed in Section 2.3.) the location of different fuel conversion zones described above can be identified quite clearly, as in that process the (back-)mixing effects are insignificant. However, in a Fluidized Bed (see Section 2.4.), due to intense mixing causing high heat and mass transfer rates between the reactants, the locations of the reaction zones will depend on the geometry of the reactor and the distribution of the feed points. Typically the engineering will aim to realize the char combustion zone close to the oxidant feed point(s), in order to increase the carbon conversion efficiency and generate the heat to drive the gasification reactions, and also to minimize the negative impact of partial oxidation on the cold gas efficiency.

2.3. Fixed Bed Reactor

The two major kinds of fixed bed gasifiers, also known as “moving bed gasifiers”, are updraft and downdraft reactors. The names are based on the directions of the flows of the fuel and the oxidant (either co- or countercurrent).

2.3.1. Updraft Gasifier

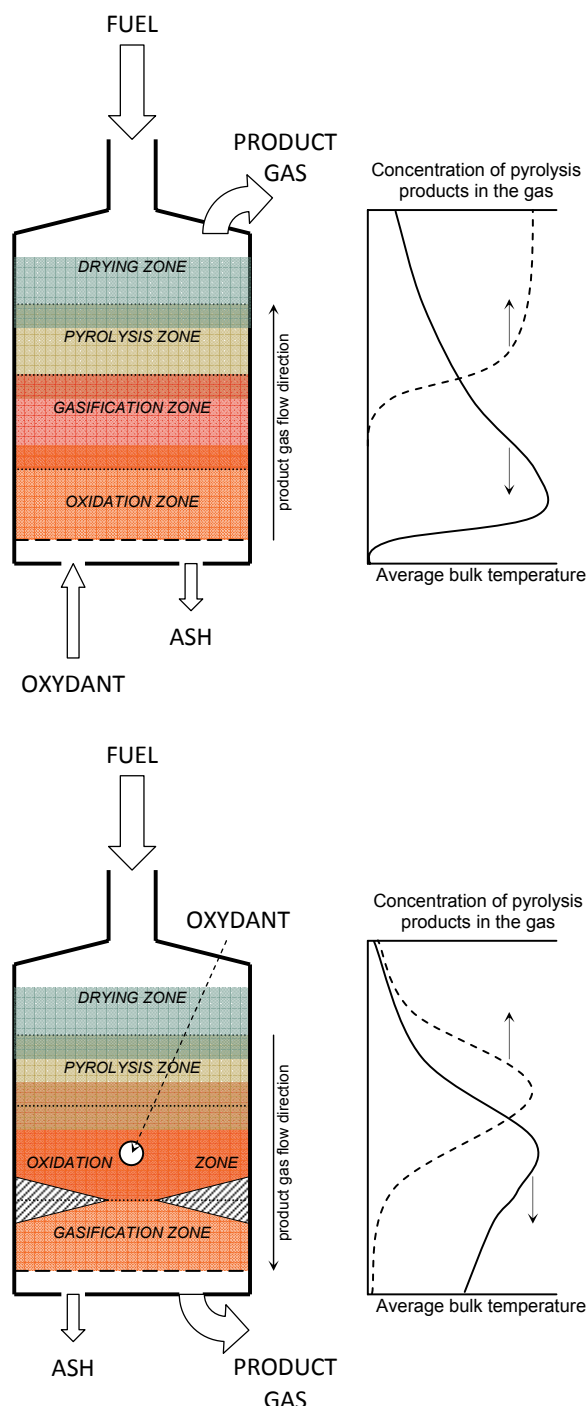
In the updraft (counter-current) gasifier the feedstock and the oxidant (e.g., air or steam) flow in opposite directions. Biomass enters from the top and gasifying agent from the bottom. In Figure 6 (top), typical zones of an updraft gasifier are shown. The biomass moves down through a drying zone (100 °C), followed by a pyrolysis zone (300 °C) where char and gaseous species are produced. Char continues to move down to react in the gasification / reforming zone (900 °C) and finally it is combusted in an oxidation zone (1400 °C) at the bottom of the gasifier by the incoming gasification agent [14]. The gaseous pyrolysis products are carried upwards by the upflowing hot gas stream. As can be seen from the figure, the product gas consists mainly of these pyrolysis products and the products of char oxidation

that pass over a relatively cold drying region. The tar in the vapor either condenses on the relatively cold descending fuel or is carried out of the reactor with the product gas; hence the high tar yield of this type of gasifier, even up to 100 g m^{-3} . The condensed tar is recycled back to the reaction zone, where it is further cracked to gas and soot. Most of the tar present in the product gas must be removed for any engine, turbine or synthesis application [42]. On the other hand, direct heat exchange with the entering feed and therefore the low gas exit temperature is beneficial for the thermal efficiency of the process. Another advantage of the updraft gasifier is its relatively low sensitivity to the amount of the ash in the fuel. This is caused by the fact that the highest temperature is achieved at the bottom of the reactor, close to the ash discharge point. Therefore there is little risk of the fusion of soft, sticky ash or solidification of slag and subsequent blockage of the reactor when proceeding to the zone with a lower temperature, as it is the case in a downdraft fixed bed reactor. Furthermore, the updraft gasifiers have simple construction and theoretically there is little scaling limitation, however, there have been no very large updraft biomass gasifiers built [14]. Probably the mostly well-known commercial application of the updraft gasifier is the Harboøre project where the produced tar from the updraft gasifier is stored for peak load CHP operation [43]. Nevertheless the process is not considered relevant for the production of liquid transportation fuels from biomass.

2.3.2. Downdraft Gasifier

In the downdraft (co-current) gasifier, the fuel and the product gas flow in the same direction. This flow can be directed up or down, although, most co-current gasifiers are of the downward flow type [45]. As can be seen in Figure 6 there is a constriction (throat) where most of the gasification reactions occur. The reaction products are intimately mixed in the turbulent high-temperature region around the throat, which aids tar conversion. Some tar conversion also occurs below the throat on a residual charcoal bed, where the gasification process is completed [14]. This configuration produces a relatively clean gas—less than 500 mg m_n^{-3} of tar is feasible with a carefully designed throat [19,44]. Due to the low tar content in the gas this technology is often applied for small scale electricity production with an internal combustion engine [14,45]. The fraction of fines (here: particles smaller than *ca.* 1 cm) in the feedstock should be low for this type of gasifier. The upper limit of the feedstock size is related to the size of the throat, and values of 30 cm in the longest dimension have been reported [14]. The size of the throat also forms a limitation for the scale-up process, and therefore the downdraft gasifier is not suitable for the implementation in a large-scale plant. Finally, due to the arrangement of the reaction zones there will be a limit to the amount of the ash in the fuel. High local temperatures in the oxidation zone could cause the melting of some of the ash constituents and the subsequent fusion of the melt to bigger lumps upon cooling in the gasification zone. These lumps would then obstruct the overall flow of the solids and the discharge of the ashes at the bottom of the reactor.

Figure 6. Fixed Bed Updraft (top) and Downdraft (bottom) reactor schematics with the indication of the different reaction zones. Also the trends of the temperature profile and the concentration of pyrolysis products in the gas phase are shown. Adapted from [44] and [19].



2.4. Fluidized Bed Reactor

The principle of fluidization is the foundation of the fluidized bed reactor. In such a reactor the fuel together with inert bed material behaves like a fluid. This behavior is obtained by forcing a gas (fluidization medium) through the solid inventory of the reactor [46,47]. Air, steam, steam/O₂ mixtures are examples of commonly used fluidization media. Silica sand is the most commonly used bed material,

but using other bulk solids, especially those that exhibit catalytic action in the process can be beneficial; see Section 3.2. Depending on the velocity of the fluidization medium in the reactor, the fluidized bed reactors are divided in bubbling fluidized beds (BFB) and circulating fluidized beds (CFB). Bubbling beds operate at relatively low gas velocities (typically below 1 m s^{-1}), while the circulating fluidized beds operate at higher gas velocities (typically $3\text{--}10 \text{ m s}^{-1}$), dragging the solid particles upwards with the gas flow. These particles are separated from the gas in the cyclone and recycled to the bottom of the fluidized bed. In both cases most of the reactions during the conversion of a fuel into a product gas take place within the dense bed region (bubbling bed); to a lesser extent they continue in the freeboard (tar conversion) [14]. The inert bed enhances the heat exchange between the fuel particles, and therefore a fluidized bed can operate under nearly isothermal conditions. The maximum operating temperature is limited by the melting point of the bed material and will typically lie between 800 and $900 \text{ }^\circ\text{C}$. At these relatively low operating temperatures and also relatively short gas residence times the (slow) gasification reactions do not reach their chemical equilibrium if no catalyst is applied. This is the reason for the presence of the hydrocarbons (tar, methane) in the product gas; the tar production falls between that of an updraft and downdraft fixed bed gasifier. The conversion rate of the feedstock is typically high.

Due to their geometry and excellent mixing properties, fluidized beds are very suitable for scaling up. The energy throughput per unit of reactor cross-sectional area is higher for a CFB than for a BFB. Both configurations can be operated under pressurized conditions, which will further increase the throughput, and will also be beneficial when the downstream process requires a pressurized input stream, as for instance in the case of Fischer-Tropsch synthesis. Intense mixing also allows the reactor to accept a wider particle size distribution of the fuel feed, starting already from relatively fine particles. Furthermore, in contrast to other reactor systems presented here, the fluidized bed gives the possibility for the use of additives, e.g., for the in-situ removal of pollutants (like sulphur) or the primary measures to increase tar conversion.

The weakest point of the fluidized bed technology emerges when fuels with high content of ash, and alkali metals in particular, are applied. When the fraction of alkali metals in the fuel is high, those compounds can form eutectics with silica present either in the bed material, or in the fuel ash itself. The presence of chlorine amplifies this effect. Those eutectics have melting points that are considerably lower than that of pure silica. Therefore they will start to melt at process temperature, likely causing stickiness of the particles, eventually leading to the formation of bigger lumps (“agglomerates”). Their presence will dramatically change the hydrodynamics of the reactor, ultimately leading to “defluidization” and necessary shut-down of the reactor. Those phenomena are discussed further in Section 3. Nonetheless, by applying proper countermeasures, the fluidized bed will still be able to accept fuels with an ash content higher than those allowable for a fixed bed reactor [44]. Van der Drift *et al.* [48] tested ten residual biomass fuels (from demolition wood to sewage sludge and verge grass) in an air-blown CFB gasifier and concluded that this technology seems to be very suitable for the gasification of all types of different biomass materials.

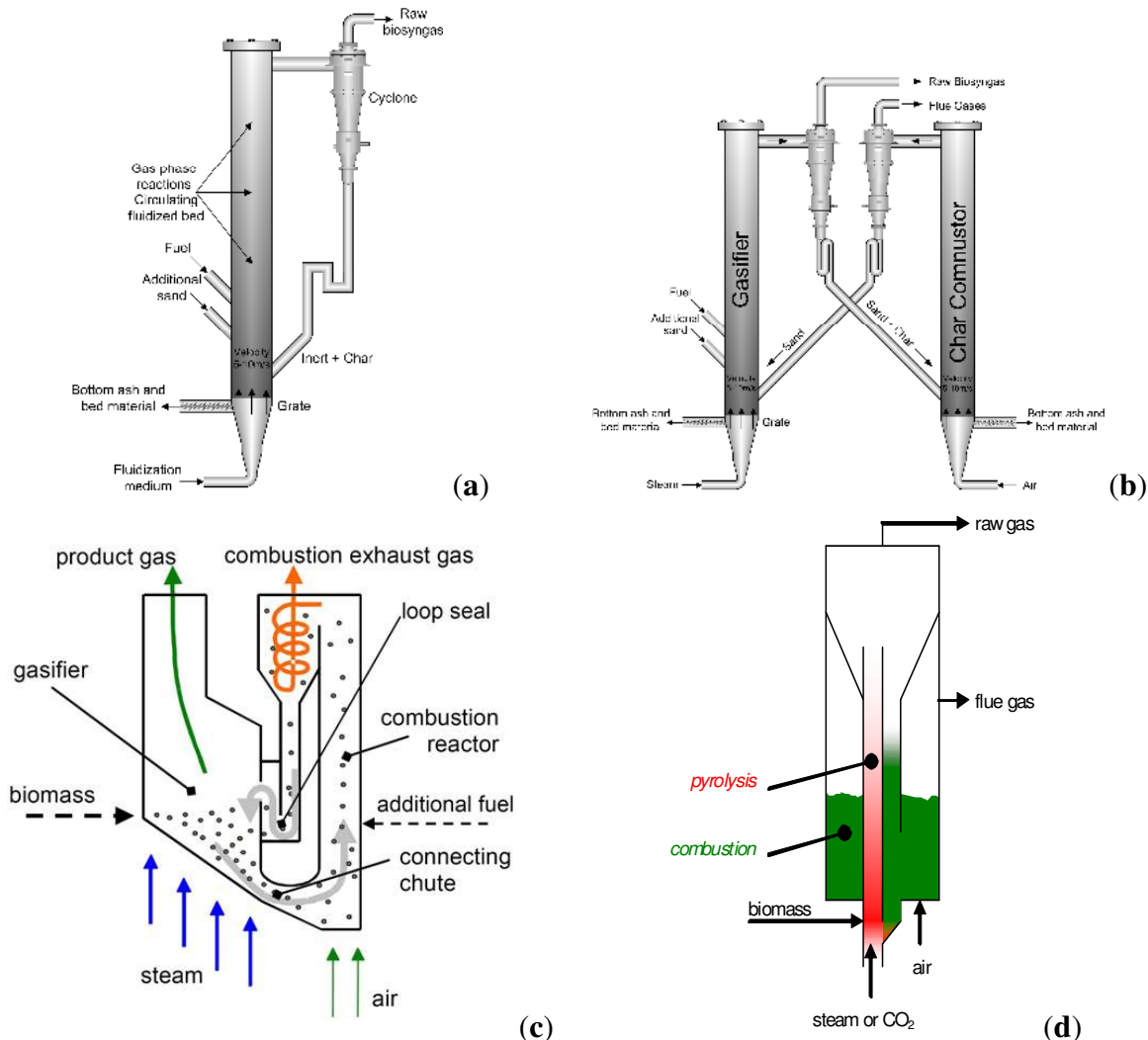
Depending on the way that heat is supplied for the gasification reactions, the (circulating) fluidized beds can be divided into the directly heated and indirectly heated units. In the directly heated concept, a part of the product of the gasification process is burned directly in the gasification reactor. Obviously the designs should be optimized for the maximal interaction of the entering oxygen with the recirculated

char. However, due to the intense mixing it is nearly inevitable to avoid the combustion of some fraction of the product gas as well. To overcome this, and to avoid the dilution of the product gas by nitrogen but without the use of pure oxygen instead of air, the indirectly heated gasifier concept has been developed. The principle of operation is based on two interconnected reactors: usually a steam-blown gasification reactor and an air-blown combustion reactor. The bed material and the char are transported from the gasification reactor to the combustion reactor where char is oxidized with air, generating the necessary heat for the gasification part. The heated bed material is recirculated back to the gasification reactor to complete the cycle. Several implementations of that concept exist. The most well-known are the Battelle's Silvagas[®] process, the Fast Internally Circulating Fluidized Bed (FICFB) developed by TU Vienna, and the Milena gasifier developed by ECN. The schematics of the classical directly heated CFB as well as of the three indirectly heated gasifier concepts are presented in Figure 7. At present it is difficult to state which process is better. Certainly, there is more practical experience with the classical CFB concept, and also with its operation under pressurized conditions. The gas produced using the indirectly heated CFB is richer in hydrogen and there is less CO₂ present, but the content of methane is also higher. Together with the relatively low product gas temperature (circa 650 °C compared to 850 °C in a directly heated gasifier) this process seems to be more suitable for tar removal by scrubbing and subsequently the production of substitute natural gas (SNG), while the directly heated concept is likely to be followed by methane and tar reforming and the production of secondary liquid energy carriers. Both reactor concepts and various combinations of downstream processes are now subject to intense investigations.

2.5. *Entrained Flow Reactor*

The entrained flow reactor (EFR) is well-known in coal combustion processes. In this type of reactor no inert added solid material is present, like it is the case in a fluidized bed. The feedstock is fed co-currently with the oxidant agent by means of a burner and the flow velocity is high enough to establish a pneumatic transport regime. EFR gasifiers operate at much higher temperatures than the previously discussed reactors (1200–1500 °C). This allows thermal conversion of tar and also of methane [14], so the composition of the product gas is very close to the chemical equilibrium composition, and therefore also close to syngas quality. However, when coal is used as a fuel it is crushed into a powder ($\approx 50 \mu\text{m}$ diameter) before feeding. This is immediately its biggest disadvantage with respect to a biomass application, as the size reduction of biomass is a very costly process in terms of energy, as stated earlier. In addition, due to the spread in particle size distribution some methane can still be expected when biomass is gasified [44]. This drawback can be partially overcome by pre-treating the biomass in the process of torrefaction [52]. However, this is a relatively novel technology and has only recently started to be demonstrated on a pilot scale [53]. In addition, in order to reach high gasification temperature more product gas needs to be oxidized, which will reduce the cold gas efficiency [54]. Finally, extreme reaction conditions pose problems to materials selection. Large quantities of molten ash (slag) will be formed during the gasification of all kinds of biomass, except for relatively clean wood, and the presence of high amounts of potassium is a concern with respect to the life of the refractory lining [55].

Figure 7. Different CFB gasification concepts: (a) classical, directly heated [49]; (b) indirectly heated dual CFB, Battelle [49]; (c) indirectly heated FICFB, TU Vienna [50]; (d) indirectly heated Milena, ECN [51].



2.6. Supercritical Water Gasifier, Heat Pipe Reforming, Chemical Looping and Other Novel Processes

The reactors described in the paragraphs above represent technologies that over the past decades gained an established place among the solid fuel conversion processes. Nonetheless, continuously new technologies are being developed, searching for the solution of the problems known from the state-of-the-art. Below three of these novel technologies are highlighted.

2.6.1. Supercritical Water Gasification (SCWG)

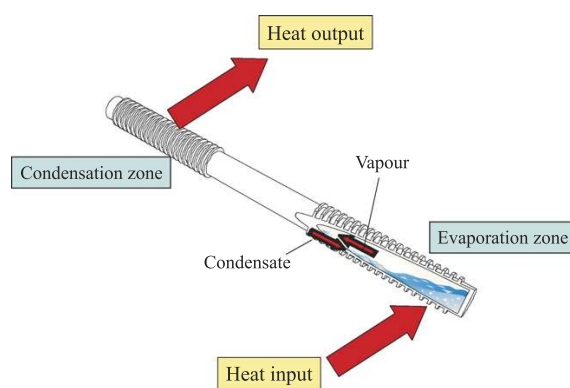
As the name already suggests, this process is carried out under supercritical conditions of water, *i.e.*, a temperature over 374 °C and pressure higher than 221 bar. Under these conditions biomass is rapidly decomposed into syngas components at high conversion efficiency—values close to 100% are reported [56,57]. The acceptance of very wet biomass (such as sewage sludge or cattle manure) and the fact that the product contains relatively low concentrations of tar and char makes SCWG an

interesting process for further development. For SCWG process to attain a reasonable thermal efficiency the system must recover enough heat to obtain the supercritical state. This is one of the challenges for the development of this process, as preheating of the slurry above 525 K will initiate its decomposition, which may cause plugging and/or fouling upstream the reactor [11,58]. Furthermore, the issue of construction materials requires attention as extensive corrosion of the reactor walls have been reported when using nickel alloys [59]. Although extensive research efforts on SCWG have been undertaken in recent years, this process is currently still in a R&D stage.

2.6.2. Heatpipe Reformer

The heatpipe reformer is a type of indirect gasifier where the heat necessary for the endothermal gasification reactions is transferred from the char oxidation zone by means of the heatpipes. A heatpipe is a modularly constructed pair of heat exchangers (a “pipe”) using an internally circulating medium to transfer the heat from the input side to the utilization side, see Figure 8. It can be seen as an equivalent of an indirect fluidized bed gasifier presented earlier (see Section 2.4.), but without the circulation of the bed material over the gasification and combustion part. As in that process, the gasification reactor (a fluidized bed) can be operated using steam only, while the necessary heat is provided from an “external” source (allothermal reactor principle). Also in the heatpipe reformer the heat is generated by the oxidation of char that has not been gasified in the gasification step [60]. An important advantage of the heatpipe reformer is the possibility of heat coupling with an SOFC that requires external cooling in order to maintain the operational temperature and consequently its conversion efficiency. However, the scale-up of this type of reactor to a megawatt-scale and larger is economically not justifiable (there being better alternatives in that plant size region), therefore its application is limited to decentralized CHP systems, and this makes it less relevant for BTL processes.

Figure 8. The operational principle of a heat pipe (from [60]).



2.6.3. Other Indirect Gasification Processes

In view of the potential benefits from the indirect gasification processes, of which the ability to use the air for oxygen supply without diluting the product gas with nitrogen is the most pronounced one, a number of alternative processes have been under investigation. Some of them turned out to be not attractive enough, due to various problems (design, technical, operational, *etc.*) and their development

has been discontinued. Examples include the Agip-Italenergie process where the heat was transferred between the gasification and the oxidation zone through the reactor wall separating the two vessels, and the Lund University gasifier which was constructed of three concentric tubes, to separate the steam gasification zone and the char combustion zone [44].

An interesting development of the indirect gasification principle is the use of reactive heat carrier instead of an inert heat carrier, mostly being the bed material, or a system similar to a heatpipe as described in previous sections. Early developments of such process combined with gasification reported by Beenackers [44] include for example the EXXON Research Oxygen Donor Process, where the heat and the oxidant are carried to the gasification zone by means of calcium sulphate (CaSO_4); no steam being used in this process. Although no results or indications of the further development of this process have been found in the literature, this kind of operation recently started to regain recognition, and is now being referred to as “Chemical Looping Combustion” (CLC). In this process the oxygen is being transferred from the air to the gaseous fuel via a metal oxide that is exothermic during its reduction (e.g., iron, copper or nickel). The advantage of CLC is the fact that, just like Solid Oxide Fuel Cell, it is a combustion technology with inherent CO_2 separation [61–63]. As this process is applied *after* the gasification step, it is not discussed here in more detail.

Another improvement proposed for the indirect gasification systems is the Adsorption Enhanced Reforming (AER) process. Here, again a solid is used to influence the gas composition, not in a catalytic way but through the adsorption of one of the gas constituents, for example CO_2 by CaO . The three main advantages of such a process are the shifting of the reaction coordinate of the water-gas shift reaction to the hydrogen side and therefore an increased hydrogen yield, the integration of the heat of adsorption and the heat of the water-gas shift reaction (both are exothermic), and the possibility for *in-situ* CO_2 capture [64–67]. The process of CO_2 adsorption by CaO is of course not new [68], and although this application is very promising the fact that this process requires relatively mild gasification conditions (temperature of approximately 700°C , may lead to an increased tar yield or reduced carbon conversion and cold gas efficiency. This will need to be verified and eventually solved by further R&D efforts.

2.7. Optimal Choice for Industrial Scale Gasification Process: Fluidized Bed Technology

In the previous paragraphs several gasification technologies have been introduced. Some of them are still in the R&D phase, whilst others are already at a more advanced stage and therefore more viable for industrial application as intended in this review paper. Each of these technologies have certain characteristics, which make them more or less suitable for the generation of high-quality product gas, or preferably even syngas. None of these technologies are free from drawbacks in that respect, and consequently the choice of the most suitable gasification system will be based on a compromise, depending on the application of the gas. Table 5 gives an overview of the main characteristics of the above-mentioned reactor types. Returning to the criteria listed at the beginning of this section and applied to the process of syngas production for the synthesis of liquid biofuels, the most suitable technology can be identified as presented in Table 6. Nonetheless, the numbers provided by the equipment manufacturers show that 75% of the gasifiers offered commercially were of the downdraft type, 20% of the (circulating) fluidized bed type and 2.5% were of the other types [31].

Table 5. Main characteristics of the five established gasification reactor types (adapted from [69]).

	Fixed Bed		BFB	CFB	EF
	Downdraft	Updraft			
Process temperature (°C)	700–1200	700–900	<900	<900	1300–1500
Oxidant	air	air	air, steam, O ₂	air, steam, O ₂	air
Feedstock size	very critical	critical	less critical	less critical	very fine particles
Tar yield	low	very high	intermediate	intermediate	none
Carbon conversion	93–96% ^a	near 100%	>90%	>90%	100%
Scale (MW _{th})	<5	<20	10–100	>20	>100
Thermal throughput ^b (MW m ⁻²)	1–2	1–2	1.2–1.6	5–7	
Investment	low	low	moderate	high	high
Control	easy	very easy	intermediate	intermediate	very complex

^a from [70] page 8; ^b from [34].

Table 6. Response of the main characteristics of the established conversion processes to application criteria related to the syngas production for the synthesis of liquid biofuels. Symbols used: + (suitable), 0 (less suitable), – (not suitable).

Criterion	Suitability for BTL Application			
	FB (Downdraft)	FB (Updraft)	BFB / CFB	EF
Scale of operation	–	0	+	+
Feed flexibility	–	0	+	–
Sensitivity to ash amount and composition	0	+	0	0
Tar yield	+	–	0	+

The assessment of gas quality is, however, also very important, as the product gas will be used as a feed for certain downstream process. Evaluating the configuration of biomass gasification and production of liquid fuels, requirements for the intermediate gas cleaning will need to be set up to comply with the impurities. Table 7 shows an overview of such requirements for the production of FT-diesel and methanol (an intermediate for DME production).

On the basis of the information presented above it can be concluded that at present, the fluidized bed reactor complies the best with the requirements for the production of bio-syngas for the synthesis of liquid transportation fuels via thermochemical gasification route. Obviously, the state-of-the art is changing continuously and new technologies are emerging, nevertheless the amount of experience with the fluidized bed technology and its characteristics make it a mature and reliable technology. What is lacking is the final technology push to solve the remaining, but important problems, and a

breakthrough in industry's hesitation to support the construction of large-scale fluidized bed gasification demonstration units.

Table 7. Syngas quality requirements (allowable concentrations of impurities) for the synthesis of secondary fuels.

Contaminant	FT Synthesis	Methanol Synthesis
Particles	0 ppb ^a , 0.1 mg m _n ³ e	low
Tar and BTX	below dewpoint ^{b,e}	
Hydrogen halides (HCl, HBr, HF)	<10 ppb ^{b,e}	<10 ppb ^e
Alkaline metals	<10 ppb ^{b,e}	
N-compounds	< 1ppm ^b , <20 ppb ^{c,e}	10 ppm _v NH ₃ , 0.01 ppm _v HCN ^e
S-compounds	< 1ppm ^b , <20 ppb ^c , 0.1 ppm ^e	< 1ppm ^d , 0.1 ppm ^e
Pressure ^d	20–30 bar	140 bar
Temperature ^d	200–400 °C	100–200 °C

^a from [118]; ^b from [35]; ^c from [119]; ^d from [70]; ^e from [49].

3. Fluidized Bed Biomass Gasification Process

In the previous section the motivation was presented to employ fluidized bed technology for the production of bio-syngas. Main characteristics of that and other possible thermochemical biomass conversion systems were presented and compared. In this section deeper background information on the fluidized beds is presented, including their principle of operation and the effect of various process parameters on the product gas quality. The presented information is based on a review of the relevant scientific publications supported by own experience and fact-findings.

3.1. Hydrodynamics and Fluidization Regimes

When a gas is blown upwards through a batch of bulk material, the behavior of the inventory will differ depending on gas velocity. Figure 9 shows the possible flow regimes, arranged by the increasing superficial gas velocity. The fluidization of particles is only possible, when the drag of the gas stream on the particles at least equals the gravitational force on those particles less their buoyancy. This is achieved when the gas reaches the so-called minimum fluidization velocity. The superficial gas velocity being higher than the minimum fluidization velocity is the basic and primary condition to achieve fluidization. The formation of gas bubbles in the bed, while the bed surface is still clearly visible will indicate the regime of bubbling fluidization; further increase of the fluidization velocity will lead to a turbulent bed, which is a highly expanded and violently active regime. Particles are thrown into the freeboard and the surface of the bed will still exist, but will be highly diffused [47]. Reaching of the so-called transport velocity is the condition to enter the fast fluidization regime. This regime can be described as a nonuniform suspension of slender particle clusters moving up and down in a dilute, upwardly flowing gas-solid continuum [47]. Circulating fluidized beds operate in the regime of fast fluidization, while the bubbling fluidized beds operate in the regime of bubbling fluidization. This difference has a number of consequences for the the gasification process, depending on which type of the fluidized bed reactor

is being used. Some characteristics of the BFB and the CFB gasifiers have already been introduced in Table 5 to show the main differences between the reactor types that could possibly be used for gasification of biomass. A more detailed comparison between industrial-size bubbling and circulating fluidized beds is given in Table 8. From the table it is clear that the CFBs have slightly better characteristics (higher carbon conversion, less tar in the product gas, higher fuel flexibility, better scale-up potential) compared to the BFBs. Therefore for an advanced application like the large-scale production of secondary fuels from biomass a CFB will be the choice of the reactor, especially when a directly heated gasifier is to be designed. The indirectly heated gasifiers have also been designed as CFBs with BFB features (CFB–BFB hybrid), as shown in Figure 7c and 7d.

Table 8. Overview of the differences between a bubbling and a circulating fluidized bed gasifier, constructed on an industrial scale.

Property	BFB	CFB	References
fluidization regime	bubbling bed	fast bed	[47]
mixing	very good	excellent	[47]
solids feed flexibility (size)	finer not desirable	fine & coarse material	
tar yield (g m_n^{-3})	avg.: 12 (moderate)	avg.: 8 (lower than BFB)	[34,47]
carbon conversion (%)	lower than CFB	typically 88–96	[71]
carbon loss by entrainment	significant	low	[72]
particle concentration in the gas (g m_n^{-3})	average: 4	average: 20	[34]
bed height / fuel burning zone (m)	1–2	10–30	[47]
therm. throughput (MW m^{-2})	1.2–1.6	5–7	[34]
process control	less complex	more complex	
scale-up potential	good	very good	

3.2. Main Process Parameters

Given a fluidized bed gasifier, the operator can alter a number of input variables or parameters to influence the process and the output variables. Table 9 shows the main input variables and the variables they affect. The definitions of the calculated process parameters reported in the table are given below, while the process variables indicated in bold face are discussed in more detail in the subsequent paragraphs. The symbol $\dot{\phi}_i$ indicates the mass flow of a component denoted by the subscript.

Stoichiometric oxygen ratio (λ):

$$\lambda = \frac{\text{external } O_2 \text{ supply / fuel supply (d.a.f.)}}{\text{stoichiometric } O_2 \text{ requirement / unit of fuel input (d.a.f.)}} \quad (12)$$

Steam-to-biomass ratio (SB):

$$SB = \frac{\text{steam mass flow}}{\text{fuel feed flow}} \quad (13)$$

Modified steam-to-biomass ratio (SB*):

$$SB^* = \frac{\text{steam mass flow} + \text{fuel moisture mass flow}}{\text{dry, ash-free fuel feed flow}} \quad (14)$$

Carbon conversion (CC):

$$CC = \left(1 - \frac{\dot{\Phi}_{C,residue}}{\dot{\Phi}_{C,feed}} \right) \cdot 100\% \tag{15}$$

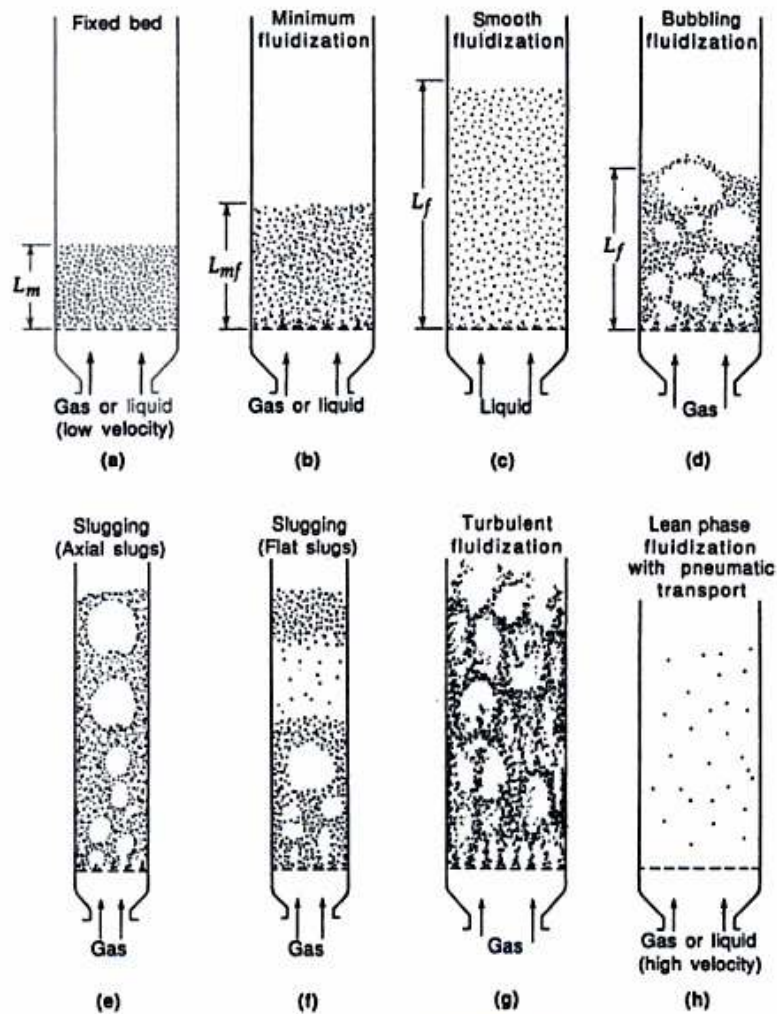
Cold Gas Efficiency (CGE):

$$CGE = \frac{\sum \dot{\Phi}_i \cdot LHV_i}{\dot{\Phi}_{fuel} \cdot LHV_{fuel}} \tag{16}$$

Superficial fluidization velocity (U_{fl}):

$$U_{fl}[m \cdot s^{-1}] = \frac{\text{actual volumetric feed gas flow rate}}{\text{cross-sectional area of the bed}} = \frac{\dot{Q}_{gas} [m_n^3 \cdot s^{-1}] \cdot T_{process}[K] \cdot 1.013[bar]}{A_{bed}[m^2] \cdot P_{process,abs}[bar] \cdot 273.15[K]} \tag{17}$$

Figure 9. Visualization of different vertical gas-solid flow regimes [46].



3.2.1. Fluidization Media

The stoichiometric oxygen ratio is commonly used for the identification of different “oxidation regimes” during a thermochemical fuel conversion process. This parameter, also called “equivalence

ratio”, “air factor” or “air ratio”, is represented by the symbol λ (lambda). From the formula given in the previous paragraph it is clear that $\lambda > 1$ refers to combustion processes, $\lambda = 0$ to pyrolysis, and $0 < \lambda < 1$ to gasification, see also Table 4. With the aim to produce a gas suitable for transportation fuels synthesis application, high yields of H_2 and CO are required; this can be achieved in low lambda value regions. On the other hand, partial oxidation of the fuel is necessary to generate heat to drive the mostly endothermic gasification reactions and allow the reactor to work in the autothermal mode.

Table 9. Main process variables and parameters, and their interactions assuming only one variable changing (increasing) at a time. Variables in bold face are discussed in more detail in the text. Symbols used: + (increase), – (decrease), OPT (optimal range exists to maximize or minimize the desired effect), x (other effect, see footnote).

Variable	Input				Output		
	λ	SB	U_{fl}, τ^a	T ^b	CC	CGE	tar yield
biomass feed rate	–	–		–	–	+	+
oxygen feed rate	+		+	+	+	–	+
steam feed rate		+	+	–	OPT	OPT	OPT
process pressure			–		–	+	–
kind of bed material			x^c		x^e	x^e	$-^d$
used additive					x^e	x^e	x^f

^a gas residence time;

^b only if the temperature cannot be controlled independently using e.g., external electrical heating;

^c no direct influence, but can impose constraints on the minimum/maximum velocity applied;

^d catalytic bed materials will have (large) influence; inert bed material will have no effect;

^e possible influence, effect depending on the kind of solid used;

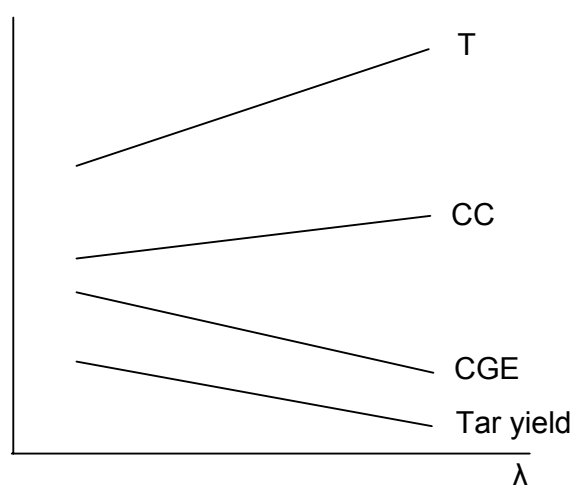
^f catalytic additives will have (large) influence, agglomeration counteracting ones less or none.

The most common fluidization and oxidation medium used in gasification processes is air. Although air is cheap and abundant, the fact that the nitrogen present in air cannot be easily separated from the product gas is a significant drawback of that gasification medium. Air gasification produces gas of low calorific value, and approximately 50% of the volume of the product is the inert nitrogen. Therefore it would be better to use a combination of gases that will either react to form useful products or will be easily separated from the final product stream. The gasification agent will typically consist of a gas that provides the necessary oxygen for partial oxidation of the fuel and a gas that will act as a moderator/fluidization medium, unless the heat to drive the strongly endothermic reactions is supplied externally, e.g., from the combustion of char, as in a dual (or: indirect) gasifier—then gasification with pure steam is possible. For a direct gasifier a mixture of pure oxygen and steam fulfils the criteria mentioned above and both gases are very common in process industry. Besides acting as a fluidization medium steam is also a reactant in many gasification reactions, therefore its presence and amount have an influence on the product gas composition. The amount of steam supplied to the process is often related to the amount of biomass feed in a so-called steam-to-biomass ratio (SB). In the literature it is not often mentioned whether the fuel feed is given on an “as received” or “dry (and ash-free)” basis.

However, in case of fuels with higher moisture and/or ash content, the difference in the calculated SB will be significant, depending on the choice of the denominator. Additionally, the moisture present in the fuel should not be neglected in the calculation of the SB, as the resulting steam will be the first to interact with the organic part of the fuel upon devolatilization in the reactor. Also in case of fuels with higher moisture content the amount of steam that originates from the fuel will not be negligible compared to the overall steam input. Considering the above, a modified steam-to-biomass ratio (SB^*) is proposed. Regarding the effect of the fuel moisture van der Drift concluded that the water content of raw biomass will be one of the most dominant fuel characteristics influencing carbon conversion, cold gas efficiency and the heating value of the gas [48].

The effect of λ on the main output parameters is depicted in Figure 10. Higher availability of oxygen will lead to increased combustion of the product gas and char, and therefore to an increase of the reactor temperature and the carbon conversion. However, the yield of the combustible products and thus also the cold gas efficiency will decrease. Tar yield will decrease with increasing λ , partially due to oxidation reactions and partially due to enhanced tar cracking caused by the increased process temperature. Considering the above, the choice of λ will be a compromise; the typical values used in fluidized bed gasification processes vary between 0.2 and 0.4.

Figure 10. Effect of the variation of λ on the main process parameters.



A similar consideration applies to the SB value. Here, however, a larger variation in the suggested optimal values has been found in the literature. Table 10 shows the results of the investigations on the effect of SB on the gasification process. Most researchers concluded that choosing the SB value between 0.3 and 1.0 will have a positive effect on carbon conversion, cold gas efficiency, hydrogen yield and tar reduction. However it has to be stated that all the investigations reported in Table 10 have been carried out using BFBs. CFBs operate at a higher fluidization velocity, and therefore a higher steam input may be needed to achieve this. Nonetheless, the higher the SB ratio the more energy is required to heat up the steam to process temperature, which at some point will cancel the positive effect on the CGE. In addition, higher values ($SB > 1$) lead to a high amount ($>60\%_{vol}$) of unreacted H_2O in the product gas, which, even when the recycling via condensation/vaporization/reheat is applied, will cause a significant

drop in the thermal efficiency of the whole process [73]. Also, the conversion of H₂O decreases with increasing SB ratio, and is typically limited to approximately 10% [73,74].

Table 10. The results of several investigations related to SB.

Literature Reference	Test Equipment	Investigated Variable	Investigated Range	Reported Optimal Range	Remarks
Corella [73]	BFB	SB	0.2–2.0	0.40–1.0	values higher than 1.2–1.5 not recommended
Campoy [75]	BFB	SB	0–0.63	0.3–0.4	slight positive effect on CC and CGE increased H ₂ yield from 8.7 to 13.3% _{vol} and 17.8 to 27.7 g kg ⁻¹ _{biomass,daf} decrease of the total yield of main combustibles from 555 to 507 g kg ⁻¹ _{biomass,daf}
Franco [76]	BFB	SB	0.4–0.85	0.6–0.7	maximum for CC, gas yield and H ₂ concentration in the gas
Gil [77]	BFB	SB	0.3–1.3	0.50–0.75	max. H ₂ concentration of 29% _{vol,dry} very difficult to obtain tar concentration below 5–10 g m ³ _{n,dry}

The increase in the hydrogen yield due to steam addition cannot be explained solely by the water-gas shift reaction, as the changes in H₂ and CO concentrations do not match. It is highly probable that the added steam acts as an oxygen donor for the oxidation of CO, char and perhaps also tar. This could be confirmed by the results presented in [75], which show a slightly increased carbon conversion and a slightly decreased cold gas efficiency when comparing the extreme SB ratios investigated there.

Kinoshita *et al.* [40] performed some tests in an air-blown bench-scale FB gasifier to test the influence of process temperature, equivalence ratio and residence time on the formation of tar species. Tar yield, expressed in g kg⁻¹_{dry,fuel} showed a maximum at the temperature of *ca.* 750 °C and decreases with increasing temperature ($\lambda = 0.22$, $\tau = 3.75$ s). Tar yield also decreased with increasing equivalence ratio (range: 0.22–0.32) at *constant* temperature, while the influence of the residence time in the studied interval (3.0–5.0 s) was negligible. Next to the total (measurable) tar, the yields of different tar classes were studied. The increase in temperature caused a large increase of the benzene fraction, while other monoaromatics decreased. At the same time naphthalene fraction increased, just as the fractions of 3 and 4-ring compounds, but the fraction of 2-ring compounds other than naphthalene decreased in the studied temperature range (700–900 °C). The oxygenated compounds (e.g., phenol) were absent in the temperatures above 800 °C. A very similar trend is observed for an increasing equivalence ratio at *constant* temperature, except the fact that here also the 2-ring compounds other than naphthalene showed an increasing trend. The effect of the residence time on the tar composition is much less pronounced than that of the temperature or the equivalence ratio; mainly a linear decrease of monoaromatic compounds other than benzene, and an increase of 3- and 4-ring compounds at higher residence times (>4.5 s) were observed. It is very likely that the influence of the residence time would be much more pronounced at lower values ($\tau \approx 1$ s).

3.2.2. Temperature

Temperature is an important process parameter in thermochemical fuel conversion. The temperature range relevant for biomass gasification in a fluidized bed lies between approximately 650 °C and 950 °C. Higher temperature will increase the carbon conversion efficiency and reduce the amount of tar produced, however, in the case of a fluidized bed reactor the maximum operating temperature is limited by the melting point of ashes or of the bed material. Additionally reactor construction materials can become an issue. In practice the reaction temperature is directly linked to λ , as for a higher temperature more product gas needs to be oxidized, which in its turn reduces the cold gas efficiency, as explained earlier. However, in (small) laboratory test rigs temperature can often be controlled by installed external heating elements, and therefore be independent of λ . This is not only interesting, but also necessary, as due to relatively larger heat losses in a small laboratory test rig it may be impossible to achieve the same temperature at a certain lambda value as in a big industrial unit solely by autothermal operation. As most gasification (equilibrium) reactions are endothermic their reaction coordinate will increase with higher gasification temperature. One of the important exceptions is the water-gas shift reaction, which being slightly exothermic will shift to the $\text{CO} + \text{H}_2\text{O}$ side as the temperature increases. This effect is, however, often of lower importance than the high temperature necessary to reduce the amount of tar and to achieve high carbon conversion.

3.2.3. Pressure

Although pressurized operation puts significant additional requirements on the design and operation of a gasifier, it is often desirable. Firstly, higher pressures result in lower volumetric gas flow rates, which means smaller size of the reactor and downstream gas cleaning and upgrading equipment. Secondly, many downstream processes using the produced syngas require pressurized conditions (e.g., Fischer-Tropsch process, gas turbines), and the fact is that it is easier to pressurize the reactants separately (lock-hopper system for the solids, compressors for the gases) than to compress hot, combustible, hydrogen-rich product gas compensates the technical and operational complications [44]. Compressing the product gas will require removal of tar and moisture below their dew points to avoid condensation during compression. Also the cooling of the gas to approximately 90 °C is required [22]. However, process improvements are still needed, for instance in the high-pressure feeding systems, although commercially available units exist [78].

Pressurized conditions will also influence the process of gasification. The equilibrium reactions that are not equimolar (reactions 6, 7, 9, 10, 11) will be driven towards the condition with the lowest volume (Le Chatelier's principle). In the list of the main gasification reactions, three out of five non-equimolar reactions involve methane, therefore the methane yield from the pressurized gasification process will be higher than from an atmospheric process performed at otherwise similar conditions. The tar yield will, however, go down with increasing pressure; this is due to the fact that during the pyrolysis phase the recarbonisation of the tar precursors will be more pronounced as the pressure increases. Some of the carbon formed will subsequently react to methane, but generally the carbon conversion will also decrease with increasing pressure [79].

Additional benefits from the pressurized conditions could be achieved by operating the gasifier under pressure conditions that favor the recarbonization of CO₂ on earth-alkaline species, typically calcium. Under atmospheric gasification conditions the typical partial pressures of CO₂ would require a temperature well below 800 °C to enter the thermodynamic region where CaCO₃ is formed. However, such a low gasification temperature will result in lower carbon conversion and an increased tar yield. By increasing the operational pressure of the gasifier and thus also the partial pressure of CO₂ the typical fluidized bed gasification temperatures can be maintained while benefiting from the CO₂ capture by recarbonization. The enhanced hydrogen production by the adsorption of CO₂ was studied by several authors: enhanced high-temperature WGS [80], adsorption enhanced reforming [64,65], HyPr-RING (Hydrogen Production by reaction-integrated novel gasification) [81], and also its application for post-combustion CO₂ removal has been investigated [82].

3.2.4. Bed Materials & Additives—Catalytic Activity on Gasification Reactions

The main purpose of the presence of the bed material in the fluidized bed is the heat storage and heat transfer between the particles undergoing exothermic processes (chemical reactions like oxidation and water-gas shift) and endothermic processes (drying, pyrolysis, and most gasification reactions). The heat produced during exothermic processes is “stored” (accumulated) in the bed material and due to intense mixing of the bed inventory (fluidization) it is transferred to the processes that require heat input. In this way large temperature peaks in the oxidation zone are avoided and a nearly uniform temperature distribution can be observed in the bubbling zone (BFB) or even throughout the reactor (CFB).

In principle the bed material is assumed to remain inert during the gasification process. To a large extent this is true for the bed material used most often—quartz sand. However, the choice of the bed material can have an important influence on the process if that bed material shows catalytic activity on some of the reactions involved, or its interaction with the fuel constituents results in a considerable change of its physical properties. The former effect is mostly desirable, as in the case of gasification it often leads to the increased conversion rate of tar, leading to an improved gas quality. In the latter case the most often observed effect is called bed agglomeration, which is highly undesirable—this will be discussed in the next section.

Using catalytically active bed materials can significantly influence the gas composition in terms of increased hydrogen yield, and reduced amounts of methane and tar, bringing the gas closer to syngas composition. These materials can also be applied as in-bed additives—an important feature of a fluidized bed. Regarding the tar decomposition, the ability to use metal oxides derived from natural rock minerals in the fluidized bed (as primary tar measures) appears to be more advantageous than the use of (commercial) Ni-based catalyst. This is due to the fact that the loss of solids, and of the fine fraction in particular, is often not negligible in these kind of reactors [39,83,84]. Dolomites (CaMg(CO₃)₂), calcites (CaCO₃), magnesites (MgCO₃) and olivines ((Mg,Fe)₂SiO₄) are potentially attractive in-bed additives or even bed materials because they are non-toxic and can be significantly active at high temperatures. The main problem of the minerals mentioned above, with the exception of olivine, is their low attrition resistance and the continuous deterioration of their mechanical strength over the reaction time. In addition, the costs of catalysts are usually high; this is especially true for metal-based catalysts, while the prices of natural rock minerals are often higher than quartz sand, but acceptable. Furthermore, most of

the additives have been tested only on (laboratory-)pilot scale, although olivine [16] and magnesite [85] have also been tested in larger plants.

Delgado *et al.* [86] reported that of the three natural rock minerals applied in the downstream fixed bed reactor for the upgrading of the product gas, calcined dolomite (CaO–MgO) showed the highest catalytic activity on tar cracking, followed by pure calcined magnesite (MgO) and calcined calcite (CaO). Also relatively low deactivation was observed for tar concentrations below 48 g m_n^{-3} (which is even higher than the typical tar concentrations measured in reasonably operating (C)FB gasifiers), at temperatures above $800 \text{ }^\circ\text{C}$, when small particles are applied ($d < 1.9 \text{ mm}$) [87]. An additional advantage was the simultaneous coke formation and its elimination by steam gasification, leading to the prolonged lifetime of the catalyst. The integration of the heats of CO_2 adsorption reaction and water-gas shift reaction into the complex network of (endothermal) gasification reactions will lead to the improvement of the product gas in terms of higher hydrogen yield and reduced amount of tar [64,83,86–89]. Hanping *et al.* [90] performed air-blown biomass gasification tests in a small-scale (*ca.* 12 kW_{th}) CFB gasifier with the addition of dolomite, magnesite and olivine, and although they reported a significant reduction ($>50\%$) of tar content in the gas, they did not report any values showing the change in the concentration of the permanent gases, except in the dolomite case where only the concentration of H_2 increased significantly. For magnesite, used both as an additive and as the bed material in a steam/oxygen blown CFB gasifier (100 kW_{th}), the positive effect on the conversion of tar and methane, and an increase of H_2 :CO ratio was presented in detail by Siedlecki *et al.* [89].

Devi *et al.* [91] compared the effect of dolomite and fresh olivine on the conversion of tar, by using these minerals as additives to a sand bed in an air-blown BFB gasifier. Both additives showed a reduced tar concentration in the product gas, as compared to pure sand bed, but the highest tar conversion was achieved with dolomite. The effect of the pre-treatment (calcination at $900 \text{ }^\circ\text{C}$) of olivine was also investigated, using steam- and dry reforming of naphthalene as the model tar conversion component and reaction [92]. Pre-treated olivine proved to be a significantly more active catalyst under the mentioned conditions than the untreated one. Also the calcination time was observed to play a role with a 30% and 80% increase in naphthalene conversion for 1 hour and 10 hours treatment, respectively. However, under model syngas atmosphere the conversion was lower than only in the presence of steam and CO_2 . This can be attributed to the presence of H_2 and CO in the gas, as these species are known inhibitors of tar reforming reactions (see also e.g., [93]). Also the origin of olivine, and more precisely its mineral composition, will influence its activity related to the conversion of tar. Rauch *et al.* [94] compared the influence of two different kinds of olivine on the tar yield and the gas composition during the operation of the Güssing 8 MW_{th} CHP demo-plant supported by detailed characterization of the bed material. The researchers came to the conclusion that the presence of free iron oxide outside the olivine structure is very likely a possible requirement for the desired catalytic activity. Siedlecki and de Jong [95] observed the lack of the activity of a certain kind of olivine on tar yield, even despite the calcination pre-treatment at two different temperatures ($900 \text{ }^\circ\text{C}$ and $1200 \text{ }^\circ\text{C}$, 10 hours). On the other hand Corella [73] compared the use of different catalytically active bed materials, using the H_2 and tar concentration (both on dry gas basis) as a benchmark for gas composition and gas quality respectively. Based on those experiments it was concluded that olivine is a promising catalytic bed material resulting in a hydrogen concentration varying between $34\text{--}52\%_{vol}$, while the reported tar content varied between $0.25\text{--}1.5 \text{ g m}_n^{-3}$ [73,94].

Char, although it is hard to call it an “additive”, as it is always present in the bed except during startup, has also been recognized as an important catalyst for the conversion of hydrocarbons—both tar [96] and methane [97]. Detailed comparison of various catalysts for tar conversion showed that the activity of char for naphthalene conversion is even higher than dolomite at 900 °C [98]. The high activity of char is partially attributed to the fact that it is continuously activated by steam and CO₂, and above that, there is a continuous supply of fresh char from biomass pyrolysis. However, in order to use char efficiently as an in-situ catalyst the fluidized bed should be designed in a way to allow long char-tar interaction times. In a standard (C)FB this is limited only to the devolatilization phase and the stochastic interaction between upflowing gas and fluidized char particles. Also Brage [99] claims that the holdup of char in the reactor results in the decreased amount of tar in the gas, being a proof of the catalytic activity of char on tar conversion mechanisms. In addition, he states that coal char is more active than biomass char, as higher coal char holdups can be achieved, due to lower reactivity of coal char.

3.2.5. Bed materials & Additives—Agglomeration Resistance and Counteractions

As already explained in the previous section, in principle the bed material is assumed to remain inert during the gasification process, but its interaction with the fuel constituents may result in a considerable change of its physical properties. This highly undesirable effect is called bed agglomeration. The research performed in this area indicates that bed agglomeration will occur upon the interaction between the silica-containing bed material and the inorganic part of the fuel (*i.e.*, ash), especially if the latter contains high amounts of alkali metals and/or chlorine. During biomass conversion when alkali compounds are released, and also when silica is present either from the bed material or biomass ash itself, then the formation of alkali-silicates (K₂O-SiO₂) can be expected. Those compounds have an eutectic point of about 770 °C, while the eutectic point of K₂O-CaO-SiO₂ structures is even lower [100]. Ergudenler [101] found that quartz sand will agglomerate in the presence of straw ash (with 1.2%_{wt} of K₂O in the dry fuel) at around 800 °C, causing defluidization. This has also been observed and investigated by other researchers [36,101–104]. From the above it can be concluded that silica-containing bed materials should be avoided when operation with “difficult” biomass fuels is intended. Natural rock minerals, already introduced in the previous section as catalytically active bed materials or additives could be an option here, but their mechanical strength is often much lower than that of silica-based materials and therefore they are very prone to attrition. As an alternative synthetic bed materials (e.g., alumina) could be employed, but their high price—especially important when applied on a larger scale—will be an obstacle here. Therefore the choice of the bed material will be a compromise between mechanical stability, agglomeration resistance, catalytic activity and price.

In case a silica-rich bed material is to be used with alkali-rich fuels the agglomeration problem can be counteracted using in-bed additives. Known additives that are supposed to reduce the agglomeration phenomena are kaolin (Al₂Si₂O₅(OH)₄), calcium oxide, calcium carbonate and bauxite [105]. Introduction of alumina-rich compounds, such as kaolin, may result in the formation of aluminosilicates (K₂O-Al₂O₃-SiO₂), which have a much higher melting temperature than the alkali silicates (K₂O-SiO₂) formed otherwise [100]. Siedlecki and de Jong [95] reported successful application of kaolin during the gasification of miscanthus and Dutch straw, both containing a high amount of alkaline elements in the ash, when silica-rich bed materials (sand and olivine) were used—no agglomeration

occurred during the operation with the additive, while agglomeration was reported during the test when no additive was used. Also the gasification tests with demolition wood (“B-quality” wood), a fuel that judging from its ash amount and composition should not cause any agglomeration-related problems, ended up with defluidization. There too the addition of kaolin proved to be a sufficient remedy.

3.3. Overview of Industrial Gasification Pilot Plants

Since the (re)gain of interest in gasification technology, now almost four decades ago, next to the small laboratory-sized units a number of industrial-size gasification plants based on fluidized bed technology have been constructed and operated. An overview of the industrial-size gasifier concepts based on the fluidized bed principle can be found in Table 11. Some of those concepts, like for example High Temperature Winkler process have been originally developed for coal gasification and the concept was applied for biomass gasification at a later stage. From the table it could be concluded, that already a significant number of biomass gasification plants at relevant industrial scale have been built and have been or are at present being operated. This is certainly true, however, it has to be stated that most these plants are fueled with wood, wood waste or similar biomass type; only at the Värnamo gasifier some runs with agricultural fuels such as miscanthus have been performed. These woody fuels are not very demanding in terms of ash-properties and the related operational issues. Furthermore the produced gas is used for co-firing in an fossil-fueled boiler, or in a gas engine. Also that application, although beneficial in terms of reduced net CO₂ emission, does not pose very high requirements with respect to the gas cleaning. As with the aforementioned applications the gas needs to be cooled down (e.g., to 100–200 °C for the gas engine application), consequently the particles can be efficiently removed using reliable low-temperature filtration techniques, alkali salts will be removed together with the particles, heaviest tar will condense in the gas cooler (a design issue!). The N and S-containing compounds are not directly problematic for the combustion application, although their amount needs to be controlled in order to meet the exhaust emission directives (NO_x, SO_x). Also, the produced gas does not need to meet the syngas composition requirements; next to the CO and H₂ all hydrocarbons including methane, volatile species (e.g., ethylene, acetylene, benzene) and tar (not condensed) will be accepted by the gas engine or the burners in a boiler.

As already mentioned at the end of Section 2., if the product gas is to be used for the production of advanced secondary fuels from biomass, it needs to comply with the far more stricter quality requirements. The following section touches upon one of the possible syngas applications, namely the production of bio-diesel by means of Fischer-Tropsch synthesis. As this topic can be considered to be equally as broad as biomass gasification an extensive review is not presented here, merely a short summary to illustrate the present status of the technology and the potential challenges of biomass gasification and Fischer-Tropsch synthesis (BGFT) coupling.

Table 11. Overview of the industrial-size gasifier concepts based on the fluidized bed principle and operated on biomass fuels. Names listed in boldface indicate plants that are currently in operation. Letters between brackets indicate the use of the product gas: ammonia synthesis (A), cement or lime kiln (C), gas engine (G), integrated gasification combined cycle (I), steam cycle—also in co-combustion mode (S) [14,17,34,49,67,106–114].

Technology identifier	HT Winkler	MINO	Renugas [®]	Lurgi	Pyroflow	Bioflow	Silvagas [®]	FICFB
Related Companies /institutes	Rheinbraun ^a	Studsvik AB, TPS AB, Ansaldo ^b ,	IGT ^b , Tampella ^e , Enviropower, Carbona Inc.	Lurgi GmbH	FW ^c Energia Oy, API ^f , VTT	FW ^c Energia Oy	Battelle CL ^d , Battelle ML ^g , FERCO	Babcock Borsig, TU Vienna
Gasifier topology	CFB	CFB	BFB	CFB	CFB	CFB	dual CFB	FICFB ⁱ
Heat supply	direct	direct	direct	direct	direct	direct	indirect	indirect
Operational pressure	10 bar	20 bar (Mino), atm. (TPS)	30 bar (max.)	atm.	atm.	20 bar	atm.	atm.
Fluidization medium	steam/O ₂	steam/O ₂ , air	air (+steam)	air	air	air	steam (gasif.), air (comb.)	steam (gasif.), air (comb.)
Operators (examples)	Oulu Kemira (A) 120 MW _{th} ,	Studsvik 2.5 MW _{th} (airblown), Grøve-in-Chianti (S) 2 x 15 MW _{th} , ARBRE (Aire Valley) (C) 8 MW _e	PICHTR 100 MW _{th} , Geertruidenberg (S) 83 MW _{th} ,	Rüdersdorf (C) 27 MW _{th} , Pietarsaari (C), 35 MW _{th} , Kymijärvi (Lahti) (S) 40–70 MW _{th} , Ruien (S) 50–86 MW _{th}	Norsundet (C) 27 MW _{th} , VVBGC (fr. Sydkraft) (C) Värnamo 18 MW _{th} ,	VVBGC (fr. Sydkraft) (C) Värnamo 18 MW _{th} ,	Burlington (S)	Güssing (G) 8 MW _{th} ,

^a Rheinische Braunkohlenwerke AG; ^b Institute of Gas Technology; ^c Foster Wheeler; ^d Columbus Laboratories; ^e Tampella Power Inc.; ^f Ahlstrom Pyropower; ^g Memorial Laboratory;

^h Ansaldo Aerimpianti Spa; ⁱ Fast Internally Circulating Fluidized Bed.

4. Industrial Application of Bio-syngas: Production of Liquid Transportation Fuels

Production of Fischer-Tropsch diesel from fossil fuels is now a well-known industrial process. There are plants owned by large oil companies, like Sasol in South Africa (initially coal-to-liquid, CTL; now gas-to-liquid, GTL) and Qatar (GTL) and Shell in Malaysia (GTL), producing over 200,000 bpd of synthesis products, including gasoline, diesel, naphtha, kerosene and other chemicals [3]. The composition of the products of FT-synthesis (“FT-syncrude”) depends mostly on the type of catalyst and the reaction conditions:

- Catalyst: iron- or cobalt-based;
- Temperature: 210–260 °C (Low Temperature FT, LTFT) or 310–340 °C (High Temperature FT, HTFT).

The LTFT produces a higher fraction of the higher-boiling (above 360 °C) hydrocarbons, and the total distillate yield is significantly higher than in the case of HTFT. However, the LTFT does not produce final fuels, but rather fuel blending stocks. On the other hand, the production facilities for HTFT are far more complex than those for the LTFT [3].

Regarding the FT catalyst, the advantage of the cobalt-based catalyst is its higher conversion rate and longer lifetime. Also less unsaturated hydrocarbons and alcohols are produced compared to the process employing an iron catalyst. On the other hand, iron catalysts do have a higher tolerance to sulphur and are cheaper. The Fischer-Tropsch synthesis can be represented by the following chemical reaction:



If the feed gas has a H₂:CO ratio lower than 2, the iron catalyst can be used simultaneously to adjust it by means of the water-gas shift reaction; the activity of Co-catalyst on the water-gas shift reaction is negligible, hence the H₂:CO ratio needs to be adjusted upstream [115].

Although the use of a product gas from an air-blown gasifier as feed gas for FT synthesis is theoretically possible, this will affect the synthesis process in a negative way. Firstly, high dilution by the nitrogen will cause the need for excessively large process equipment, leading to higher investment costs. Besides, high nitrogen partial pressures would make it act as an “inhibitor” on the catalytic processes, considerably reducing the reaction rates. Also, at certain elevated pressures the ammonia/nitrogen/hydrogen equilibrium may start shifting to the ammonia side. Consequently, the use of an air-blown gasifier upstream the FT process should be evaluated very carefully and processes producing a nitrogen-free gas, like steam-O₂ or indirect gasification, should be considered instead.

As with most catalytic processes, as in the FT process, there is a potential risk of the deactivation of the active sites by pollutants or catalyst poisons. To avoid frequent replacement of the catalyst, which would not be acceptable mainly from an economical point of view, the feed gas needs to meet certain purity criteria. These criteria have been summarized in Table 7. Given a typical product gas from fluidized bed gasification of biomass and the gas requirements mentioned above, the typical gas cleaning train will consist of the following steps:

- Hot gas filtration: the particles need to be removed as they will otherwise pollute or foul the downstream equipment. This should preferably be done at the temperature close to the gasification

temperature to reduce the thermodynamic losses before the next high-temperature upgrading step, namely:

- Methane and tar reforming: although advanced tar removal technologies based on scrubbing do exist (e.g., OLGA technology [116,117]), in the case of gas upgrading for advanced synthesis processes there is a benefit of combined (catalytic) conversion of tar and methane. When tar is removed by means of a scrubbing process, the methane will remain in the gas, but not being a feedstock for the synthesis process it will lead to a decreased product yield. However, if a catalytic process is to be applied here it will pose additional requirements on the capture of particularly sulphur species in the gasifier, to avoid the premature deactivation of the catalyst;
- Alkali and residual particle removal: as the gas is cooled down after the high-temperature upgrading steps an additional filtration step may be necessary. This is due to the formation of solid alkali salts from their vapors, present at temperatures of around 800 °C and above;
- Removal of *N*- and *S*-compounds: in this final upgrading step typical catalyst poisons are removed, if they have not already been removed before the catalytic hydrocarbon reforming.

Due to the relatively low temperature of the FT process compared to e.g., Solid Oxide Fuel Cell application, the gas cleaning is slightly easier as not all the cleaning steps need to be carried out at elevated temperatures. Of course the application of a heat regenerator could enable the use of low temperature cleaning steps followed by the reheat of the gas, but the total energy efficiency of the process is reduced due to the losses associated with the Second Law of thermodynamics.

Catalytic hot gas filtration (so a combined particle removal and hydrocarbon reforming step) was investigated by Simeone *et al.* [120] using model gas and tar compounds, and by Rapagna *et al.* [121] using a ceramic candle filter installed directly in the freeboard of a small laboratory-scale steam-blown bubbling fluidized bed. Both investigations showed promising results in terms of tar conversion. The removal of contaminants from the product gas downstream a steam-blown BFB and a particle filter was investigated e.g., by Cui *et al.* [122] using columns containing different sorbents. Although CH₄, tar and NH₃ were successfully converted to permanent gases using a nickel catalyst, and H₂S was reduced below 1 ppm_v using a commercial ZnO sorbent, the authors indicate that the application of catalysts and sorbents for product gas cleaning remains a challenging task. Boerrigter *et al.* [35] performed a demonstration campaign of 650 hours based on the gasification of clean wood followed by Shell FT process. Tar was removed in a high-temperature tar cracker, while NH₃ and H₂S were removed using wet scrubbing followed by active carbon and ZnO filters. Total removal of BTX (benzene, toluene, xylenes) is indicated as the design guideline for the FT process, as otherwise the BTX in the gas would cause rapid saturation of the active carbon filters. With this approach the tar problem is immediately solved as BTX are more difficult to remove / convert than tar. In a Finnish project “UltraClean Gas” the gas cleaning followed by FT synthesis is being tested in the slip-stream (5 MW_{th}) of the 12 MW_{th} atmospheric biomass gasifier in Varkaus [123], while the development of a pressurized unit and the construction of a first commercial scale BGFT-plant is currently scheduled for 2012–2014 as an industrial follow-up project [124].

5. Conclusions and Outlook

This paper has reviewed the application of fluidized bed technology in the process of biomass gasification that produces a feed stream for the synthesis of advanced secondary energy carriers, Fischer-Tropsch products in particular.

With the disadvantages of the extensive exploitation of the fossil fuel resources and its consequences being very evident now, alternative renewable and sustainable sources of primary energy are being sought. The current annual world's primary energy demand amounts to approximately 490 EJ, of which 250–270 EJ could be covered by biomass that is available on a sustainable basis and at competitive prices. However, raw biomass is not very convenient to use, mainly due to its solid appearance and low volumetric energy density. Out of combustion, pyrolysis or gasification routes the latter one proves to be very suitable, especially when production of advanced secondary energy carriers is opted for. If the process is to be carried out at large industrial scale (100 MW_{th} order of magnitude), then the fluidized bed technology shows the best balance between the advantages and disadvantages. The strong points are related to the already established acquaintance with fluidization engineering in thermochemical conversion processes, acceptance of a wide variety of the feedstock regarding the size and the chemical composition, good scalability of the reactor, moderate amount of the tar formed and the ability of using the *in-situ* additives to improve the conversion process. The main vulnerability is related to the fuel ash issues, and especially the presence of alkali metals together with silica in the reactor which can lead to the formation of bigger bed material lumps (agglomerates) and cause undesirable interruptions in the operation. However, by using appropriate additives (e.g., kaolin) this issue can be managed. The composition of the product gas and the process efficiency (usually expressed in terms of the carbon conversion and the cold gas efficiency) strongly depends on the operational parameters of the gasifier. The elimination of nitrogen is crucial for obtaining medium calorific value gas and is achieved either by using steam/O₂ blown gasifier or an indirect gasification concept. The choice of the bed material will be of utmost importance, due to a proven catalytic activity of minerals like dolomite, magnesite and olivine on the hydrocarbon conversion reactions and the water-gas shift reaction, which makes them more attractive than quartz sand. The bed materials with low silica content also show a significantly better agglomeration resistance. Additional benefits can be obtained from pressurized gasification, although the reactor design and operation are significantly more complicated than in the case of an atmospheric gasifier.

Gas produced in the fluidized bed gasification process is not yet of the syngas quality. The design of the gas cleaning and upgrading system, although less demanding than the one required, for instance, for an SOFC application, needs to be done carefully to benefit from the fact that some steps can be carried out at the temperature of the FT process, instead of at the elevated gasification temperature.

Nowadays only a few (C)FB biomass gasifiers are being operated at industrial scale using woody (thus "easy") fuels, and they produce gas for co-firing in a boiler. This application poses significantly lower requirements on the gas cleaning than the fuel cells or synthesis processes. Fischer-Tropsch production plants also exist, but they use fossil fuels as feedstock. The combination of biomass gasification and the production of advanced secondary fuels has not left the demo-scale yet, but this step is currently "work in progress".

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