*Проект SWorld*

*Львович И.Я., Преображенский А.П., Толбатов В.А., Червоный И.Ф., Чопоров О.Н. и др.*

# НАУЧНОЕ ОКРУЖЕНИЕ СОВРЕМЕННОГО ЧЕЛОВЕКА:

## ТЕХНИКА И ТЕХНОЛОГИИ

входит в **РИНЦ SCIENCE INDEX**
присвоен DOI: **10.30888/978-617-7414-28-4.0**

## *МОНОГРАФИЯ*

Одесса
*Куприенко СВ*
2018

УДК 001.895
ББК 94
Н 34

*Авторский коллектив:*

Капитанова Л.В. (1), Львович И.Я. (2), Преображенский А.П. (2), Чопоров О.Н. (2),
Верховлюк А.М. (3), Червоный И.Ф. (3), Горбач А.С. (4), Куликов А.В. (4),
Писарева М.Ю. (4), Рогачева В.А. (4), Тюрина В.Н. (4), Бойко П.Н. (5),
Бондар Н.В. (5), Куц А.М. (5), Головкина Л.В. (6), Крестьянполь Л.Ю. (7),
Гармаш С.Н. (8), Вакал С.В. (9), Смоляров Г.А. (9), Толбатов А.В. (9),
Шандиба А.Б. (9), Ляховецкий Л.М. (10), Орешков В.И. (10), Яневич А.К. (10),
Агаджанова С.В. (11), Агаджанов-Гонсалес К.Х. (11), Вьюненко О.Б. (11),
Толбатов А.В. (11), Толбатов В.А. (11), Толбатова Е.А. (11)

Н 34 **Научное** окружение современного человека: Техника и технологии : монография / [авт.кол. : И.Я.Львович, А.П.Преображенский, В.А.Толбатов, И.Ф.Червоный, О.Н.Чопоров и др.]. – Одесса: КУПРИЕНКО СВ, 2018 – 181 с. : ил., табл.
ISBN 978-617-7414-28-4

Монография содержит научные исследования авторов в области техники и технологий. Может быть полезна для инженеров, руководителей и других работников предприятий и организаций, а также преподавателей, соискателей, аспирантов, магистрантов и студентов высших учебных заведений.

**УДК 001.895**
**ББК 94**
**DOI: 10.30888/978-617-7414-28-4.0**

ISBN 978-617-7414-28-4

# ГЛАВА 5.
# БИОМАССНАЯ ГАЗИФИКАЦИЯ В ПРОИЗВОДСТВЕ БИОЭТАНОЛА

## Вступление / Introduction

The biomass gasification process is an alternative approach for producing ethanol from lignocellulosic biomass. This method involves controlled burning of biomass to produce synthesis gas, or syngas, and then conversion of syngas to ethanol. And, later, there are two methods to convert biomass-derived synthesis gas to ethanol. The first method is to use biocatalysts and the second method is to use metal-based chemical catalysts. This article is an introduction to this process, where chemistry of syngas formation and gasifier designs that are used to make syngas from biomass is discussed. Syngas produced from biomass can be converted to ethanol by two alternative methods, as shown in Figure 1. One of the principal differences in this gasification approach and the aqueous-phase biomass hydrolysis process is that in theory all the carbon in cellulose, hemicellulose, and lignin can be transformed to carbon in ethanol in the gasification method, whereas in the aqueous phase route only cellulose and hemicellulose are used in making ethanol; lignin is separated as a byproduct.

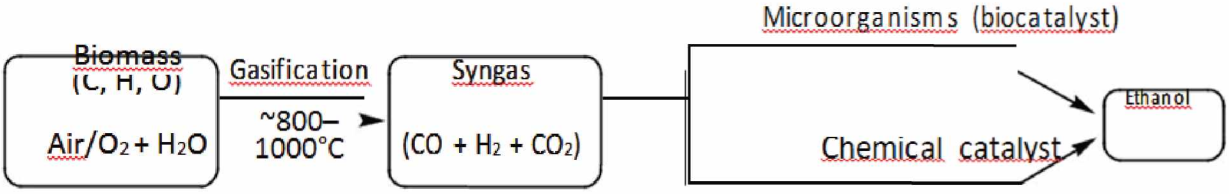

**Figure 1** Biomass gasification, then syngas to ethanol conversion process.

Any form of biomass rich in carbon-like agricultural waste, forest residues, municipal wastes dedicated energy crops, and grasses can be converted to syngas by controlled burning in a gasifier. In fact, syngas technologies were originally developed as far back as the early 1800s for conversion of coal to syngas, and syngas can be used directly as a fuel in internal combustion engines and gas turbines as well [1].

Direct gasification of biomass with air produces a syngas of heating value in the range of 4–12 MJ/m3 [2, 3]. Low energy density and difficulties in storage are the major drawbacks in using syngas directly as a fuel, however, the conversion of syngas to liquid fuels with high energy density and easy storage is an attractive proposition. There are a number of approaches for conversion of syngas mixture to liquid fuels like the Fisher-Tropsch method for conversion to gasoline, diesel-like hydrocarbon fuels as well as conversion to alcohol and ether-type oxygenated fuels. This chapter will focus on the production and properties of biomass-derived synthesis gas.

## 5.1. Chemistry of the Conversion of Biomass to Syngas

Synthesis gas, or syngas, is a gas mixture that contains hydrogen, carbon monoxide, and often some carbon dioxide as the major components. The term synthesis gas was given to this gas mixture since it can be used as a feedstock for the synthesis of various types of fuels and chemicals. This type of gas mixture can be prepared by multiple routes, which includes steam reforming of natural gas, liquid hydrocarbons, and gasification of coal or lignocellulosic biomass. Syngas is combustible, can be used directly as a fuel in internal combustion engines and gas turbines, or as an intermedi-ate for the production of liquid fuels and other chemicals. A comprehensive overview of syngas production from biomass is found gasification. The other technique is to supply the heat from an external source, which is known as indirect or allothermal gasification. Lignocellulosic biomass is first chipped into smaller pieces to feed the reactor, and this will provide higher surface area and faster reaction rates.

Biomass material undergoes several different complex chemical processes during gasification. These processes in increasing order of temperature can be outlined as follows:

1. Dehydration – typically, the moisture content of biomass feed ranges from 5% to 35%. Dehydration occurs at around 100°C, resulting in the loss of adsorbed water from the biomass. The moisture content in the biomass is reduced to below 5% at this initial stage. The resulting steam is mixed into the gas flow and may be involved with subsequent chemical reactions.

2. Pyrolysis – this process occurs at around 200–300°C. During this step biomass undergoes a thermal decom-position in the absence of oxygen or air, and volatile matter in the biomass is reduced at this stage. This results in the release of hydrocarbon gases, reduc-ing the biomass to solid charcoal. These hydrocarbon gases can condense at a sufficiently low temperature to generate liquid tars.

3. Combustion – in this step C, H, O in biomass and some of the char produced in the pyrolysis stage reacts with oxygen to produce carbon dioxide, water and carbon monoxide. The proportion of CO to $CO_2$ produced depends on the amount of oxygen available. This is a reaction between solid carbonized biomass and oxy-gen in the air, resulting in formation of $CO_2$. Hydrogen present in the biomass is also oxidized to generate water. A large amount of heat is released with the oxidation of carbon and hydrogen. If oxygen is present in substoichiometric quantities, partial oxidation of carbon may occur, resulting in the generation of carbon monoxide. Combustion or biomass oxidation reaction can be summarized by the following equation:

$$C_2H_2O + O_2 \rightarrow CO_2 + H_2O + CO \qquad (1)$$

4. Reduction – a number of reduction reactions take place at this stage in the absence (or sub-stoichiometric presence) of oxygen. The reactions which occur in the 800–1000°C temperature range are mostly endothermic, and the key reactions in this category are summarized below.

The gasification process occurs as the char reacts with steam to produce carbon monoxide and hydrogen.

$$C + H_2O \rightarrow H_2 + CO - 131.4\ \text{kJ/mol} \qquad (2)$$

Bounded reaction:

$$C + CO_2 \rightarrow 2CO - 172.6\ \text{kJ/mol} \qquad (3)$$

Water gas shift reaction is a very important reversible reaction that occurs at high temperatures. This reaction reaches equilibrium very fast at high temperatures in a gasifier and controls the balance of carbon monoxide, steam, carbon dioxide and hydrogen.

Water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ - 42 kJ/mol} \qquad (4)$$

Methane reaction:

$$C + 2H_2 \rightarrow CH_4 \text{ - 75 kJ/mol} \qquad (5)$$

### *5.1.1. Composition of the Syngas*

Composition of syngas depends on the gasifier design, type of biomass used and operating conditions. Indicative compositions and lower heating values (LHV) of syngas produced in allo thermal, auto thermal, and entrained flow types of gasifiers are shown as an example in Table1 [3]. The last column in the table shows the composition of syngas produced from coal in an entrained flow gasifier.

**Table 1 Indicative compositions of biomass-syngas produced in allo thermal, auto thermal, and entrained flow gasifiers, and comparison with coal-syngas produced in a entrained flow gasifier.**

| **Syngas properties (vol%, dry)** | **Biomass, Allo thermal** | **Biomass, Auto thermal** | **Biomass, Entrained flow** | **Coal, Entrained flow** |
|---|---|---|---|---|
| $H_2$ | 40 | 26 | 39 | 32 |
| CO | 25 | 20 | 38 | 55 |
| $CO_2$ | 21 | 35 | 20 | 8 |
| $CH_4$ | 10 | 13 | 0.1 | 0 |
| $C_2H_4$ | 2.5 | 3 | 0 | 0 |
| $N_2$ | 1.5 | 3 | 3 | 3 |
| $H_2$/CO | 1.6 | 1.3 | 1.0 | 0.6 |
| LHV ($MJ/m^3$) | 14 | 12 | 10 | 11 |

### *5.1.2. Classifications of Biomass Gasifiers*

Biomass gasifier design is an important aspect in the efficient conversion of biomass to syngas. There are a number of research publications and good review articles on this subject [6,7,23].

Classifications of biomass gasifiers are complex, given that there are several criteria to consider. A relatively simple method of classification is based on three main factors: gasification agent, heat source, and gasifier pressure. Additionally, gasifiers can be classified according to reactor design as well.

1. *Classifications by gasification agent*:

a. Air-blown gasifiers

b. Oxygen gasifiers

c. Steam gasifiers

2. *Classification by heat source*:

a. Auto-thermal or direct gasifiers, where heat is provided by partial combustion of biomass.

b. Allo-thermal or indirect gasifiers, where heat is supplied by an external source via a heat exchanger or an indirect process. The fuels for this external heat source are normally the char and tar residues from the gasification process itself.

3. *Classification by gasifier operating pressure*:

a. Atmospheric

b. Pressurized

4. *Classification by reactor design*:

a. Fixed-bed gasifier

b. Fluidized-bed gasifier

c. Bubbling fluidized-bed (BFB) gasifier

d. Circulating fluidized-bed (CFB) gasifier

e. Allothermal dual fluidized-bed (DFB) gasifier

f. Entrained flow gasifier

### *5.1.3. Fixed-Bed Gasifier*

Fixed-bed gasifier has a bed of solid fuel particles through which the gasifying media and gas moves. This design can be divided into three groups depending on the gas flow direction as gas moving up (updraft), moving down (downdraft) or introduced from one side of the reactor and released from the other side on the same horizontal level (crossdraft). Fixed-bed gasifier is the simplest type of gasifier, typically consisting of a cylindrical space for fuel and gasifying media with a fuel-feeding unit, an ash-removal unit and a gas exit. The plan of an updraft fixed-bed gasifier is shown in Figure 2. In this gasifier design the fuel bed moves slowly down the reactor as the gasification take place, and air is fed from the bottom, whereas the syngas is removed from the top of the chamber.

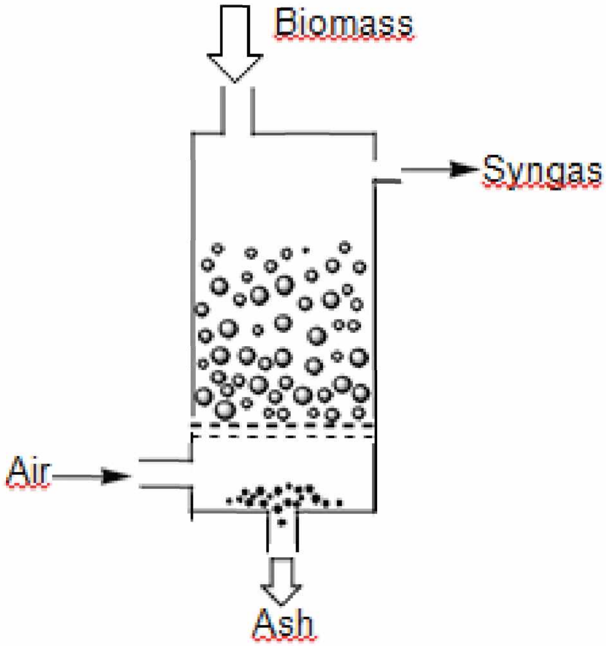

**Figure 2 Updraft fixed-bed gasifier design.**

In fixed-bed gasifiers, the char bed gasification zone where char is converted into syngas plays a major role in terms of efficiency and control of the process. Teixeira and coworkers have investigated the mechanical and thermochemical behavior of the char bed gasification zone and focused particularly on bed compaction when wood pellets are used as the biomass feed. In this study they found that pelletization has no effect on char bed compaction, final char conversion and syngas quality [8]. Generally, fixed-bed gasifiers are simple to construct and normally operate with high carbon conversion, long solid residence time, low gas velocity and low ash carry-over.

### *5.1.4. Fluidized-Bed Gasifier*

In this design the gasifying agent is blown through a bed of solid particles at a sufficient velocity to keep the particles in a state of suspension. Fuel particles are introduced at the bottom of the reactor and are very quickly mixed with the fluidized-bed material. The fuel is almost instantaneously heated up to the bed temperature by hot solid bed material. As a result of this treatment, the fuel is pyrolyzed very fast, resulting in a component mix with a relatively large amount of gaseous materials. In this type of reactor gasification and tar-con-version reactions occur in the gas phase. All fluidized-bed gasifiers use a bed material, which can be inert sand, the ash from the fuel or catalytic active-bed material like dolomite or olivine. Dolomite is Ca- and Mg-containing mineral rock material composed mainly of $CaMg(CO_3)_2$. Olivine is a mineral rock material mainly composed of magnesium iron silicate with the formula $(Mg,Fe)_2SiO_4$. The purpose of the bed material is to distribute and transport the heat in the gasifier to prevent local hot spots. The bed material facilitates the mixing of fuel with the gasification gas and promotes the gasification process. Since fluidized-bed gasifiers can handle a wide variety of biomass forms with limited pretreatment, this design is more suitable for large-scale biomass to syngas conversion processes.

Fluidized-bed gasifiers can be further divided into three main categories depending on the actual engineering design. The most common designs are: bubbling fluidized-bed (BFB), circulating fluidized-bed (CFB) and indirect or allo thermal dual fluidized-bed (DFB) types of designs. These designs are shown in Figure 3.

### *5.1.5. Bubbling Fluidized-Bed (BFB) Gasifier*

The bubbling fluidized-bed (BFB) gasifier is the simplest fluidized-bed gasifier, where biomass is normally fed in or above the fluidized bed. The bed material is fluidized by a gas (air or an oxygen steam mixture) entering the gasifier through nozzles distributed over the bottom of the reactor. Combustion of part of syngas and/ or the oxidation of char produced provide the energy required for heating the biomass and the endothermic gasification process. Gas velocity in this type of gasifier is typically around 1 m/s.

Bed material plays an important role in bubbling fluidized-bed and other fluidized-bed reactors, and sometimes catalytic materials like transition metal salts are added to the bed material to improve yields and product profile. These catalysts are added to the bed material to promote char gasification, water-gas-shift and steam reforming reactions, and reduce tar yield. There is a great interest in in-bed catalytic

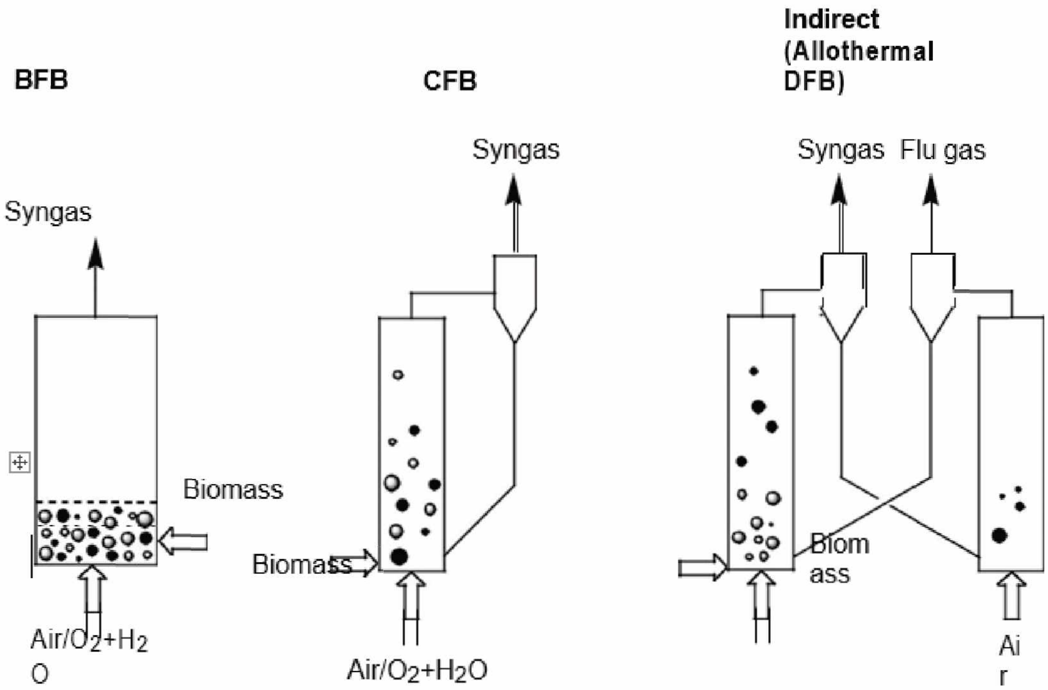

**Figure 3. A comparison of three fluidized-bed gasifiers: bubbling fluidized-bed (BFB), circulating fluidized-bed (CFB), and indirect or allothermal dual fluidized-bed types of gasifiers**

additives, as these catalysts can improve the quality of the syngas. Consequently, the use and need for more complex and expensive downstream cleaning methods can be simplified [9].

Natural minerals such as dolomite, limestone, olivine and iron ores, and synthetic minerals, Ni-supported olivine, Fe-supported oliv-ine, alkali metal-based material, and even char can be used as cata-lytic materials. Char in the reactor can act as a tar cracking material as well, however, as char itself gets converted during the process, an external continuous supply of char into the gasifier is required [9]. In addition to this, sorbents such as limestone can retain sulfur compounds like H2S and COS further simplifying downstream gas cleaning steps. Even though several in-bed catalysts have shown good results for improving the quality of the synthesis gas, some of them are quite expensive and a number of these catalysts leave contaminated residues behind. Additionally, there have been erosion problems and loss of catalytic activity. For example, Ni-based catalysts are quickly deactivated due to carbon deposition and sulfur poisoning [9]. Therefore, development of good quality and inexpensive catalytic bed materials remains a high priority research area.

In one study where bed materials impregnated with different catalysts have been compared, inert quartzite was used as a reference case, olivine, dolomite as natural catalysts, and nickel-alumina as the artificial catalyst [10]. In this experiment gasifications were carried out on a bubbling fluidized bed and it was found that artificial catalyst has the highest effectiveness in enhancing the hydrogen yield as well as in tar reduction. A stable activity of the nickel-alumina catalyst was observed for the whole duration of the reaction, suggesting that no deactivation phenomena occurred due to coke deposition or morphological modifications of the particles [10].

There are a number of important features in bubbling fluidized-bed (BFB) design, which include:

1. High fuel flexibility in terms of both size and type
2. Flexibility of operation at loads lower than design load
3. Ease of operation
4. Low feedstock inventory
5. Good temperature control and high reaction rates
6. Good gas–solid contact and mixing
7. In-bed catalytic processing possible
8. Production of syngas with moderate high heat value (HHV) but low tar levels and high particulates
9. Carbon loss with ash
10. High conversion efficiency
11. Suitable for large-scale capacities (up to 1MW or even higher).

### *5.1.6. Circulating Fluidized-Bed (CFB) Gasifier*

In the circulating fluidized-bed (CFB) gasifier, air/O2 and H2O mixture is entered from the bottom while the biomass is added from the side of the gasifier similar to BFB, but higher gas velocities are used in this reactor compared to the BFB reactor. At higher gas velocities, part of the bed material gets entrained with the fuel and gets circu-lated inside the reactor. Representative gas velocity in the circulating fluidized-bed gasifiers are between 3 and 10 m/s. The entrained bed material, which is not completely converted fuel particles or char, are removed from the synthesis gas produced by a cyclone-type separation device. These particles are normally returned back to the bottom of the gasifier as shown in the CFB reactor plan in Figure 3.

Some of the most important features in circulating fluidized-bed (CFB) design are:

1. High fuel flexibility in terms of both size and type
2. Flexibility of operation at loads lower than design load
3. Ease of operation
4. Low feedstock inventory
5. Good temperature control and high reaction rates
6. In-bed catalytic processing possible
7. Production of syngas with moderate tar levels but high particulates
8. High carbon conversion
9. Good gas–solid contact and mixing
10. Suitable for large-scale capacities (up to 1MW or even higher)
11. High conversion efficiency
12. Very good scale-up potential

### *5.1.7. Allothermal Dual Fluidized-Bed (DFB) Gasifier*

In the dual fluidized-bed (DFB) type design, gasification of the biomass and the combustion of the remaining char occur in two separate chambers as shown Figure 3. The biomass enters the first reactor, where it is gasified with steam at 700–900°C, and the synthesis gas produced in the first reactor exits the gasifier with char to a cyclone for gas cleaning. Next, the char separated is transported to the combustion reactor, where it is burnt with air to produce heat. This heat is transported from combustion reactor to gasifier by the circulating bed material. The heat required for heating the biomass and gasification comes from the combustion reactor. The fuel conversion in indirect gasifiers is higher than in CFB- or BFB-type gasifiers (direct gasifiers) because all the char is combusted. The remaining ash contains virtually no carbon, which benefits the overall efficiency of the process. There are two separate exits for syngas and flue gas. Consequently, dual fluidized-bed (DFB) type designs produce two gases; syngas with little or no nitrogen and a flue gas.

Circulating-type dual fluidized-bed gasifiers (DFB) with steam as the gasification agent have turned out to be a potential technology for large-scale biomass gasification. Steam can be easily produced and facilitate the enhancement of hydrogen content in the syngas [3]. There are a number of advantages in using the DFBG technology.

Some of the important features of DFB gasifiers are:

1. Many forms of biomass samples can be used directly or after minimum pretreatment
2. Easy feeding of biomass
3. Low temperature operation
4. Relatively complex construction and operation
5. Production of syngas with moderate heat value, and moderate tar levels
6. Good cleaning of gas required before use in engines
7. In-bed catalytic conversions possible
8. Good gas–solid contact and mixing
9. Relatively low efficiency
10. Suitable for high specific capacities (>1MW)
11. Good scale-up potential but relatively complex design

The dual fluidized-bed (DFB) type of gasifier is a popular design in biomass gasification. Some major dual fluidized-bed-type biomass gasifiers in the world and their locations are summarized in Table 2.

Modeling of biomass gasification processes by simulators such as Aspen Plus is a powerful tool to assess mass, energy balances, and to optimize process designs. A model for biomass gasification in dual fluidized-bed (DFB) reactors by coupling Aspen Plus and dedicated Fortran has been reported by Abdelouahed et al. [11]. In this study, DFB reactor was divided into three modules according to the main chemical phenomena: biomass pyrolysis, secondary reactions, and char combustion. The calculated compositions of permanent gases, tars, flow rates, and lower heating values were compared with experimental data for two DFB technologies, Tunzini Nessi Equipment Companies (TNEE) and Battelle High Throughput Gasification Process (FERCO). During these studies, Abdelouahed and coworkers found that the syngas composition and flow rate are very sensitive to the water-gas shift reaction (WGSR) kinetics [11].

### *5.1.8. Entrained-Flow Gasifier*

The entrained-flow gasifier is a downdraft type of direct gasifier, where the biomass feedstock, steam, and oxygen or air is introduced at the top of the gasifier.

**Table 2 Some major dual fluidized-bed (DFB) biomass gasifiers in the world [2].**

| **Name/location/ operation start** | **Capacity as fuel input (MWth)** | **Feedstock** | **Design (gasifier/ combustor)** | **Bed material** | **Temperature (gasifier/ combustor,°C)** | **Syngas composition** |
|---|---|---|---|---|---|---|
| Gussing FICFB/ Austrian Energy, TU Vienna 2001 | 8 | Biomass chips | BFB/CFB | Olivine | 900/1000 | CO: 20–30<br>$H_2$: 35–45<br>$CO_2$: 15–25<br>$CH_4$: 8–12<br>$N_2$: 3–5 |
| Chalmers (GoBiGas)/ Sweden 2008 | 2 | Wood pellets | BFB/CFB | Sand | 812/1000 | CO: 33.1<br>$H_2$: 25.1<br>$CO_2$: 14.8<br>$CH_4$: 11.8 $N_2$: 9.3 |
| Silva Gas, Vermont/USA 1998 | 90 | Wood pellets | BFB/CFB | Sand | 812/1000 | CO: 50<br>$H_2$: 15<br>$CO_2$:10<br>$CH_4$: 15<br>$N_2$: ? |
| Blue Tower Herten/ Germany 2001 | 15 | Wastes | BFB/CFB | Ceramic balls | 600/950 | CO: 20<br>$H_2$: 50<br>$CO_2$: 20<br>$CH_4$: 5<br>$N_2$: ? |

The basic design of this gasifier is shown in Figure 4. Within this gasifier, high temperature, pressure, extremely turbulent gas and fuel flow causes a rapid biomass to syngas conversion, achieving a high throughput. Relatively higher temperatures are involved in this type of reactor compared to other designs, and this may shorten the life of reactor system components. Also, it may be necessary to add fluxes or blend feedstock to achieve good slagging characteristics in entrained flow gasifiers.

The use of entrained flow gasifiers with biomass is a relatively new development, and there are reports on testing this type of reactor on wood, straw, and dried lignin [12]. Hernandez et al. have studied [13] the effect of the addition of steam to air as gasifying agent in biomass entrained flow gasification. The entrained flow gasifier can be seen as a promising technology due to its commercial availability, high efficiency and high potential for the production of biofuels and chemicals from biomass.

Several research groups have recently studied the performance of entrained flow gasifiers using different biomass forms such as wood powder [14], raw and torrefied bamboo [15], oil palm residue [16], and coir dust [17]. In one study Hernandez and coworkers used deal-coholized marc of grape as fuel in the entrained flow gasification.

In these experiments they found that a higher temperature increases the CO and $H_2$ content in the product gas for air gasification, whereas air-steam gasification leads to a boost in the $H_2$ production at higher temperatures, as well as an increase in the $CH_4$ content [18].

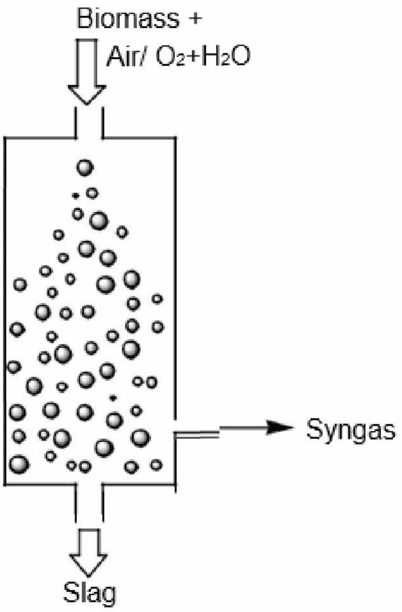

**Figure 4. Entrained flow gasifier design.**

Some important features of entrained flow design are:

1. High fuel flexibility in terms of both size and type
2. Flexibility of operation at loads lower than design load
3. Ease of operation
4. Low feedstock inventory
5. Good temperature control and high reaction rates
6. In-bed catalytic processing possible
7. Production of syngas with moderate tar levels but high particulates
8. High carbon conversion
9. Good gas–solid contact and mixing
10. Suitable for large-scale capacities (up to 1MW or even higher)
11. High conversion efficiency
12. Very good scale-up potential

### *5.1.9. Syngas Cleaning*

Crude syngas from the biomass gasifier contains impurities such as solid ash with metal oxides, carbonates, silicas, and tars; therefore it is necessary to clean the syngas before many applications, including the metal-catalyzed or microorganism-based biocatalyzed conversions to ethanol. Biomass syngas cleaning is an active research area and has been reviewed in recent literature [1,19]. The amount of impurities in the biomass-derived syngas totally depends on the factors like reactor design, operating conditions and type of biomass used in the reactor. However, it is interesting to see the maximum concentrations reported for different impurities before the purification, and Table 3 summarizes these maximum concentrations reported for common impurities.

The gas cleaning can basically be divided into two types: dry hot gas cleaning and wet gas cleaning. In addition to these, tar treatment can also be considered as a part of the syngas cleaning process.

**Table 3 Common biomass syngas impurities and their highest reported concentrations.**

| Gaseous impurity | Maximum concentration (mol%) | Reference |
|---|---|---|
| $CH_4$ | 15 | [20] |
| $C_2H_2$ | 0.69 | [21] |
| $C_2H_4$ | 5.3 | [22] |
| $C_2H_6$ | 0.8 | [20] |
| $C_6H_6$ | 0.3 | [20] |
| $C_{10}H_8$ | 0.3 | [20] |
| $NH_3$ & HCN | 0.28 | [20] |
| $H_2S$ & COS | $1.0x10^{-4}$ | [20] |
| $SO_2$ | 0.055 | [20] |
| $NO_X$ | 0.123 | [20] |

### *5.1.9.1. Hot Gas Cleaning*

Hot gas cleanup has been traditionally used in the removal of particulate matter and tar with the goal of minimizing maintenance of syngas combustion equipment. In this technique high temperature gas is cleaned directly at the neck of the gasifier. This is a highly efficient and reliable method. Many common gas cleaning technologies have been applied to hot gas particulate cleanup, most of which are based upon one or more of the following physical principles: inertial separation, barrier filtration, and electrostatic interaction. A summary of hot gas cleaning technologies that can be used in particulate removal in biomass-derived syngas is shown in Table 4.

### *5.1.9.2. Inertial Separation Using Cyclone*

A cyclone is a hot gas cleaning device used in all types of gasifiers [1]. The inertial separation devices like cyclones operate using mass and acceleration principles for separation of heavier solids from lighter gases. A cyclone can be operated at temperatures in excess of 1000°C, and is one of the oldest and most commonly employed devices for solids separation in syngas. They utilize cen-tripetal acceleration to reduce the long times otherwise required for small particles to settle by gravity. A basic design of a cyclone used in the syngas cleaning is shown in Figure 5 [1]. As shown, the gas stream enters a “double vortex” that first forces particulate outward and downward in an outer vortex. This outer swirling motion separates particulate matter from the vapors by inertial forces. The gas stream is then redirected into an inner and upward moving vortex before exiting the device through a “vortex finder.” Several approaches to cyclone design are based on the characteristics of particles and the gas stream [24]. In general, a “cut point” is technology, established where a certain size particle obtains a balance between centrifugal and drag forces. Even though cyclones are a mature technology, process advancements are still occurring in this field.

**Table 4 A summary of hot gas particulate removal technologies [1,23].**

| Device | Collection efficiency (%) | Pressure drop (kPa) | Flow capacity ($m^3 s^{-1} m^{-2}$) | Energy required |
|---|---|---|---|---|
| **Cyclones** | | | | |
| Conventional | Low (~ 90) | Moderate to high (7.5–27.5) | Very high | Low |
| Enhanced | (>90–95) | Moderate to high | Very high | Moderate to high |
| **Granular filters** | | | | |
| Fixed | Good (>99) | Moderate (6–10) | High (0.15–0.2) | High |
| Moving | - | Moderate | High | Moderate to high |
| **Rigid barrier filters** | | | | |
| Ceramic candle | Excellent (>99.5) | Moderate to high (5–25) | Moderate to high (0.03–0.07) | Moderate |
| Cross-flow | - | Low to moderate (2.5-7.5) | Moderate to high (0.03–0.07) | Low to Moderate |
| Ceramic tube | - | Moderate (8–12.5) | Moderate to high (0.03–0.05) | Moderate |
| Metallic | - | Moderate to high | Moderate to high | Moderate |
| Electrostatic precipitators | - | Very low (0.3–0.6) | Low to moderate (0.01–0.03) | Moderate to high |

There are some new designs in cyclones, and one new design operates as a reverse flow gas cyclone using partial recirculation, and it has shown a separation efficiency that is superior to the classical Stairmand high efficiency (HE) designs [24]. Simple design and lack of moving parts are important features in cyclones. Cyclones can be operated at high temperature, which is typically limited only by mechanical strength and stability of the construction materials. They are often operated hot to prevent condensation of water, tar, and other contaminants that might otherwise foul or corrode the cyclone. With their robust nature and efficient removal of particulate matter larger than 5 mm, cyclones are typically the first cleanup device applied to a gas stream. However, many processes require more stringent particulate matter removal down from sizes below 1 mm. Therefore, gas cleaned in the cyclone is typically sent to a filtration-type gas cleaning system. These second-stage cleanup systems can remove much smaller particles in the gas stream [1].

### *5.1.9.3. Gas Cleaning Filters*

Filters are one of the most common methods for removing particu-late matter and are effective for a very wide range of particle sizes. Barrier filtration occurs when a gas stream passes around fibers or granules or through a porous monolithic solid [1].

Particulate matter is removed during filtration by a combination of four different mechanisms:

1. Diffusion
2. Inertial impaction
3. Direct interception

4. Gravitational settling

There are different types of filtration devices that can be used in biomass syngas cleaning. These include: fabric filters, rigid filters, and both fixed- and moving-bed granular filters.

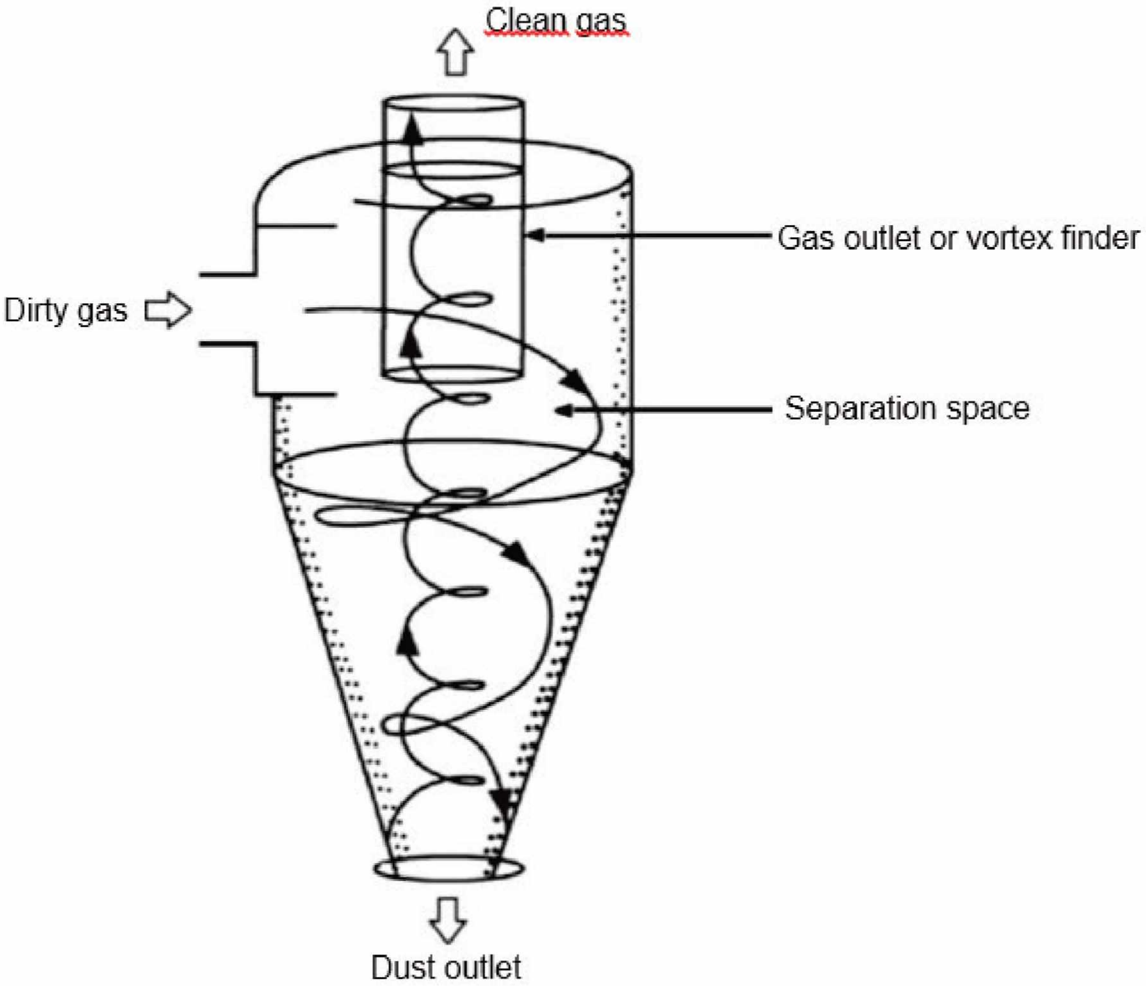

**Figure 5 Cyclone used in biomass syngas cleaning.**

Fabric filters are effective in removing particulate matter even smaller than 1 mm to concentrations less than 1 mg/m3. However, the operation temperature of the fabric filters are generally limited to around 250°C, which classifies them as a warm gas cleanup method [25]. Filters made from ceramics and metals can stand much higher temperatures, and these are also known as rigid filters. They have advanced in recent years to the extent that they can remove 99.99% of particulate matter smaller than 100 mm while operating at temperatures beyond 400°C [26]. Candle filters are another type of high temperature gas cleaning devices. These filters are prepared in the form of hollow tubes, and are primarily composed of porous ceramic materials. In this technique, dirty gas passes through the outside of a long, closed-end tube (or cone), depositing the particles on the surface before exiting through the top of the tube. The resulting accumulation of particulate matter, known as filter cake, is periodically removed with a reversed pulse of gas, typically nitrogen. Several candle elements are placed in parallel to form an array so that several filters are always operating while others are being cleaned. Candle filters are commonly constructed of clay-bonded silicon carbide (SiC) as well as materials such as monolithic and composite ceramics [27,28].

### *5.1.9.4. Electrostatic Separations*

Electrostatic separation is another syngas cleaning method, and is particularly useful in removing very fine particulate matter. In this technique, particles become charged by a strong electric field and are removed due to their difference in dielectric properties com-pared with the gas molecules [1]. Electrostatic forces acting on fine particulate matter (less than 30 mm) can be more than 100 times stronger than the force of gravity, making electrostatic precipitators (ESPs) very effective in removing particulate matter from gas streams. Two configurations are commonly employed in the design of electrostatic separators: a tube-type precipitator and a parallel-plate precipitator [1]. Although simple in concept, performance depends on several factors including geometry of the device, applied voltage, electrical resistivity of gas and particles, and size and shape of particles.

### *5.1.9.5. Cold Wet Gas Cleaning or Conventional Gas Cleaning*

Cold gas cleaning (CGC), or conventional gas cleaning, is another common technique used in the purification of biomass-derived syngas. In this method gas is washed by exposure to a solvent or a liquid adsorbent. The operating temperature in cold gas cleaning may be as high as the condensation point of the water used for tar and particulate scrubbing, or as low as −62°C for chilled methanol used in removing acid gases. Particulate matter is typically removed at ambient temperatures using water as a “wet scrubbing” agent. Wet scrubbing is widely deployed in industry given its relative simplicity and effectiveness. Cold gas scrubbing can be characterized according to operating principles: spray scrubbers, wet dynamic scrubbers, cyclonic spray scrubbers, impactor scrubbers, venturi scrubbers, and electrostatic scrubbers [1].

Wet gas cleaning can be used for removal of particulate matter, tars, acid gases like HCl and other trace organic and inorganic components. Conventional acid gas removal processes can be carried out with techniques such as the Rectisol process. In the Rectisol process (licensed by both Linde AG and Lurgi AG), cold methanol at −40°C is used to absorb the acid gases from the feed gas at rela-tively high pressure, usually 2.7 to 7.0 MPa. Another widely used scrubber is the solvent identified in the trade name Selexol, and the use of this solvent is known as the Selexol process. In the Selexol process (now licensed by UOP LLC), the Selexol solvent absorbs the acidic gases such as carbon dioxide and hydrogen sulfide from the feed gas at relatively high pressure, usually 2 to 14 MPa. The pressure in the rich solvent containing the acid gases is then reduced or steam stripped to release the acid gases from the solvent. This process can operate selectively to recover $H_2S$ and $CO_2$ as separate streams so that the $H_2S$ can be sent to separate reactors for conversion to elemental sulfur or sulfuric acid [1].

Scrubbers that undergo chemical transformations with impurities in biomass-derived syngas are known as chemical scrubbers. Alkanol amine has been used to remove acidic gases such as HCl, $H_2S$, and $CO_2$. One such solvent is aliphatic amine methyldiethanol-amine (MDEA). For example, HCl in the gas stream can be removed by reacting with MDEA as shown in the equation in Figure 6, which separates as the ammonium salt. Chemical scrubber solvents are favorable at low acid-gas partial pressures, whereas physical solvents are typically used at high acid-gas partial pressures.

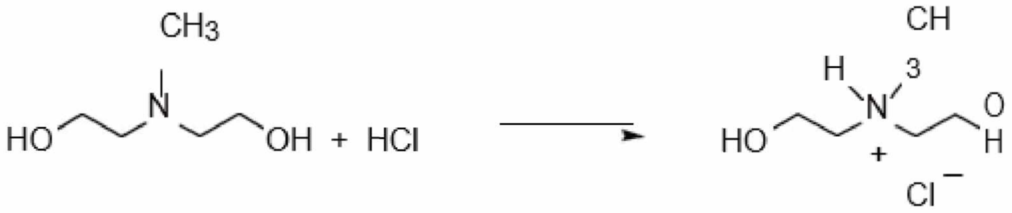

**Figure 6 Methyldiethanolamine (MDEA) as a chemical scrubber for removal of HCl in biomass-derived syngas.**

### *5.1.10. Tar Control and Treatment Methods*

Tar formation is a side reaction in biomass gasification. When the gas cools, tar condensation can foul filters and can make deposits in pipes, making tar control a high priority in biomass gasification. In fluidized-bed gasifiers the tar concentration in biomass-derived syngas is typically in the order of 10 g/m3. In these gasifiers, fouling is not a significant problem as long as all the tar is present in the gas phase. Additionally, tar content in the syngas can be controlled by means of tar prevention and treatments inside the gasifier. The primary measures for reduction and elimination of tar in biomass gasification processes are discussed in two review articles by Devi et al. [9] and Han et al. [29].

A number of techniques are known to reduce tar concentration in the syngas produced. Some common techniques are: optimization of the gasifier design, optimization of the operation conditions, addition of catalytic bed materials, and controlling the biomass properties. The use of catalyst promoters in the bed material is also a popular method for controlling the tar content in syngas. Metallic elements such as Ni or Co and their metal oxide are added as promoters to the typical bed catalyst materials dolomite, limestone, olivine sand, bauxite, natural alumina, clay minerals and iron ore. Internal reforming of tars by inclusion of a catalytic hot gas filter in the freeboard of the gasifier and at the gasifier outlet is a smart technology for tar reduction. Monolith reactors or ceramic blocks containing a honeycomb structure with a thin layer of catalytically active material on the channel walls such as a Ni-based coating, have also been used in the internal reforming of tars [2].

### Conclusion

The conventional of biomass into syngas by gasification processes is another route in the bioethanol production. Using of this technology depend from final price of production and, of course, its influence on the price of bioethanol.