

Chapter 8

Pre-combustion Air Emission Control

Air emission control is enforced when the ambient air quality or the source air emission rate does not meet certain standards. There are three basic approaches to air emission control: pre-, in-, and post- combustion air emission control. The most cost-effective is to control before combustion, which reduces the load of downstream units. The last choice is add-on devices for flue gas cleaning. These *extra* devices contribute significantly to the capital and operating costs of the plant; they also reduce to some degree the thermal efficiency, because the devices may also reduce some of the power output of the plant. Many of these devices also produce another form of waste, usually solid or liquid being discharged to the environment.

This chapter is focused on the following pre-combustion air emission control technologies.

- Fuel cleaning,
- Fuel substitution,
- Fuel conversion, and
- Alternative energy resources.

8.1 Fuel Cleaning

8.1.1 Coal Cleaning

One of the most cost-effective approaches to the control of air emissions is the removal of the unwanted chemicals from the fuels before combustion.

Two most common engineering practice examples are coal washing, and oil and gas refinery. In the United States, about 50 % of all coals supplied to power plants are washed before delivery. In Germany, almost all coals are washed before firing. The oils and gases are refined globally following the specific government regulations. Fuel cleaning is the most effective way to reduce the contents of sulfur, ash-forming

compounds, and trace elements. Basic principles of coal cleaning and related technologies have been well documented (e.g., [27]), and they are briefly introduced as follows.

Coal cleaning methods may be classified into conventional physical cleaning and advanced cleaning methods. Advanced cleaning methods include advanced physical cleaning, aqueous phase pretreatment, selective agglomeration, and organic phase pretreatment. Of these alternatives, conventional physical cleaning is widely used for the sake of low cost and relatively high efficiency.

Conventional coal cleaning involves the following steps:

- (1) **Crushing of the coal:** Grinding into smaller particles with diameters less than 50 mm. It also liberates ash-forming minerals and inorganically bound sulfur.
- (2) **Particle screening:** The crushed coal particles are screened into three modes; coarse, intermediate, and fine.
- (3) **Flotation:** It involves the separation of ash and sulfur compounds from the coal before it is pulverized and introduced into combustion chamber. The lighter coal particles float on top while the heavier minerals sink to the bottom in a stream of water.
- (4) **Drying:** In this step wet coal particles are dried using a dewatering device, generally a vacuum filter, centrifuge, or a cyclone, to separate water from the solid, followed by further drying in hot air.

Coal washing can remove about 60 % of ash-forming materials. It is often necessary to reduce the excessive amount of ash-forming materials from the coal especially for steel processing applications. For example, the lignite from India and Greece may contain more than 50 % wt ash-forming material. A significant amount of Pyrite (FeS_x), As, Se, and Hg can be removed by coal pre-cleaning.

Coal washing alone can remove up to 50 % of the pyretic sulfur, which is equivalent to 10–25 % removal of the total sulfur content of the coal. Ninety percent of the inorganic fuel sulfur, especially pyritic sulfur, FeS_2 , can be easily removed by coal washing. The organically bound sulfur cannot be removed by physical cleaning methods; however, it can be removed with biological or chemical methods.

Biological treatment can remove both inorganic and organic sulfur. For example, a bacteria, *Thiobacillus ferrooxidans* is capable of converting FeS_2 into water-soluble FeSO_4 , whereas a mutant of *Pseudomonas*, called Coal bug 1 (CB₁) can consume organic sulphur in thiophene groups. However, these techniques are time-consuming and may require very small coal particles.

Chemical methods can remove organically bound sulfur and involves treatment with alkaline or caustic solutions, oxidative leaching, and chlorinolysis with chlorine-based chemicals. However, these chemical methods may change the property of the coal and reduce its potential for use as a fuel.

Like any other process, there are pros and cons for physical coal cleaning. The advantages are as follows

- Reduced SO₂ formation in the flue gas:
The reduction could be 10–40 % lower than burning coals without pre-cleaning.
- Decrease of ash content:
This allows the cleaned coal to be used for pulverizer and boiler. It also reduces the load of downstream particle separators such as ESPs and bag houses.
- Lower maintenance costs for boilers:
The reduction of ash content leads to less wear and tear on coal preparation before combustion and on boiler during combustion.
- Smooth operation:
Less operational problems such as boiler slagging and fouling.

Meanwhile, one has to bear in mind the disadvantages of coal washing. Intensive energy is required for coal grinding and drying. And moisture added to the coal may reduce the efficiency of the boiler and the entire plant. There may be 2–15 % of energy loss to the preheating of coal.

In addition to these technical issues, one should also consider the environmental regulations and the price of cleaned coal. In some countries, the price of coal is the same regardless of its cleanness. In addition, the waste liquid stream from coal cleaning may contain acidic toxic metals, which pose an extra challenge and cost in waste treatment or disposal. More and more stringent regulations have been introduced in the United States and China, for example, to prevent dumping of these toxic acidic streams into the environment without prior treatment.

8.1.2 Oil and Gas Refinery

Crude oil and raw natural gas contain tens of thousands of kinds of hydrocarbon compounds. By refinery, crude oil is decomposed into various fractions and transformed into fuels including oil and gas and other products.

The oil and gas after refinery process contains specified amount of sulfur, nitrogen, and ash contents. For example, sulfur compounds in the crude oil or raw natural gas can poison many of the catalysts used for the treatment of hydrocarbons in the petrochemical industry. More and more stringent environmental regulations also require reduced sulfur compounds in the final petroleum products. The average sulfur content in Canadian diesel was 350 ppm in 2000, and ultra-low sulfur diesel with 15 ppm sulfur became mandatory in North America for highway vehicles in 2006. In 2009, all EU vehicles will run on 10 ppm sulfur diesel including off-roads.

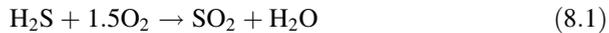
Due to stringent regulation on sulfur content in fuels, a large amount of sulfur compound is produced as a byproduct of oil refinery. The elemental sulfur is often an important byproduct of oil refining and it is also a major raw material for the productions of fertilizer and sulfuric acid.

Sulfur compounds are first separated from the refinery stream by absorption using amine followed by another separation process to recover the amine and to

concentration the H₂S gas stream. The concentrated H₂S streams usually contain >50–60 % of H₂S. H₂S smells like rotten eggs; it is corrosive and toxic. H₂S loaded gas streams must be further treated [5].

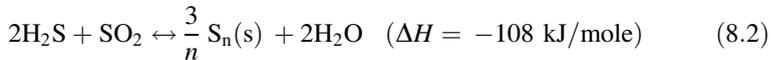
8.1.2.1 Claus Process

One of the common practices is to convert H₂S to nontoxic and elemental sulfur by the Claus process, which was first developed by London chemist Carl Friedrich Claus in 1883. A Claus process converts H₂S into elemental sulfur by two steps, thermal step and catalytic step [1, 8, 33, 43]. In the thermal step 1/3 of the H₂S is oxidized into SO₂ and water by the oxygen in the air.



The resultant gas steam contains H₂S and SO₂ in a 2:1 mol ratio. This step requires a high-reaction temperature of 1,000–1,400 °C.

In the following catalytic step, SO₂ reacts with the remaining H₂S in presence of a catalyst to form elemental sulfur. With the catalysts, the reactions in the catalytic step proceed at a much lower temperature of 200–350 °C.



where typical value of n is 8. Following Eq. (3.27), the equilibrium constant of Eq. (8.2) can be described as

$$K_P = \frac{y_{\text{H}_2\text{O}}^2 y_{\text{S}_8}^{3/8}}{y_{\text{H}_2\text{S}}^2 y_{\text{SO}_2}} P^{\frac{5}{8}} \quad (8.3)$$

The reaction described in Eq. (8.2) is exothermic and equilibrium-limited reaction that calls for low temperatures. However, low temperatures will result in low elemental sulfur yield rate. That is why a catalyst is necessary. Typical catalysts for Claus processes are activated alumina, activated bauxite, or cobalt molybdenum hydrogenation catalyst [33, 43]. In addition, a multistage process with interstage timely removal of elemental sulfur by cooling and sulfur condensation further improves the conversion rate.

By two- or three-stage processes the H₂S conversion efficiencies could reach about 95 or 97 %, respectively.

Alternatively, with the super-Claus process and special catalysts, efficiencies of >99 % can be achieved because it prevents the formation of SO₂. However, a separate hydrogenation reactor has to be employed between the second and third stage. Oxygen enrichment of the air to the burner in the final Claus stage also reduces soot formation and poisoning of the catalysts.

8.1.2.2 Adsorptive Claus Process

Recently, increasing restrictive low-sulfur fuel regulations challenge the conventional Claus process. Depletion of low-sulfur feedstocks for the petroleum industry demands more improved or new technologies to maximize the H₂S conversion. Elsner et al. [13] proposed an improved process called adsorptive Claus process based on the Le Chatelier's principle [47], which implicates that the removal of a reaction product results in an equilibrium displacement to higher conversion.

Unlike the conventional Claus process, where elemental sulfur is removed by in situ condensation, the adsorptive Claus process removes water by selective adsorption. According to the reaction equilibrium constant described in Eq. (8.3), removal of water vapor would have a greater impact on the conversion rate than sulfur removal, because there are 2 mol of water per 3/8 mol of sulfur in the product.

As introduced in Chap. 5, there are several water vapor adsorbents, and one of them is zeolite which can be regenerated by inert sweep gas. A challenge to this process is the chemical resistance of the catalyst and the zeolite to the aggressive gas system, where SO₂ and water may react and produce sulfuric acids.

8.1.2.3 Natural Gas Sweetening

Natural gas sweetening is important to both environment and final product quality. Natural gas contains a large amount of methane (CH₄), and all kinds of impurities as shown in Table 8.1. The mole amount of a substance in a raw natural gas depends highly on the gas field.

In industry, sour gas is referred to high contents of H₂S and CO₂. These acidic gases in the raw natural gas are removed at the gas well to reduce technological challenges to downstream gas transportation in the pipeline, and equally important, to reduce SO_x and CO₂ emissions.

First of all, it prevents the formation of gas hydrate (commonly called dry ice). CO₂ hydrate can clog the system during the liquefaction of the natural gas. Furthermore, it reduces the corrosion resulted from H₂S and CO₂ in the presence of

Table 8.1 Typical composition of raw natural gas out of the well

Gases	Mole ratio
CH ₄	70–95 %
H ₂ S	0–15 %
C2+	0–15 %
CO ₂	0.1–8 %
N ₂	0–0.2 %
Temperature	30–40 °C
Pressure	5–120 atm

Source Ramdin et al. [40]

water and the toxicity of H_2S . Removal of CO_2 also improves the heating value of the natural gas because CO_2 is not combustible and it simply lowers the combustion efficiency.

The great partial pressure of H_2S and CO_2 allows them to be removed by physical adsorption and membrane separation from the natural gas outside of the well. Physical solvents like Rectisol, Purisol, and Selexol are preferred over chemical solvents for high pressure gas purification processes. However, the most popular technology is amine-based absorption. The separated H_2S can be converted into elemental sulfur as explained above. The treatment of separated CO_2 will be elaborated in Sect. 12.6.

8.2 Fuel Substitution

As introduced previously the air emissions are dependent on the fuels. Relatively speaking, natural gas is cleaner than gasoline, and coal is the dirtiest fossil fuel. Solid fossil fuels, biomass, and waste-derived fuels generate a wide spectrum of air pollutants in addition to solid waste. From this point of view gaseous or liquid fuels are considered cleaner because they hardly contain ash-forming elements, which make them suitable for application in internal combustion engines and gas turbines. As a result, the emissions per unit heat or power generated by liquid/gaseous fuels are less than solid fuels.

It is technically feasible to use fuel substitution such as co-combustion of oil and coal, in order to reduce the air emissions. In reality, other factors, likely economical consideration, also contribute to the final decision of which fuel is used for certain process. So far, coal is still the cheapest and most polluted fuel in environment. In the United States, coal is mainly used as an electric utility fuel. Although oil is more expensive than coal to recover, it can be easily transported by pipelines. Like oil, natural gas is more expensive to recover from wells, but contrary to oil, it cannot be easily stored or shipped. Nonetheless natural gas is widely used because of its ease, efficiency, and cleanliness of combustion.

It is obvious that replacing a high-sulfur fuel with a low-sulfur fuel will reduce the amount of SO_x in the flue gas. Replacing solid fuel with oil or gas can also reduce the ash formation. In some regions, local authorities may enforce fuel substitutions to reduce the local air pollution. For example, low-sulfur coals must be burned in the plants within the capital of China.

The success of fuel substitution depends on the fuel-flexibility of the burner and the economics of operation with another fuel. It is relatively easy to retrofit a coal-fired boiler with natural gas; however, it may not be the same using oil. Furthermore, we have to consider the operation of downstream air cleaning units. For example, sulfur content in the fuel affects the dust separation performance of an electrostatic precipitator (ESP). In-depth analysis will be introduced Chap. 10 for post-combustion air emission control approaches.

Replacing gasoline with natural gas or propane can reduce the emissions of VOCs. This replacement is not limited to stationary combustion sources, and some engines can be powered by compressed natural gas or propane. Extensive research and development being conducted in the petroleum industry to improve the combustion properties, handling, and use of natural gas as a substitute of gasoline to dominate the auto fuel market, although it is still not the case yet.

Biodiesel, which will be introduced shortly as one type of alternative fuels, is being used as a substitute for petroleum diesel fuels for diesel engines. Intensive experimental and computational studies on biodiesel have been carried out in the past decades. B20, a mixture of 20 % of biodiesel and 80 % of petroleum diesel, is now widely adapted by the US government for transportation industry. It is characterized by near-zero emissions of sulfur and net-nitrogen. But there is controversy data in the literature about the emissions of particulate matter.

8.3 Thermochemical Conversion of Fuels

Solid fuels such as coal or biomass may be converted to liquid or gaseous fuels by a thermochemical conversion (TCC) process. A TCC process is a chemical reforming process in which the depolymerization and reforming reactions of organic matter take place. There are many TCC processes that convert a wide variety of feedstock into different fuels through different types of reactions. They can be small or large in scale. Overall, TCC processes can be divided into three categories.

- Pyrolysis
- Gasification, and
- Liquefaction

8.3.1 *Pyrolysis*

Pyrolysis is a process where organic matter is degraded by thermal reactions in the absence of added oxidizing agents. Pyrolysis, being as old as civilization, was widely employed in the seventeenth and eighteenth centuries for conversion of charcoal to fuels for the smelting industry.

With wood as a feedstock, pyrolysis is also referred to as carbonization or destructive distillation. Pyrolysis decomposes a fuel with larger molecules into smaller fractions such as C_2H_6 , CO, CO_2 , H_2 , H_2O , oily liquids, and a solid carbonaceous char residue. The actual products depend on the TCC process. The mixture of gases, liquids, and solids require further separation in order to produce the final fuel products. The principles introduced in Chaps. 5 and 6 sets the foundation of the engineering designs of the related equipment and processes.

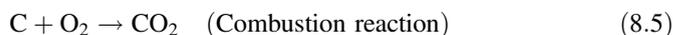
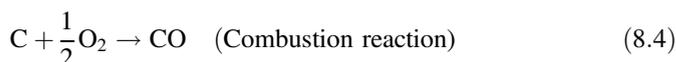
For conventional pyrolysis, where the heating rate is below 10 °C/s and the residence time is long, the primary products are tar and char. In order to maximize the production of oil, flash pyrolysis with rapid heating of about 100–10,000 °C/sec is employed. External heating is also applied for the process to allow pyrolysis in the absence of combustion. The char and tar can be burned with air for heating.

8.3.2 Gasification and Syngas Cleaning

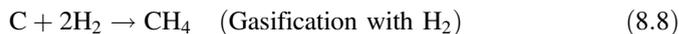
8.3.2.1 Gasification Chemistry

Gasification is a thermal chemical conversion process in which carbonaceous materials are converted to gases by incomplete oxidation. Gasification is actually fuel rich combustion operating at 25–40 % of the oxygen that would be needed to convert the hydrocarbon fraction of the fuel to CO₂ and H₂O. In this process part of the fuel is combusted to provide the heat needed to gasify the rest.

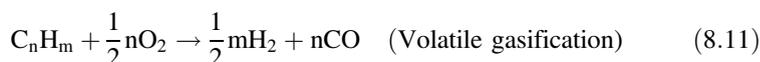
Major reactions involved in the gasification process are as follows [36].

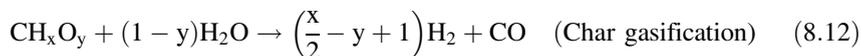


Steam is produced by oxidation of hydrogen atoms in the fuel. There are also other minor chemical reactions including gasification with hydrogen, water gas shift reaction, and methanation.



A more complicated way to present the gasification of solid or liquid feedstock involves devolatilization to produce volatile hydrocarbons and chars. Then both the chars and volatile hydrocarbon are further gasified to produce syngas and other compounds.





If we consider the formula of char containing C, H, O, N, S, and mineral matters, the chemical reactions are much more complicated. With the presence of steam, the sulfur content usually is converted into H_2S . Part of the H_2S can react with CO_2 to produce COS.



The primary gasification products are synthesis gas also known as syngas, which is composed of CO , H_2 , CH_4 , and many others. This syngas has to be cleaned before H_2 , CH_4 , and/or CO can be separated as clean fuels.

8.3.2.2 Gasifiers

A gasifier is the main chamber where all the main gasification chemical reactions take place. Various types of gasifiers have been developed over the last centuries. Conventional gasifiers (Fig. 8.1) include

- fixed bed gasifiers,
- fluidized bed gasifiers, and
- entrained flow gasifiers.

These gasifiers are widely used in integrated gasification and combined cycle (IGCC) plants. Most of the coal is gasified in fixed bed gasifiers [36, 42]. Updraft and downdraft moving bed gasifiers are suitable for smaller scale gasification, where fluidized bed gasifiers are often used for solid feedstocks other than coal. The entrained bed gasifiers are most suitable for coal. All these gasifiers have been well commercialized by different companies. Each has its features aiming at different applications. They are only briefly introduced as follows in order to focus on the main scope of this book.

In entrained bed gasifiers, feedstock particles concurrently react with oxidants in suspended (i.e., entrained) fluid flow mode. Entrained bed gasifiers require pulverized feedstocks. The sizes of solid fuel particles have to be less than 1 mm for effective suspension. The gasification temperature may exceed 1,500 °C and the residence time is in the order of 1 s only. The units are usually operated at high pressure (2.94–3.43 MPa). With this high gasification temperature, the syngas stream is almost free of tars, oils, and phenols. On the other hand, the corresponding raw syngas exiting the gasifier usually requires significant cooling before it can be handled by the downstream gas cleaning units. Such a high temperature also requires expensive burners and sophisticated high-temperature heat exchangers to cool the syngas.

In a fixed bed gasifier, preheated feedstock is fed from the top of the gasifier. The feedstock falls through different zones before it reaches the grates. From top to

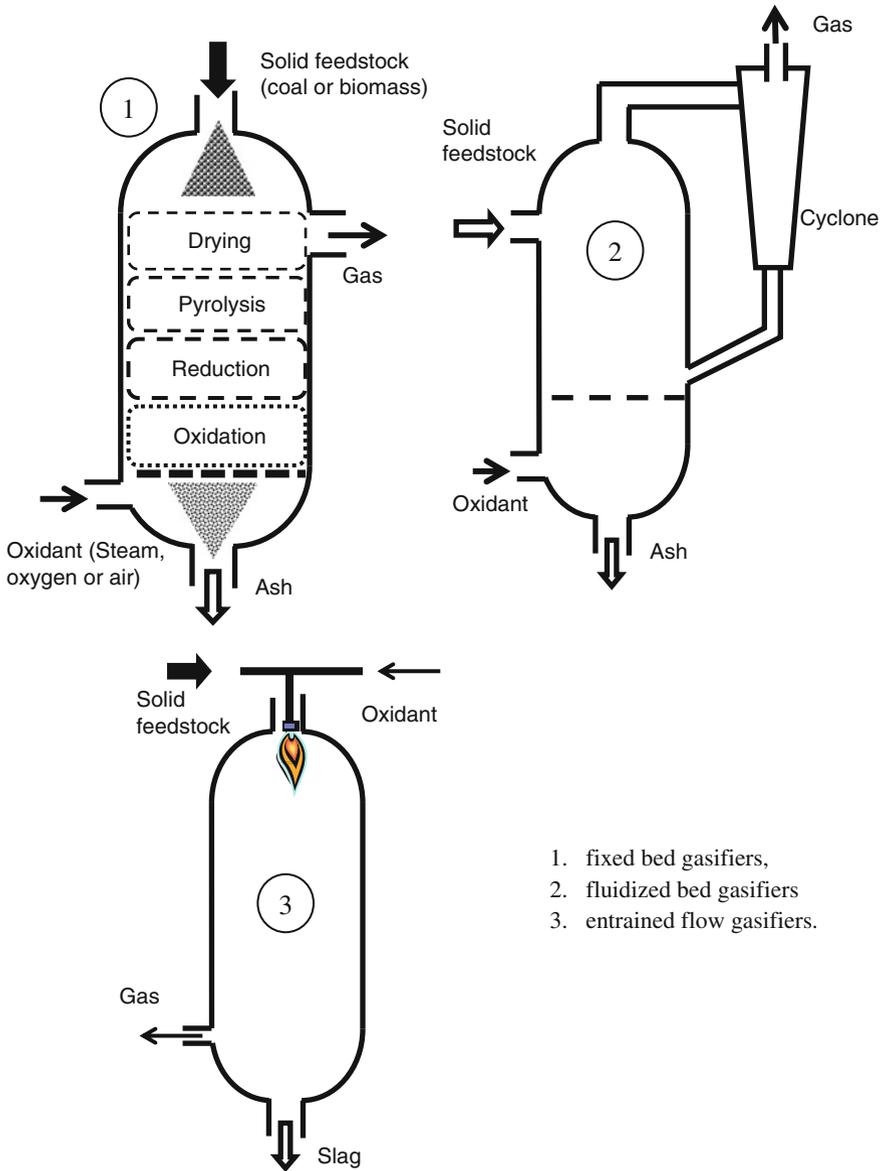


Fig. 8.1 Different gasifiers

bottom, the feedstock is preheated, dried, devolatilized/pyrolysed, gasified, and combusted. Maximum temperature in the combustion zone can be as high as 1,800 °C, mostly greater than 1,300 °C, depending on the reactor design. Post-combustion ash leaves at the bottom and the syngas exits at the top to the syngas

cleaning units. The temperature of the syngas leaving the top is about 400–500 °C. The feedstock particle size is normally in the order of tens millimeters and the residence time is about 15–30 min.

In a fluidized bed gasifier, both the feedstock and the oxidants can enter from the bottom of the gasifier. And they travel upward together. As a result of effective mixing, the temperature within the air-based gasifier is relatively uniform and it is in the range of 900–1,050 °C to minimize ash melting. In order to maintain the fluidity of the particles, the feedstock particles are smaller than those in a fixed bed gasifier. It is in the range of 0.5–5 mm. And the residence time of feedstock in the gasifier is typically 10–100 s, which is much shorter than a fixed bed gasifier [19]. Right at the exit of a fluidized bed gasifier, an optional cyclone is usually used to recycle the large unspent feedstock. Large particles will be recycled for further gasification. Smaller ones penetrating through the cyclone become the particulate matter in the syngas stream. As we learned in Sect. 6.4, a cyclone is effective in separating particles of a few micrometers. Therefore, particulate matter in the syngas stream is primarily in the micron range or smaller. Most of these particles can be separated using electrostatic precipitators or filters.

8.3.2.3 Syngas Cleaning and Separation

Raw syngas compounds depend on the feedstock and the gasifier. Among various carbonaceous feedstocks, coal, petroleum coke, and petroleum residues have been used for gasification. Recently, biomass has been tested too as a feedstock.

A sample raw syngas compounds produced from coal, pet coke, and petroleum residues are listed in Table 8.2. Most raw syngases contain considerable amount of CO, H₂, CO₂, H₂S and COS, and particulate matter. CO₂, H₂S and COS are also collectively called acidic gases because they can be converted easily into acids with moisture. CO₂ is also considered as a greenhouse gas.

Table 8.2 Pre-combustion syngas after water gas shift reaction

Gas	Mole fraction (%)
H ₂	55.5
CO ₂	37.7
N ₂	3.9
CO	1.7
H ₂ O	0.14
H ₂ S	0.4
Others	0.66

Source Ramdin et al. [40]

The exact syngas properties depend on the type feedstock, gasifier, operating pressure, temperature, and residence time. In general, higher temperature leads to greater carbon conversion. However, overheated feedstock may result in ash fusion and/or ash agglomeration [52]. Most of the commercial gasifiers operate at elevated pressures (~ 2.94 MPa) [18] for the equilibrium consideration. However, the pressure does not alter the syngas composition very much.

Particulate removal

Particulate cleaning of the hot syngas is necessary not only to reduce air emissions, but also to prevent corrosion and erosion of downstream gas separation components. For all gasifiers, char materials along with ash can be removed by water spray (quenching) followed by carbon scrubber. Around 95 % of the char carbon can be removed by direct water spray. The residual carbon is handled in the following wet scrubbers. Because of the cooling of the syngas, the thermal efficiency is greatly reduced in the entire process if the syngas will be used immediately, like in an IGCC process.

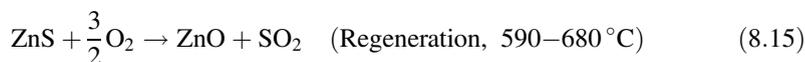
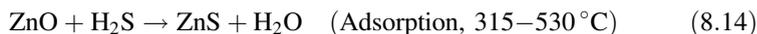
An alternative approach is hot gas filtration. Particulate filtration at temperatures above 260 °C is called hot gas filtration; sometimes it can reach 900 °C [23]. This high temperature demands special filtration materials that can endure the high temperature as well as the acidic gases in the raw syngas. The filter housing is also expected to be stable against temperature, pressure, and chemical composition of gas and dust.

Common materials in hot gas filtration are ceramic and metallic. These materials allow rigid self-supporting filter elements that can be employed at high temperatures due to their high mechanical strength. The filters can be shaped like candles, as long as a few meters, or honeycomb structure. High costs and system failure due to filter clogging are the main challenges to hot gas filtration.

8.3.2.4 Acidic Gas Removal and Sulfur Recovery

Gas separation follows particulate removal. Engineering designs are based on the principles introduced in Chap. 5, most commonly by adsorption or absorption. There are many options for CO_2 separation from the syngas too. CO_2 capture and storage will be introduced in detail in Chap. 12.

H_2S separation can be achieved by both absorption and adsorption. Physical or chemical adsorption followed by conventional Claus sulfur recovery units has been proven successful in petroleum industry. ZnO/CuO , Cr_2O_3 , and Al_2O_3 can adsorb H_2S components. The simplified adsorption and adsorbent regeneration reactions are as follows, using ZnO as an example [48].



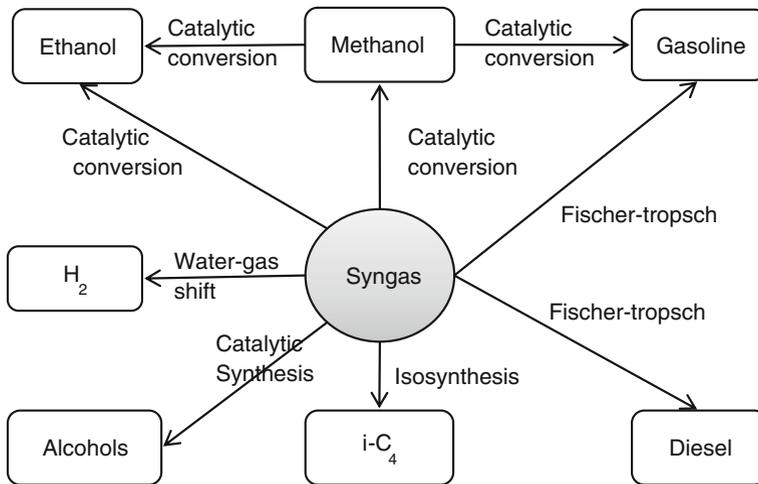


Fig. 8.2 Syngas to fuels

Purified syngas ($\text{H}_2 + \text{CO}$) is a great building block for energy industry. It can be directly burned for power generation through gas turbines. This is so-called combine cycle technology, which will be introduced in next section. Pure hydrogen produced from syngas can be used in hydrogen-based fuel cells. In addition, syngas can be converted into many other products. Some of these conversions pathways are shown in Fig. 8.2. The most well known is syngas to diesel/gasoline through Fisher-Tropsch process.



8.3.3 Combined Cycle Technologies

Since the 1970s, combined cycle technologies have been developed for gaseous fuels based on gas turbine technology. The fuel gas, which is either natural gas or a syngas from gasification, is burned in a gas turbine and the exhaust is used for a steam cycle. The thermal efficiency of a natural gas fired combined cycles (NGCC) can be in the order of 60 %. In coal-fired integrated gasification combined cycle (IGCC), the thermal efficiency could reach 46 %. The main advantage of combined cycle is that the exhaust is “cleaner” since gaseous fuels are used and less oxygen is used than conventional combustion. Liquid and gaseous fuels do not or hardly contain ash-forming elements. As a result, air emissions per unit heat or power generated are smaller for liquid/gaseous fuels than for solid fuels, however, all this comes with a high cost, especially for IGCC.

8.4 Biofuels

With the depletion of fossil fuels and the growing concern of climate change, renewable energy emerges on to the global stage. On the scale of centuries, the supplies of fossil fuels will be severely depleted. The only sources that could supply energy indefinitely beyond that time horizon are likely to be nuclear fusion and renewable energy. Heat and energy can be produced by solar, fuel cell, wind, geothermal, etc. There is minimal fuel combustion in these energy production processes and consequently are believed to be able to dramatically reduce the air emissions from fuel combustion.

On the other hand, cost is the major barrier preventing these technologies to be commercialized at large scales. Thus far, these alternative energy resources are still at the research and development stage with limited applications. In addition, it also takes energy to produce the devices for energy harvesting and conversion. The net benefit of these technologies should be evaluated based on a life-cycle analysis.

Among all the relevant alternative energy technologies, biofuels are closely related to the scope of this book. Thereby the following is focused on biofuels. Biofuels are produced from biomass, which is biological material derived from living organisms. They grow on the planet earth by converting carbon dioxide (CO_2) with solar energy into HC organic compounds. Biomass can be simply divided into three categories (Table 8.3), lignocellulosic, starch based, and triglyceride-producing biomass.

The type of biofuels produced from biomass depends on the feedstock and the process. Table 8.3 summarizes the platforms for biofuels from biomass. Like fossil fuels, biofuels can also be solid, liquid, and gaseous.

8.4.1 Solid Biofuels

As seen from Table 8.3, solid, liquid and gaseous biofuels can be produced from different biomass following different engineering processes. Without deviating too much from the main scopes of this book, typical processes are briefly introduced as follows.

8.4.1.1 Pulverized Biomass

After drying, biomass can be pulverized and mixed with coal for power generation, and it is expected to reduce the net carbon emission because carbon in the biomass is from CO_2 in the atmosphere. Biomass drying consumes energy. Due to the high moisture content in biomass, loss in thermal efficiency is also a concern. Other technical questions about fuel feed, boiler combustion chemistry, and ash deposition and disposal have been raised too [37].

Table 8.3 Biomass and biofuels platforms

Biomass		Biofuel production			
Type	Examples	Technology	Intermediate products	Post processing	Final biofuel products
Lignocellulosic biomass	Wood, grass	Pulverization	Powder		Co-firing utility fuel
		Pelletization			Pellets
		Anaerobic digestion	Biogas	Gas separation	H ₂ , CH ₄ , CO
		Gasification	Syngas	Fischer-Tropsch Fermentation	FT-diesel, jet fuel, ethanol
Starch-based plants	Corn, sugarcane	Pyrolysis	Bio-oil	Refining	Bioler oil, diesel
		Liquefaction	Bio-oil	Refining	Bioler oil, diesel
Triglyceride-producing plants	Canola, soybean, safflower	Hydrolysis	Sugar	Fermentation	Bioethanol, biobutanol
		Extraction	Edible oil	Transesterification	Biodiesel
		Purification		Transesterification	Biodiesel

8.4.1.2 Wood Pellets

Biomass can be processed into wood pellets for effective transportation and efficient combustion too. The feedstock can be any lignocellulosic biomass, and wood is the most widely used one. Wood pellets can be burned in stove for indoor air heater or in specialized furnace for energy production. They burn like high quality coal, with much lower air emissions.

There are several steps that we can follow to make wood pellets. While the exact procedure may be different from plant to plant and the product quality may vary accordingly [30], the common steps are summarized in Fig. 8.3 for guidance only.

- The first step is biomass drying. The moisture content in the raw biomass must be reduced to a level of about 10 % before the pelletizing process begins. Otherwise, it is difficult to pelletize and consequently affects the quality of the final product. This step is especially important when recycled biomass is used as a feedstock.
- The next step is to remove the impurities from the dried wood. Metal, for example, can be removed by magnets and a screen. This step is especially important for recycled biomass too.
- After the removal of the impurities, the raw material is ground in a hammer mill and it becomes wood powder. The powderous particles can be separated using a cyclone or surface filter. This size reduction is necessary for pelletization. Typical powder sizes are below 5 mm in diameter.
- Right before pelletization, the powder is heated to 70 °C or so. Heating and softening ensure that the lignin in the wood is released and the particles can be bonded effectively together in the final product.

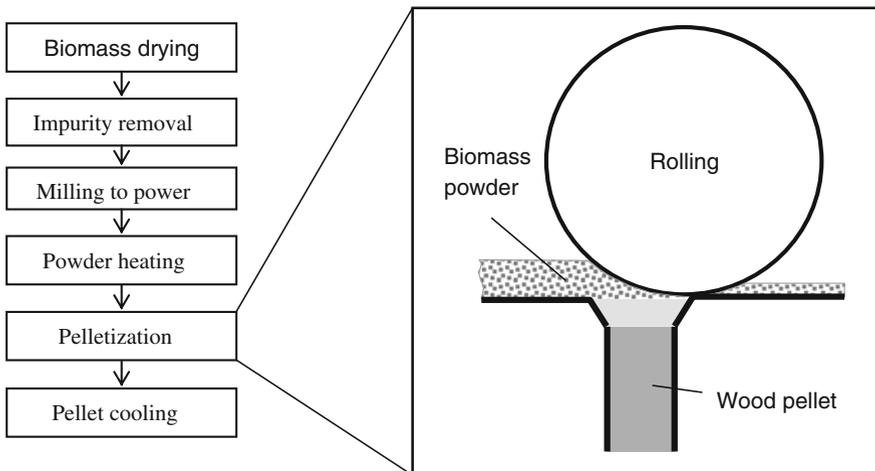


Fig. 8.3 Pellet processing

- Pelletization is a process that reforms the wood powder into certain shapes. As depicted in Fig. 8.3, the powder is pressed down into the die block and is compressed into cylindrical the pellets.
- The last step is to cool the pellets to increase their durability.

The environmental impact assessment for biomass pellet production should be conducted from feedstock harvesting to the delivery of pellets to the end user. Magelli et al. [32] conducted an assessment for wood pellet production in Vancouver, Canada with end users in Sweden by streamline life-cycle analysis. They compared the total emission factors (in g/kg fuel) between wood pellet and natural gas as fuels. The results in Table 8.4 show that wood pellets as a fuel has a great potential in reducing air emissions. The reduction could be greater if the pellets were produced and consumed locally without international transportation. On the other hand, we have to realize that wood pellets cannot replace natural gas because each of them has its uniqueness due to the phase difference.

8.4.2 Biodiesel

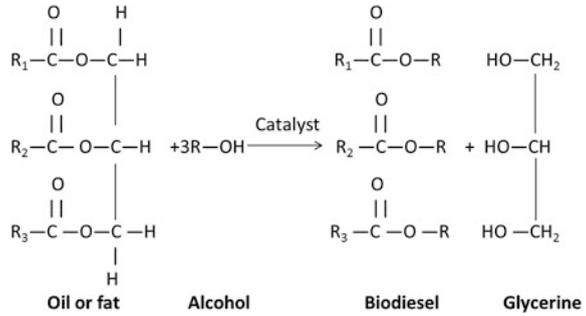
Biodiesel has some substantially different properties than petroleum diesel because of its different structure. Biodiesel is described as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (in ASTM Standard D6751-03). Typical biodiesel has the cetane number that is close to the high end No. 2 petroleum diesel. For example, the biodiesel viscosity–temperature relationship is similar to that of No. 2 diesel fuel, which followed the Vogel equation [54].

Table 8.4 Emission factors for pellet and natural gas production

Air emissions		Pellet (g/1,000 kg fuel)	Natural gas (NG) (g/1,000 kg fuel)	Emission factor ratio (Pellet:NG)
Pollutant	CO	1,196	1,213	0.986
	NO _x	6,420	6,452	0.995
	VOC	169	384	0.440
	PM	496	505	0.982
	SO _x	2,958	3,040	0.973
	NH ₃	6	9.8	0.612
GHGs	CO ₂	281,550	446,750	0.630
	N ₂ O	7.8	10.7	0.729
	CH ₄	53	972	0.055

Based on the data in Magelli et al. [32]

Fig. 8.4 A simplified representation of biodiesel production



$$\ln v = A + \frac{B}{T + C} \quad (8.17)$$

where v (mm^2/s) is the kinematic viscosity of the biodiesel at temperature T (K); A , B , and C are correlation parameters, which can be determined from viscosity measurements at three or more temperatures.

Nowadays most of the biodiesel fuels are produced through the base-catalyzed transesterification of oils or fats. In this process, the vegetable oil or animal fat is combined with alcohol, producing biodiesel and a valuable byproduct glycerin. Figure 8.4 shows a simplified representation of this reaction, where R is the short hydrocarbon chain of an alcohol. R can be either methanol or ethanol or isopropanol. R_1 , R_2 , and R_3 are fatty acid chains. For naturally occurring oils or fats, these fatty acids are largely palmitic, stearic, oleic, linoleic, and linolenic acids.

The exact chemical compositions of biodiesel depend on feedstock, the source of fatty acids and the alcohol used in production. Since alcohol is relatively constant, fatty acids are the main factor that determines the chemical composition of biodiesel. Most of the fats and oils contain 16 and 18 carbon chains. A large number of vegetable oils contain predominantly unsaturated acids, whilst animal fats like cattle tallow contain 60 % saturated acids and mono unsaturated acids as the remainder.

8.4.2.1 Air Emissions from Biodiesel Combustion

Biodiesel is generally considered to be oxygenated, sulfur-free, biodegradable, and nontoxic.

From an environmental point of view, biodiesel is believed to be biodegradable, renewable, and reduces CO_2 emission. Since most of the carbon in the fuel was originally removed from the air by plants, there is very little net increase in carbon dioxide levels.

The post-combustion exhaust gas from biodiesel combustion is characterized with low carbon monoxide, low unburned hydrocarbons, and low particulate emissions from diesel engines; hence it reduces further already low carbon monoxide and unburned hydrocarbons. Although particulate emissions, especially the

black soot portion, are greatly reduced for biodiesel engines, NO_x emissions are usually high.

The NO_x emissions from biodiesel may be 10 % more than that produced by petroleum diesel. Biodiesel combustion usually has more widespread high-temperature distribution areas than petroleum diesel fuel [53]. As we have learned from combustion chemistry, higher combustion temperature leads to more thermal NO_x formation. This partially explains the reason behind the high NO_x emissions typically measured from the engine exhaust produced by biodiesel fuels. However, ethanol could act as an effective NO_x reducing additive [20]. Strategies for reducing NO_x emissions from biodiesel combustion include increasing spray cone angle, retarding start of injection, exhaust gas recirculation (EGR), and charge air cooling [55].

8.4.2.2 Challenges to Biodiesel

The specific gravity of biodiesel ranges from 0.86–0.90, which is higher than that of No. 2 diesel. This may result in a higher fuel mass of biodiesel injection through an unmodified diesel injection system than does a No. 2 petroleum diesel. The high heating value of biodiesel is slightly above 17,000 Btu/lb, and it is lower than that of No. 2 petroleum diesel (19,300 Btu/lb). As a result, the total thermal energy delivered from biodiesel is less than that of No. 2 diesel.

The main barrier for commercialization of biodiesel is its higher cost than petroleum diesel. The price of biodiesel is almost double that of petroleum diesel if subsidies are not taken into account.

Fuel stability is another major concern to biodiesel. Biodiesel is less saturated and normally has poorer thermal stability, oxidative stability, and storage stability than petroleum. A study performed at the University of Idaho showed that biodiesel placed in water degraded 95 % by microorganisms in 28 days, while petroleum diesel fuel degraded only 40 % in same time [56]. At low temperatures, biodiesel will gel or crystallize into a solid mass that cannot be pumped; as a result the engine cannot run.

Another emerging challenge is the food crisis as it is unethical to convert edible food to biodiesel to feed the SUVs instead of the starving people. There was a great rise in the price of food (especially corn) and fertilizer from 2006–2008, partially because quite a lot of corn in North American was used for biodiesel production. Research and development should be focused on waste to biodiesel instead.

8.4.3 Bioethanol

Bioethanol (C₂H₅OH) can be produced from starch in corn, sugar in sugar cane, or cellulose from the cellulosic biomass. Starch and sugar based bioethanol is considered as the first generation bioethanol, while cellulosic bioethanol the second.

Corn is the well-developed feedstock in United States, while sugar cane is a tropical and subtropical crop that is the primary feedstock in Brazil, India, and Colombia. Cellulosic bioethanol is a more recent development that is not well commercialized yet. Regardless of the feedstock, the sales price of bioethanol must be competitive with that of petroleum gasoline. However, profit margins in bioethanol production processes are still low. Nonetheless, our focus here is a briefly introduction rather than an in-depth discussion.

Depending on the biomass feedstock, there are several major steps that may apply to bioethanol production [26].

- Feedstock pre-treatment
- Hydrolysis
- Fermentation
- Separation
- Storage.

8.4.3.1 Feedstock Pretreatment

Feedstock pretreatment is necessary to convert most of the carbohydrates in the feedstock into sugars. The first step is size reduction and breakdown of the cell wall structures surrounding the target compounds, mainly cellulose. Some lignin is dissolved in the solution. Sugar cane is crushed followed by juice extraction; corn goes through dry grinding or wet milling according to the downstream conversion technology. The feedstock is then pretreated using chemicals, such as dilute sulfuric acid or ammonia.

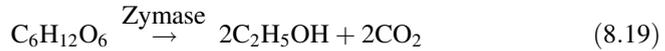
After pretreatment, a large amount of water is separated from the hydrolysate slurry. Meanwhile, other unwanted chemicals such as acetic acid and furfural are also removed from the slurry. Then hydrolysate slurry is cooled by dilution water and further chemically conditioned for next step.

8.4.3.2 Hydrolysis and Fermentation

In this step, the starch and cellulose are converted into sugars, primarily being glucose, by cellulose enzymes. It is also called enzymatic hydrolysis. A cellulase enzyme breaks down cellulose fibers and ultimately converts them into glucose monomers.

The resulting glucose and other sugars from feedstock pretreatment are to be converted into bioethanol by fermentation. This process may take several days to complete. The simplified chemical reactions for hydrolysis and fermentation are





where $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ stands for sucrose, $\text{C}_6\text{H}_{12}\text{O}_6$ glucose, and $\text{C}_2\text{H}_5\text{OH}$ ethanol.

Example 8.1: Conversion rate of bioethanol

According to Eqs. (8.18) and (8.19), what is the stoichiometric mass ratio of conversion by fermentation.

Solution

According to Eqs. (8.18) and (8.19), 1 mol of sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ can be converted into 4 mol of ethanol, $\text{C}_2\text{H}_5\text{OH}$, and 4 mol of CO_2 . The overall reaction can be described as



The molar weights of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, $\text{C}_2\text{H}_5\text{OH}$ and CO_2 are 342, 46, and 44 g/mol, respectively. Therefore, the maximum theoretical mass conversion ratio of ethanol is

$$\frac{4 \times M_{\text{C}_2\text{H}_5\text{OH}}}{M_{\text{C}_{12}\text{H}_{22}\text{O}_{11}}} = \frac{4 \times 46}{342} = 53.8 \%$$

The rest goes to CO_2 and its production ratio is 46.2 %.

This example shows only the theoretical maximum conversion rate. In reality, no more than 47 % of the fermented carbon hydrates is converted to (bio)ethanol.

8.4.3.3 Bioethanol Separation

The product of fermentation is called both or beer. It contains water, ethanol, combustible solids, and much more. Ethanol is separated from this mixture by a few steps. Distillation and molecular sieve adsorption are the core technologies for this purpose.

Distillation can be accomplished in two or three columns depending on the required purity of the ethanol. In the first column, called beer column, water, and dissolved CO_2 are first removed from the mixture. The second column is called rectification column, where ethanol is concentrated to a level of 92.5 % of ethanol. Then it can be further dehydrated to 99.5 % by vapor-phase molecular sieve adsorption.

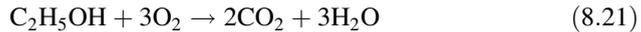
Both adsorption and desorption principles are employed in the aforementioned separation process. There are two columns in the molecular sieve adsorption process, one works as an adsorption tower while the other is being regenerated. All the other gaseous emissions are treated by absorption using pure water.

Solid-liquid separation devices are employed to recover the solids in the stillage from the beer column. Although the principles were not deliberately introduced in this book, hydraulic cyclones and filters can be used for this purpose. After drying,

the solids can be used as alternative fuel for combustion too. The rest of the water goes to a water treatment facility.

8.4.3.4 Bioethanol Combustion

Bioethanol is mainly mixed with petroleum gasoline for combustion in light engines. The overall stoichiometric combustion formula can be described as follows, although the actual chemical reactions are much more complicated.



On a volumetric base, bioethanol (or ethanol) has only $2/3$ of the heating value of petroleum gasoline [6]. There is a great power reduction if pure ethanol (E100) is used to power an automobile. Therefore, bioethanol is mixed with gasoline for sale.

Water contamination remains a challenge to the bioethanol industry. The challenge to bioethanol-gasoline mixed fuels is the phase separation induced by water contamination. Ethanol absorbs water readily in a storage tank or transport pipeline. This resultant water in the fuel negatively affects the engine operation.

8.4.4 Hydrothermal Conversion of Biomass to Biofuels

8.4.4.1 Properties of Hot Compressed Water

Before we introduce hydrothermal conversion of biomass to biofuel, we have to start with the phase behavior of hot compressed water. Water exhibits unique properties at a critical point of $374\text{ }^\circ\text{C}$, 22 MPa . Above this critical point, water is in a homogeneous phase known as a supercritical fluid. Supercritical water exists simultaneously as both a liquid and a gas. Subcritical water is marked by a higher density and the presence of two phases, one being liquid and the other being vapor [29].

The first special property of hot compressed water is its ionic constant. The ionic products are H^+ and OH^- ions:



The ionic constant of subcritical water is considerably higher than those of supercritical water and regular water. As such, subcritical water is a special reaction medium due to its dual acid-base catalysis nature, which enables rapid conversion of biomass compounds to biofuels.

Another special property of hot compressed water is its density. Under low density conditions, diffusion of radicals through the solution is enhanced; under high-density conditions, ionic reaction mechanisms are promoted.

The third parameter of concern is the dielectric constant of hot compressed water. The dielectric constant of water decreases with the increase of temperature. As a result, hot compressed water is much less polar than normal water. It performs more like an organic solvent. The decreasing dielectric constant of hot compressed water is likely to affect organic reactions. One benefit of the changing dielectric constant of water is that it works like an organic solvent during reaction conditions, and it returns to its normal polarity after cooling. This unique property is believed to be beneficial to the production and voluntary separation of alkanes from biomass [11].

The changing reaction environment around critical point approach causes a significant change in reaction mechanisms of hydrothermal conversion of biomass [7, 28]. Both ionic and free radical reactions may take place in hydrothermal conversion of biomass, the latter being preferred above the critical point.

Depending the status of hot compressed water it can convert biomass into both gaseous and liquid fuels. Without catalyst, the higher the water temperature, the more gas, and the less liquid fuels. As a result, hydrothermal conversion processes are divided into hydrothermal liquefaction and hydrothermal gasification.

The overall process of decomposition of biomass is illustrated in Fig. 8.5. Hydrolysis plays an important role in forming glucose/oligomer, which can quickly decompose into, oil, char, and gases. Without catalyst, oil can be converted into char and gases; however, the addition of alkali catalyst will result in more oil production because it inhibits the char production from the oil intermediates. The presence of water in the feedstock is a key factor for the conversion reaction. At temperatures between 250 and 350 °C, organic molecules in liquid water undergo chemical reactions.

Temperature is an important factor that affects the HTC conversion products, liquid, or gas. As shown in Fig. 8.6, more liquid products are produced at lower temperature. As the temperature increases, more gaseous products are produced at the expense of the liquids and because of additional carbon conversion.

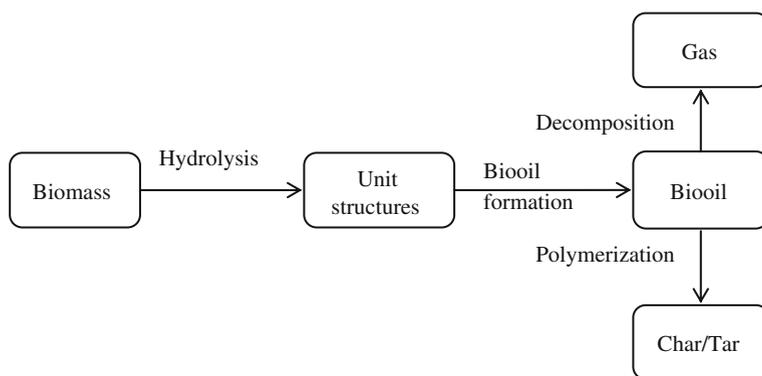
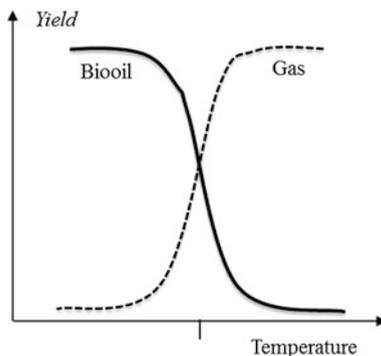


Fig. 8.5 Conversion of cellulose to bio-oil

Fig. 8.6 Effect of temperature on the HTC product



Water goes through dramatic changes in both physical and chemical properties when heated. As the temperature rises from 25 to 300 °C under standard pressure, the density and dielectric constant of water decreases from 997 to 713 kg/m³ and 78.85 to 19.66, respectively, while the ionic product increases from 10^{13.99} to 10^{11.30}. These changes in physical properties make the solvent properties of water at 300 °C roughly equivalent to those of acetone at 25 °C. Ionic reactions of organics are favored by the increase of solubility in water. The increase in the dissociation constant increases the rate of both acid- and base-catalyzed reactions in water far beyond the natural acceleration due to increased temperature. Water itself can also act as an acidic or basic catalyst, and its reactivity can often be reinforced by autocatalysis from water-soluble reaction products.

Under high-temperature high pressure conditions, water shows even more unique properties as a reaction medium, especially with the presence of suitable catalysts. At supercritical condition (385–400 °C, 35 MPa) the reaction for HTC conversion can be completed within a minute.

Residence time is another factor for a successful conversion. The HTC bio-oil yields under acidic, neutral, and alkaline conditions all decrease with increasing residence time. Despite the similar trends of HTC bio-oil yields against conversion temperatures and the residence time, the conversion mechanisms behind them are likely quite different. Under acidic HTC conditions, the decrease in bio-oil yields at high temperatures and long residence time is mainly attributed to the formation of residual solids. Under acidic conditions, 5-HMF, the main component of acidic HTC bio-oil, tends to form hydrothermal char/solid by polymerization. Under neutral conditions, the decrease in HTC bio-oil yield at high temperatures and long reaction residence time is mainly caused by the formation of residual solids and the gas products. Under alkaline HTC conditions, the gas formation from the decomposition of alkaline HTC bio-oil mainly resulted in the bio-oil yield decrease at the high temperatures (>300 °C).

In continuous operation, slurry feeding is a challenge because of the water evaporation at the end of the pipe. Poor conversions were reported because of the loss of water by condensation. Serious erosion and/or corrosion occurred on several spirals of the auger where the reaction was actually took place before the feedstock enters the reactor. Char formation was found to occur downstream because of lack of water brought about by back condensation. Some differences have been found in the chemical composition of the oil from the batch process and the semi-continuous process. A higher percentage of aromatic and/or unsaturated carbon was found in the oil produced using the semi-continuous process.

8.4.4.2 Hydrothermal Liquefaction

Hydrothermal liquefaction employs reactive hydrogen or carbon monoxide carrier gases to produce liquid fuel from organic matter at moderate temperatures. Temperatures between 300 and 400 °C correspond to the maximum yield of oil products [50]. Direct liquefaction involves rapid pyrolysis to produce liquids and/or organic vapors, whereas indirect liquefaction employs catalysts to convert non-condensable, gaseous products of pyrolysis, or gasification into liquid products.

Technically, any matter with high organic content can be converted into another form by thermochemical conversion, but the conversion rate depends on the feedstock and the process itself. A variety of feedstocks are proven technically successful including high-carbon content materials such as coal, peat, and ligno-cellulosic material. Low-quality feedstock includes municipal and industrial wastes and agricultural residues. Studies on thermochemical conversion of biomass were predominantly focused on materials that are highly cellulosic, until recently an emerging interest in liquid waste such as livestock manure (e.g., [50]) and algae [34].

Many factors affect the conversion rate of a HTC process. They include, but not limited to, temperature, pressure, retention time, reactant gases, feedstock, catalysts, if any, and the reactor design. These parameters were found to be most important as they dictate the yield and quality of the products. Regardless of the process, the new fuel is inevitably more expensive than its parent fuel due to the extra energy and equipment required for the conversion.

Hydrothermal conversion is a process that is similar to cooking of food. The major differences between this process and other processes are use of wet feedstock as raw material because it saves energy from drying the feedstock. Also, the presence of water is beneficial for the conversion process.

The primary reactions in the conversion of biomass to oil likely involve the formation of low-molar weight, water-soluble compounds such as glucose. Water also acts as solvent and alkaline catalysts. More importantly, water plays a critical role in the water-gas shift reaction



The resultant hydrogen with other oxygen-containing functional groups, eliminating the oxygen element and yielding hydrocarbon-like compounds.

8.4.5 Biogas

In addition to the thermochemical conversion approach, biomass can also be converted into gaseous fuels by a biological approach called anaerobic digestion. And the resultant gas is sometimes called biogas. It is well known that typical biogas from a well-controlled anaerobic process contains 60 % CH₄ and 40 % CO₂ and other trace compounds.

Anaerobic digestion is a complex biochemical reaction that involves the following four steps.

- Hydrolysis:
It is the process where complex organic matter is decomposed into simple organic molecules. It is done with the existence of water that splits the chemical bonds of the organic matter.
- Fermentation:
It is also called acidogenesis, the process where carbohydrates are decomposed by bacteria, enzymes, molds, or yeasts in the absence of oxygen.
- Acetogenesis:
It is the process where the products of the fermentation process are converted into H₂, CO₂, and acetate by acetogenic bacteria.
- Methanogenesis:
It involves the formation of CH₄ from acetate, H₂, and CO₂ by methanogenic bacteria.

In the anaerobic digestion process, the methanogenic bacteria are very sensitive and are easily upset by sudden changes in temperature or pH, and toxic substances such as arsenic, copper, and antibiotics.

There are mainly two types of anaerobic digesters:

- Mixed digester
- Plug-flow digester

Mixed digesters are usually employed for liquid feedstock and the latter for semi-solid feedstock (about 13 % solids). In a mixed digester solids are kept in contact with the bacteria for reaction and the mixing is usually maintained either mechanically or by bubbling. Plug-flow digesters eliminate the need for mixing by slowly moving the waste through a tube-shaped vessel. A lagoon is another commonly used method for waste treatment, where aerobic bacteria use oxygen to

convert organic matter into CO₂, water, and more bacteria. Therefore, there is no biogas produced in aerobic digestion.

The main drawback of natural anaerobic digestion is its slow reaction. A properly designed anaerobic digester provides better control over the environment for the anaerobic digestion process. A digester is like a reactor, which can be sealed, heated, and agitated to shorten the time needed to stabilize the waste. It also offers a good control of odor emission and easy capture of the gaseous products like methane. Due to the shorter process time requirement, a typical anaerobic digester can be 100 times smaller than a natural anaerobic lagoon.

Regardless of the type of fuels produced from biomass or petrochemical process. Their applications were primarily for energy production by combustion. The combustion processes of these many types of fuels do not always follow the same simplicity, rather they depend on the physical designs of the process.

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