Chapter 6
Fossil Fuels and Alternative Fuels

6.1 Introduction

A “fuel” is generally defined as any material that can be altered to release energy in a controlled manner in the form of heat and/or work. Fuels can be solids, liquids, or gases. *Conventional fuels* are of two types: fossil fuels and nuclear fuels. The word “altered” in the above definition signifies a chemical or physical process to which the fuel is subjected to release energy. Nuclear fuels, such as fissionable uranium, are “altered” through a chained nuclear reaction of fission to generate useful energy in the form of high temperature heat. Fossil fuels represent fossilized biomass, which stores carbon out of the natural carbon cycle in sediments for a long time. When combusted, fossil fuels release the carbon into the atmosphere in the form of carbon dioxide, thus contributing to global warming. Biomass also emits carbon dioxide when combusted; however, the emitted carbon is only returned in the global carbon cycle in this way; thus, biomass is considered a renewable energy resource. Biomass represents biological material of recently living organisms, which is regarded both as an alternative fuel and as a source of materials for synthetic fuels production.

Alternative fuels are nonconventional fuels that can be obtained from biomass (in which case they are called *biofuels*) or from fossil fuels (in which case they are called synthetic fossil–based fuels). Blends of fossil-derived fuels and biofuels are also considered alternative fuels (e.g., gasoline + bioethanol blends). The classification of fuels is represented graphically in Fig. 6.1.

Sustainable energy development requires alternative fuels, which are viewed as a cleaner means of chemical energy storage with respect to fossil fuels. In this chapter, fossil fuels and alternative fuels are introduced and compared in terms of energy and exergy per stored mass and volume and associated environmental impact.

6.2 Fossil Fuels

There are three types of fossil fuels: coal (solid), petroleum (liquid), and natural gas (gaseous).

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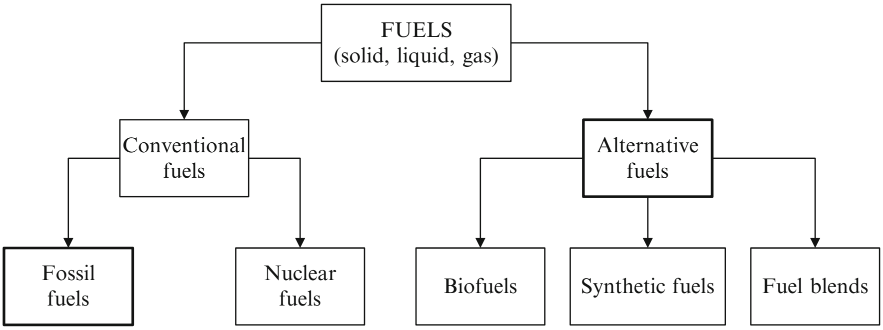

Fig. 6.1 Classification of fuels

All fossil fuels are natural hydrocarbons with a density in increasing order, starting from natural gas to the light and heavy oils, to bitumen, kerogen, sapropels, and humic coals. While the density increases, the ratio between hydrogen and carbon atoms (H/C) for 1 mol of substance decreases from about 4 for natural gas (comprising mainly methane) to 0.7 specific to coal. In a hydrocarbon, the H/C ratio indicates the *aromaticity*, which is the capability of the molecule to form aromatic rings of covalent bonds. Because of higher aromaticity, the molecules of heavier hydrocarbons are more stable and thus more difficult to crack. We discuss in this section the main features of coal, petroleum, and natural gas.

6.2.1 Coal

Coal is a sedimentary rock obtained by exposure to high pressure and temperature of fossilized organic matter and comprises primarily carbon and some smaller quantities of hydrogen, sulfur, oxygen, and nitrogen. The variety of coal rock is large with respect to composition, moisture content, and calorific value. Three of the chemical elements containing coal generate heat when combusted. These are carbon, hydrogen, and sulfur. The formation enthalpy of the oxidation products of these elements, listed in Table 6.1, is the factor contributing to the calorific value of coal. Therefore, the concentration of carbon, hydrogen, and sulfur in coal plays the major role with respect to coal value from an energy point of view.

Coal is of four main types according to the *coal rank*. The coal rank represents a conventional measure to characterize the heating value of coal in correspondence to its fixed carbon and volatile matter content and caking properties. The types of coals in the standard classification, listed from higher to lower rank, are as follows: anthracite, bituminous, subbituminous, and lignite; their characteristics are summarized in Table 6.2.

The presence of water in coal is explained by the process of its geological formation, where humid biomass was squeezed under the pressure of sediment layers. Water is both chemically and physically bound in the coal structure and is

Table 6.1 Formation enthalpy and chemical reactions of the main oxidation products of coal

Element	Symbol	Chemical reaction	Formation enthalpy, kJ/mol
Carbon	C	$C + 0.5O_2 \rightarrow CO_2$	−393,486
Hydrogen	H	$H_2 + 0.5O_2 \rightarrow HO_2$	−241,811
Sulfur	S	$S + O_2 \rightarrow SO_2$	−296,792

Note: Data calculated with Engineering Equation Solver Software (Klein 2010)

commonly denoted with the term *moisture content*. Table 6.2 shows that the moisture content in coal varies from 2% to 45% by weight. When coal is combusted, a part of the combustion heat is consumed by water evaporation; the drier it is, the higher the calorific content of coal.

Ash represents the residue that remains after the complete combustion of coal and comprises various sulfates and oxides and other inorganic chemicals. Coal embeds two types of mineral matter that ultimately led to the formation of ash by combustion: extraneous mineral matter (gypsum, shale, sand, pyrite, clay, marcasite, calcium, magnesium) and inherent mineral matter (some of the constituents of the biomass from which coal was formed).

Volatile matter is the percentage of products that are volatile—that is, they can be released as gases during pyrolysis process. Volatile matter refers to all other components, except the water vapor, which result from mixture evaporation. The loss of carbon dioxide from mineral embedded in coal structure is an example of volatile matter; other examples are hydrogen emanated by chloride minerals or sulfur from pyrite.

If the mass of volatiles, ash, and moisture is extracted from the mass of coal, the remaining quantity is known as *fixed carbon*. For anthracite, the fixed carbon is 75% to 85% by weight, while for bituminous, subbituminous, and lignite coal, it is 50% to 70%, 30% to 57%, and 25% to 30%, respectively (see Speight 2005).

The calorific value of solid fuels is usually given in two forms: gross (GCV) and net (NCV) calorific values. Note that for liquid and gaseous fuels the terms used for GCV and NCV are higher heating value (HHV) and lower heating value (LHV), respectively. The calorific values are defined as follows:

- GCV or HHV represents the heat of combustion in the case when all products are brought to the reactants' (fuel and oxidant) temperature and condensing all water vapor.
- NCV or LHV is determined by subtracting the heat of evaporation of water from GCV (HHV) and corresponds to the case when all products are brought to the reactants' temperature, but water remains in the vapor phase.

The estimation of the gross calorific value of coal can be made with Mason and Gandhi's (1983) formula, which is given as a function of the weight percentages of the main coal components:

$$\begin{aligned}\mathrm{GCV} = 2.326 \times [&0.198(\%\,\mathrm{C}) + 0.6203(\%\,\mathrm{H}) + 0.0809(\%\,\mathrm{S}) \\ &+ 0.04495(\%\,\mathrm{A}) - 5.153],\end{aligned} \tag{6.1}$$

Table 6.2 Classification of coal by rank

		Composition[a]								
Rank	Description	C, %	H, %	O, %	S, %	N, %	Ash, %	Moisture, %	GCV, MJ/kg[b]	Density, kg/ dm^3
Anthracite	Brittle, hard, black lustrous	75–85	1.5–3.5	5.5–9.0	0.5–2.5	0.5–1.0	4.0–15.0	3.0–6.0	27.9–31.4	1.35–1.70
Bituminous	Black to dark brown, dense	65–80	4.5–6.0	4.5–10.0	0.5–6.0	0.5–2.5	4.0–15.0	2.0–15.0	27.9–33.7	1.28–1.35
Subbituminous	Dark brown to bright black, dull	55–70	5.5–6.5	15.0–30.0	0.3–1.5	0.8–1.5	3.0–10.0	10.0–25.0	17.4–23.3	1.35–1.40
Lignite	Brownish black with high moisture	35–45	6.0–7.5	38.0–48.0	0.3–2.5	0.6–1.0	3.0–15.0	25.0–45.0	13.0–17.4	1.40–1.45

[a] Percent by weight
[b] Ash-free basis

given in MJ/kg. It is useful to express the NCV on a wet basis; this can be done with the equation presented in Van Loo and Koopejan (2008):

$$\mathrm{NCV} = \mathrm{GCV}(1 - w_\mathrm{w}) - 2.444\, w_\mathrm{w} - 21.839\, w_\mathrm{H}(1 - w_\mathrm{w}), \tag{6.2}$$

where w_w is the moisture content by weight.

The estimation of coal entropy and chemical exergy is of utmost importance for the second law analysis of energy systems involving coal combustion. For specific exergy content of dry and moisture-free coal, Eiserman et al. (1980) give the following regression formula, based on the concentration of main elements expressed in kmol per kg dry and ash-free coal (where c, h, o, n, and s are the concentrations of carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively):

$$\begin{aligned} s_\mathrm{DAF} = c\Bigg[&37.1653 - 31.4767\exp\left(-0.564682\left(\frac{h}{c+n}\right)\right) + 20.1145\left(\frac{o}{c+n}\right) \\ &+54.3111\left(\frac{n}{c+n}\right) + 44.6712\left(\frac{s}{c+n}\right)\Bigg], \end{aligned} \tag{6.3}$$

where index DAF stands for *dry coal and ash-free* basis, and the entropy results are in kJ/kg K.

The chemical exergy of coal, dry and ash-free basis, can be calculated with the formula obtained by Kaygusuz (2009), which reads

$$\begin{aligned} ex^\mathrm{ch}_\mathrm{DAF} = \mathrm{GCV} - T_0\Bigg[&s_\mathrm{DAF} + \left(c + \left(\frac{1}{4}h\right) + s - \left(\frac{1}{2}o\right)\right)s_{\mathrm{O}_2} - c \times s_{\mathrm{CO}_2} \\ &- \left(\frac{1}{2}h\right) \times s_{\mathrm{H_2O}} - s \times s_{\mathrm{SO}_2} - \left(\frac{1}{2}n\right) \times s_{\mathrm{N}_2}\Bigg] + c \times ex^\mathrm{ch}_{\mathrm{CO}_2} \\ &+ \left(\frac{1}{2}h\right) \times ex^\mathrm{ch}_{\mathrm{H_2O}} + s \times ex^\mathrm{ch}_{\mathrm{SO}_2} + \left(\frac{1}{2}n\right) \times ex^\mathrm{ch}_{\mathrm{N}_2} \\ &- \left(c + \left(\frac{1}{4}h\right) + s - \left(\frac{1}{2}o\right)\right)ex^\mathrm{ch}_{\mathrm{O}_2}, \end{aligned} \tag{6.4}$$

where the exergy value results are in $\mathrm{MJ/kg_{DAF}}$. The chemical exergy of good-quality coals varies between 7 and 8.2 MJ per kg dry ash-free basis. The contribution of ash to chemical exergy is negligible; therefore, the specific chemical exergy of coal, wet basis, can be estimated with

$$ex^\mathrm{ch} = (\%\mathrm{coal_{DAF}}) \times ex^\mathrm{ch}_\mathrm{DAF} + \frac{(\%\mathrm{H_2O})}{M_{\mathrm{H_2O}}} \times ex^\mathrm{ch}_{\mathrm{H_2O}}, \tag{6.5}$$

where $(\%\mathrm{coal_{DAF}})$ is the percent of dry coal and $(\%\mathrm{H_2O})$ is the percent of water, both by weight.

For every 12 g of carbon, there is 1 mol of carbon content in coal, which by complete combustion is converted into 1 mol of CO_2 weighing 44 g. Therefore, if (%C) is the percent of carbon per weight on a dry basis, and w_w is the moisture content by a wet basis, the carbon dioxide emission for 1 kg of coal by a wet basis is

$$\mathcal{M}_{CO_2} = \frac{44}{12}[\%C] \times (1 - w_w), \frac{\text{kg}\,CO_2}{\text{kg wet}}, \tag{6.6}$$

where [%C] is the carbon fraction given in kg carbon per dry coal ash-free; thus, the carbon dioxide emission per unit of NCV wet basis is

$$\mathcal{M}_{CO_2,\text{NCV}} = \frac{\mathcal{M}_{CO_2}}{\text{NCV}}, \frac{\text{kg}\,CO_2}{\text{MJ wet}}. \tag{6.7}$$

Figure 6.2 shows the amounts of carbon dioxide emissions per unit of energy in MJ corresponding to the net calorific value of coal. The moisture content is considered according to the typical ranges. The ranks with more carbon content emit more CO_2 even if high ranks have a better calorific value. Equations (6.6) and (6.7) and data from Table 6.2 were used to draw Fig. 6.2.

6.2.2 *Petroleum*

The term *Petroleum* comes from the Latin terms *petra* meaning rock and *oleum* meaning oil. Petroleum is extracted from sediments in an oil well in liquid form. Several kinds of fossilized biological matter containing mostly lipids, amino acids, carbohydrates, and lignins contribute to the formation of petroleum currently existing in oil wells. Petroleum is a mixture of hydrocarbons that range from light ones (carbon number lower than 5) to heavier ones such as paraffins dissolved in liquid. Petroleum is toxic and flammable, and apart from carbon (83–87%) and hydrogen (10–14%), it comprises sulfur (0.5–6%) and some metals. The range of hydrocarbons that constitute petroleum (or crude oil) are as follows:

- Naphthas, with 5 to 7 carbon atoms in the molecule (used mainly as solvents).
- Gasoline, with 8 to 11 carbon atoms, which is the basis of gasoline fuel for autos.
- Kerosene, with 12 to 15 carbon atoms, from which diesel fuel is extracted.
- Lubricating oils, with 16 to 19 carbon atoms; they have a high normal boiling point.
- Solid hydrocarbons, with over 20 carbon atoms; they have melting point at higher values than the ambient temperature and are classified, in order of increased molecular weight, as paraffins, wax, tar, and asphaltic bitumen.

Petroleum is not used in practice in the form in which it is extracted (crude oil); rather, it is subjected to a distillation process in refineries. Table 6.3 summarizes the fuels derived from petroleum. Regarding jet fuels, there are currently two main

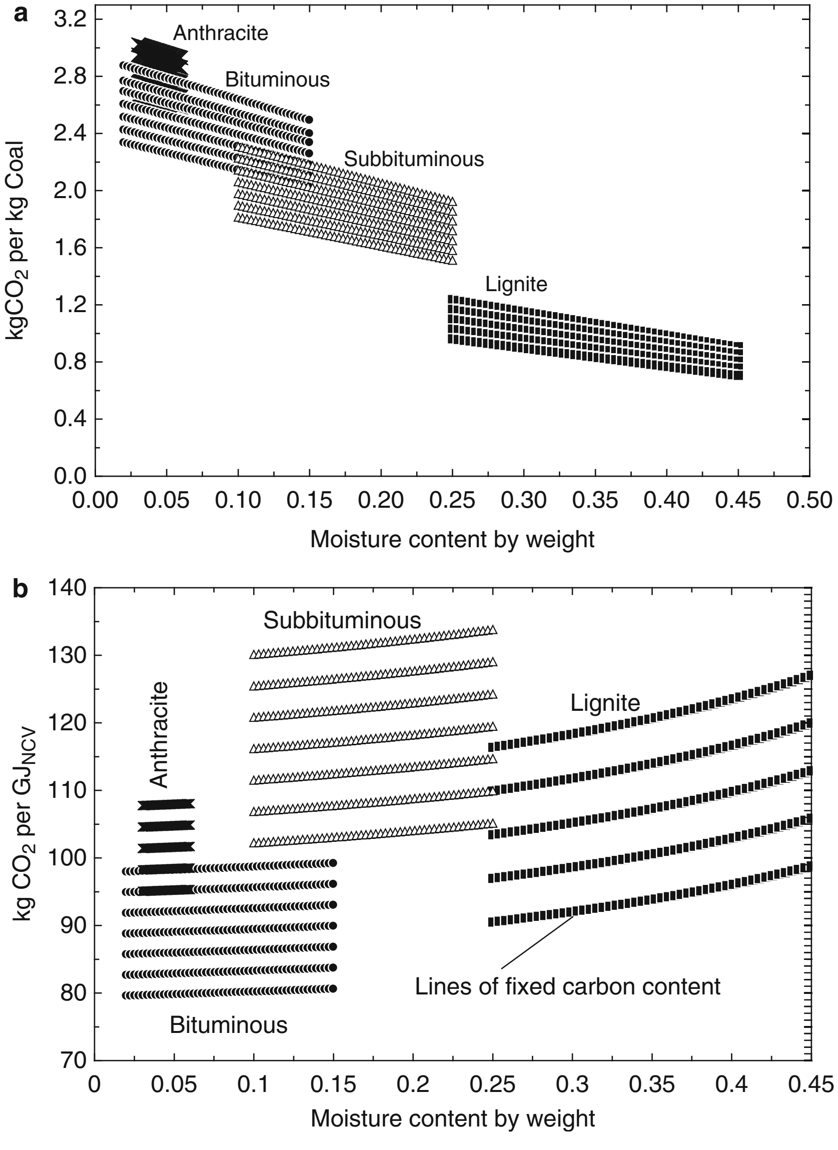

Fig. 6.2 Carbon dioxide emissions per kg and per GJ (NCV) for coal by rank

grades: jet A-1 and jet A, which are both kerosene-type fuels. There is another grade of jet fuel, jet B, which is a wide-cut kerosene (a mix of gasoline and kerosene), but it is rarely used, except in very cold climates. Jet A is a kerosene-based type of fuel, produced to an ASTM (American Society for Testing and Materials) specification and normally only available in North America. It has the same flash point as jet A-1, but a higher freeze point maximum (−40°C). Jet B is a distillate covering the

Table 6.3 Petroleum-derived fuels and their properties

Fuel name	Boiling point, °C	Molec. weight, kg/kmol	Density, kg/m^3	Carbon, wt%	LHV, MJ/kg	HHV, MJ/kg	Chemical exergy, MJ/kg	$\mathcal{M}_{CO_2}$, kg$_{CO_2}$/GJ$_{LHV}$
Light naphtha	0–150	100–150	~750	83.7	44.9	48.1	44.5	68.2
Gasoline	35–200	114	~745	85.1	43.5	46.5	47.5	71.9
Heavy naphtha	150–205	150–215	~850	85.4	43.0	46.1	49.0	64.2
Diesel fuel	150–370	233	~747	85.6	42.8	45.8	44.2	73.3
LPG	–43	44	~580	81.8	46.0	52.0	54.9	65.3
Kerosene	205–260	170	~795	84.7	43.1	46.2	49.1	71.9
Jet fuels	156–293	185	800	76.0	43.2	46.9	45.3	63.4
Fuel oil	260–425	>200	~990	85.4	40.1	42.9	41.4	78.1

LPG liquefied petroleum gas (assimilated as propane)

naphtha and kerosene fractions. It can be used as an alternative to jet A-1. Because it is more difficult to handle (higher flammability), there is significant demand only in very cold climates, where its better cold weather performance becomes important. In Table 6.3, the row for jet fuels lists the average properties of jet A and B fuels. On average, jet fuels can be approximated with the chemical formula $C_{12}H_{23}$; see Nojoumi et al. (2009).

The chemical exergy of liquid fuels can be determined, as illustrated, for example, in Szargut (2005) and Al-Najem and Diab (1992), based on the chemical composition of the fuel, expressed with respect to the molar carbon in the molecule, namely,

$$
\begin{aligned}
ex_{\text{fuel}} = \text{LHV}\Bigg[& 1.0374 + 0.0159\left(\frac{\text{H}}{\text{C}}\right) + 0.0567\left(\frac{\text{O}}{\text{C}}\right) \\
& + 0.5985\left(\frac{\text{S}}{\text{C}}\right)\left(1 - 0.1737\left(\frac{\text{H}}{\text{C}}\right)\right)\Bigg],
\end{aligned}
\tag{6.8}
$$

where H, O, S, C represent the number of atoms of hydrogen, oxygen, sulfur, and carbon, respectively.

The fuel that is used mostly in road transportation is gasoline, which is a blend of aliphatic and aromatic chemicals obtained by distillation of petroleum in refineries. Diesel fuel is also very common for road transport—especially for large capacity vehicles—and marine ships and rail locomotives. Processing of petroleum to obtain diesel fuel is simpler with respect to that of gasoline. The important aspect in diesel processing is the reduction of the sulfur content. The liquid petroleum gas (LPG) is based mainly on propane but often is mixed with butane in a 60/40 proportion. The gases that compound LPG are all extracted from petroleum in the refinery processes. The density of LPG is about the average of that of liquid propane and liquid butane at 25°C. Alcohol-based fuels, such as ethanol and methanol, can be

Table 6.4 Typical composition ranges of fossil natural gas

Component	Methane	Ethane	Propane	Butane	Pentane	Hexane	CO_2	O_2	H_2
Concentration	87.1–96.0	1.5–5.1	0.1–1.5	0.02–0.06	<0.18	<0.06	0.1–1.0	0.01–0.1	<0.02

Table 6.5 Principal properties of natural gas

Parameter	Unrefined	Refined
Molecular mass, g/mol	20	16
Density, kg/m^3	1.832	0.733
Normal boiling point, °C	N/A	−162
Autoignition temperature, °C	540	560
Octane number	120	130
LHV, MJ/kg	18.2	50.7
HHV, MJ/kg	20.2	56.2
ex^{ch}, MJ/kg	18.8	52.4
% C by weight	73	75
% CO_2 by weight[a]	2.68	2.75
CO_2, kg/MJ$_{LHV}$	147.2	54.2

[a] Assumed complete combustion

produced using petroleum as a fossil fuel source. However, these fuels are mostly produced from biomass through fermentation, and they are categorized here as alternative fuels.

6.2.3 Natural Gas

Fossil natural gas consisting mainly of methane is a natural resource found mainly either in natural gas fields or in oil well fields (where it is in association with oil). Other important sources of natural gas are coal-bed methane and in the form of hydrate sediments present under permafrost regions. The typical composition of natural gas is listed in Table 6.4. The existence of noncombustible components such as carbon dioxide, nitrogen, and oxygen in natural gas detracts from its heating value. One practical aspect is that natural gas is less inflammable than other hydrocarbon-based fuels, even though methane, its principal constituent, is highly flammable. When confined, natural gas presents explosion danger. Methane is a chemical with a high greenhouse effect, having 72 times higher potential than that of carbon dioxide for a time horizon of 20 years. Its lifetime in the atmosphere is 12 years.

Refining natural gas involves several processes aimed to remove humidity (water), sulfur, carbon dioxide, helium, solid particle, and liquid hydrocarbons existing in the gas. Through refining, the carbon content and the associated heating value are increased. Table 6.5 compiles the main physical properties of natural gas in unrefined and refined form.

6.3 Alternative Fuels

The classification introduced in Fig. 6.1 shows three alternative fuels to fossil fuels, namely, biofuels, fuel blends, and synthetic fuels. The need for alternative fuels is explained by two reasons: (1) fossil-based fuels deplete, thus new fuel sources must be discovered; (2) high carbon dioxide emissions are associated with fossil fuel combustion, and it is desired to limit these in order to have a better environment and avoid the danger of global warming. The three kinds of alternative fuels can be briefly described as follows:

- Biofuels are fuels derived from biomass though various physical and/or chemical (biochemical) processes. They can be solids, liquids, or gases.
- Synthetic fuels can be produced using either renewable or nonrenewable sources starting from materials such as water, air, and carbon dioxide, or starting from fossil fuels. For example, electrolysis of water can be used to obtain hydrogen, or the Fischer–Tropsch process can be used to obtain synthetic diesel fuel from coal or biomass.
- Fuel blends are blends of conventional and synthetic fuels or biofuels that are very attractive as a transition solution toward a cleaner transportation sector. A typical example is gasoline–ethanol blend, which is used in many countries. Blends help in reducing CO_2 emissions.

6.3.1 Biofuels

Biologic matter, such as wood, crops, manure, and wastes, is generally called biomass. Any fuel derived from biomass can be called a biofuel. A more exact definition of biofuel, taken from Speight (2008), is any biomass-derived fuel with at least 80% content by volume being materials sourced from living organisms harvested within 10 years preceding the manufacture. If the fuel is a gas, the common term is *biogas*. If the fuel is a solid (e.g., wood) the term *biomass* is customarily used. If the fuel is a liquid, the common term is *biofuel* (e.g., biodiesel). We discuss in this section the main types of biomass-derived fuels, their characteristics and properties, and the main methods for their synthesis. Using biofuels creates the opportunity to mitigate carbon dioxide emissions. It is important to assess the carbon mitigation potential for each specific case when a biofuel is used.

Since living species rely ultimately on solar energy for life, it appears that biomass is a true renewable energy resource. The most common way to use biomass energy is through direct incineration to generate heat. The thermal energy obtained can then be converted into electricity with the help of heat engines (viz., Rankine cycle). There are other ways to use biomass energy, including gasification, fermentation to produce biogas or alcohols, and so on. Other uses of biomass, besides the energy (heat or power) production, are in the chemical and pharmaceutical industries, and even in civil engineering works as construction material. Examples of biomass are as follows:

- Wood: trees, tree stumps, dead trees, branches, and wood residuals from forestry and wood-processing industries.
- Agricultural residues: straw, sugarcane fiber, rice hulls, animal wastes, and dried dung.
- Biodegradable wastes from municipal and industrial sources.
- Vegetable oils: palm oil, corn oil, peanut oil, soy oil, and canola oil.
- Energy crops: *Miscanthus*, *Sorghum*, switchgrass, hemp, sugarcane, corn, poplar, eucalyptus, willow, and aquatic plants.

Because it has lower sulfur content and ash-forming components, biomass combustion is cleaner than fossil fuel combustion. Plants absorb carbon dioxide from the atmosphere and convert it into carbohydrates and fiber through photosynthesis. By combusting biomass, the same carbon dioxide is released back to the atmosphere. Consequently, biomass is a CO_2-free renewable source. The general chemical model of biomass is $C_{X_C}H_{X_H}O_{X_O}N_{X_N}S_{X_S}ash_{X_{ash}}(H_2O)_{X_w}$; X_i is number of constituents of species i. Dry biomass has the chemical formula $C_{X_C}H_{X_H}O_{X_O}N_{X_N}S_{X_S}ash_{X_{ash}}$. Molecular mass of dry biomass can be calculated as follows:

$$M = 12 \times X_C + X_H + 16 \times X_O + 14 \times X_N + 32 \times X_S + M_{ash}X_{ash}. \tag{6.9}$$

Dry basis percent by weight of each component (C, carbon; H, hydrogen; O, oxygen; N, nitrogen; S, sulfur) is

$$\begin{aligned} w_C &= 12 \times \frac{X_C}{M}; w_H = \frac{X_H}{M}; w_O = 16 \times \frac{X_O}{M}; w_N = 14 \times \frac{X_N}{M}; w_S \\ &= 32 \times \frac{X_S}{M}; w_{ash} = M_{ash} \times \frac{X_{ash}}{M}, \end{aligned}$$

where typically $w_{ash} = 0.5$–12% dry basis. The moisture content is $w_w = 0$–50% wet basis and the molecular mass of wet biomass becomes

$$M_{wet} = M + X_w \times 18. \tag{6.10}$$

Thus, the correlation between moisture content by weight and molar is

$$w_w = \frac{18X_w}{M + X_w \times 18}, \tag{6.11}$$

or

$$X_w = \frac{w_w M}{18(1 - w_w)}. \tag{6.12}$$

The gross calorific value (GCV) on dry basis is, according to Speight (2008),

$$\begin{aligned}\mathrm{GCV} = {} & 34.91\,w_{\mathrm{C}} + 117.83\,w_{\mathrm{H}} + 10.05\,w_{\mathrm{S}} - 1.51\,w_{\mathrm{N}} - 1.034\,w_{\mathrm{O}} \\ & - 2.11\,w_{\mathrm{ash}}.\end{aligned} \tag{6.13}$$

Net calorific value (NCV) is calculated based on GCV using the same equation as for coal (6.2). According to Szargut (2005), the chemical exergy of biomass (the contribution of the sulfur is negligible) is

$$ex_{\mathrm{Bmass}}^{\mathrm{ch}} = NCV \times \left(1.0347 + 0.014\frac{X_{\mathrm{H}}}{X_{\mathrm{C}}} + 0.0968\frac{X_{\mathrm{O}}}{X_{\mathrm{C}}} + 0.0493\frac{X_{\mathrm{N}}}{X_{\mathrm{C}}}\right). \tag{6.14}$$

The complete biomass combustion with stoichiometric oxygen is written as follows:

$$\begin{aligned}& \mathrm{C}_{X_{\mathrm{C}}}\mathrm{H}_{X_{\mathrm{H}}}\mathrm{O}_{X_{\mathrm{O}}}\mathrm{N}_{X_{\mathrm{N}}}\mathrm{S}_{X_{\mathrm{S}}}\mathrm{ash}_{X_{\mathrm{ash}}}(\mathrm{H_2O})_{X_{\mathrm{w}}} + X_{\mathrm{O_2}}\mathrm{O_2} \\ & \quad \rightarrow X_{\mathrm{C}}\mathrm{CO_2} + X_{\mathrm{H_2O}}\mathrm{H_2O} + X_{\mathrm{N}}/2\mathrm{N_2} + X_{\mathrm{S}}\mathrm{SO_2} + X_{\mathrm{ash}}\mathrm{ash},\end{aligned} \tag{6.15}$$

where

$$X_{\mathrm{O_2}} = 2X_{\mathrm{C}} + X_{\mathrm{H}}/2 + 2X_{\mathrm{S}} - X_{\mathrm{O}};\ X_{\mathrm{H_2O}} = X_{\mathrm{H}}/2 + X_{\mathrm{w}}.$$

Table 6.6 compiles the calorific properties of main biomass types. Combustion is the most direct method to convert biomass energy into useful thermal energy (and if it is the case, subsequently, thermal energy conversion into electricity). The additional advantage of direct combustion is the possibility to completely use the fuel.

Other methods such as gasification involve incomplete combustion—that is, partial oxidation—and production of a gaseous fuel comprising methane, hydrogen, and carbon monoxide. The conventional gasification is used as an old technology, in which biomass is heated at high temperatures to disengage combustible gas. Optimal gasification conditions were found to be about 500°C, atmospheric

Table 6.6 Calorific properties of the main biomass types

Biomass	GCV, MJ/kg (d.b)	Moisture, w% (w.b.)	NCV MJ/kg (w.b.)	NCV MJ/dm^3 (w.b.)
Wood pellets	19.8	10	16.4	9.8
Wood chips	19.8	30–50	8.0–12.2	2.8–3.9
Grass	18.4	18	13.7	2.7
Cereals	18.7	15	14.5	2.5
Bark	20.2	50	8.2	2.6
Sawdust	19.8	50	8.0	1.9
Straw	18.7	15	14.5	1.7
Oilve	22.0	58	7.3	6.3

Data from Van Loo and Koopejan (2008)

Note: *w%* percent by weight; *d.b.* dry basis; *w.b.* wet basis pressure, and a steam/biomass ratio equal to 10:1. In the presence of a nickel catalyst, hydrogen at 65% (volume) was produced under these conditions. At temperatures from 800°C to 900°C, biomass is converted completely to CO and H_2, although in practice some CO_2, water, and other hydrocarbons including methane remain in the output stream. The char compositions produced by the fast pyrolysis of biomass can be gasified with gasifying agents. Air, oxygen, and steam are widely used gasifying agents. There are three typical gasification reactions:

- *Oxygen gasification*: It yields a better quality gas of heating value of 10 to 15 MJ/Nm^3. In this process, temperatures between 1,000°C and 1,400°C are achieved. O_2 supply may bring a simultaneous problem of cost and safety.
- *Air gasification*: It is the most widely used technology, as it is cheap, it forms a single product at high efficiency, and it does not require oxygen. A low heating value gas is produced containing up to 60% N_2 having a typical heating value of 4 to 6 MJ/Nm^3 with by-products such as water, CO_2, hydrocarbons, tar, and nitrogen gas. Reactor temperatures between 900°C and 1,100°C have been achieved.
- *Steam gasification*: Biomass steam gasification converts carbonaceous material into permanent gases (H_2, CO, CO_2, CH_4, and light hydrocarbons), char, and tar. This method has some problems such as corrosion, poisoning of catalysts, and minimizing tar components.

In addition, another method for gasification is supercritical water gasification (SCWG), which uses the property that water is miscible with organic substances above the critical point. This method is preferred especially for high-moisture biomass. One of the key works on supercritical gasification of wood is by Modell et al. (1978); a patent was issued for their work in 1978. They reported the effect of temperature and concentration on the gasification of glucose and maple sawdust in water in the vicinity of its critical state (374°C and 22 MPa). No solid residue or char was produced. Hydrogen gaseous concentrations up to 18% were observed.

When used for power generation, the synthetic biogas (biosyngas) produced by the gasification process needs a good amount of excess air for achieving satisfactory fuel utilization. Biosyngas can be used further for hydrogen production. The available methods for producing hydrogen from biomass are reviewed in Kalinci et al. (2009).

Another method for biomass conversion is pyrolysis, which implies heating in the absence of oxygen. Pyrolysis allows the release of volatile matter that is recovered as gas, char, and tar. Pyrolysis is an important process for obtaining energy from biomass. Valuable hydrogen-rich gas can also be generated by pyrolysis. As reviewed in Kalinci et al. (2009), there are three methods for producing hydrogen-rich gas. First, hydrogen can be produced by steam reforming of the pyrolysis liquid obtained from the pyrolysis of biomass. Second, the pyrolysis process is carried out at around 700°C, including the removal of the tar content of the gas and improving the quality of the product gas. In the second stage, catalysts, normally dolomites and Ni, high temperatures, steam, and oxygen could be used. In the third option, the pyrolysis occurs at a lower temperature (<750°C), and a catalyst is incorporated into the same reactor where the pyrolysis of biomass occurs. Catalytic pyrolysis/gasification is one of the promising options for tar elimination from the product gas. Fast pyrolysis of plant material, such as wood or nutshells, at temperatures between 800°C and 900°C leaves as little as 10% of the material as solid char and converts some 60% into a gas rich in hydrogen and carbon monoxide. This makes fast pyrolysis a competitor of conventional gasification methods. Pyrolysis may be defined as an incomplete thermal degradation of carbonaceous materials into char, condensable liquids (tar, oils, or bio-oils), and noncondensable gases in the absence of air or oxygen. Fast pyrolysis is a thermal or thermocatalytic conversion process that can be characterized by rapid heating rates, quick quenching, and exclusion of oxygen from the reaction zone. It yields valuable chemical intermediates as well as synthesis gas from biomass. Fast pyrolysis is interesting, as a liquid is produced that offers advantages in storage and transport and versatility in applications, although it is still at a relatively early stage of development. Typical properties and characteristics of wood-derived crude bio-oil have been investigated. Water comes from moisture in the feed and reaction water and cannot be separated. The values can range from 15% to 35%. Bio-oil has an HHV of about 18 MJ/kg, as it is produced with about 25 wt% water that cannot be separated.

The main methods to convert biomass into useful forms of energy are presented schematically in Fig. 6.3. Apart from combustion (which generates thermal energy and/or power), gasification, and pyrolysis processes, as discussed above, additional methods are the biophotolysis process that uses bacteria (e.g., genetically modified cyanobacteria) to generate methane or hydrogen, and fermentation processes. Gasification, pyrolysis, and biophotolysis all produce mixtures of combustible gaseous fuels. The fermentation process results in liquid fuels of the alcoholic type or in biogas. The major content of biogas is methane (55–65% by volume),

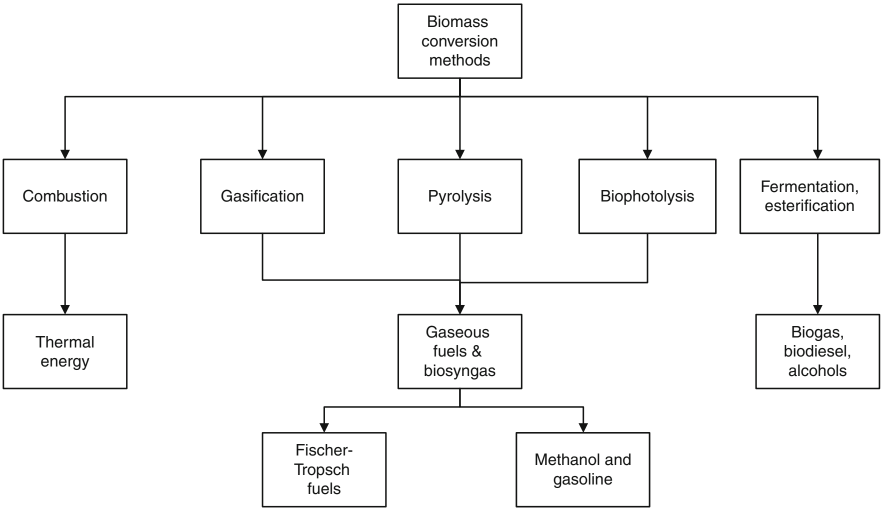

Fig. 6.3 Biomass conversion methods

while the rest is mainly carbon dioxide (35–45% by volume) and other gases (hydrogen, nitrogen, oxygen, and ammonia). Biophotolysis, fermentation, and other methods such as artificial photosynthesis and the biological water-gas shift process can be classified as biological methods for biomass conversion.

Fermentative methods can be produced using anaerobic organisms and/or photo-fermentation. Also, many phototropic organisms can produce hydrogen with the aid of solar energy, which is called photosynthesis conversion. Furthermore, some bacteria may easily perform water-gas shift reactions. Berberoglu et al. (2008) reported a factor 5.5 increase in hydrogen production by *Anabaena* variables ATCC 29413 using the Allen–Arnon medium compared with BG-11 and BG-110 media. The results were obtained with a flat panel photobioreactor made of acrylic and operated in two stages at 30°C. Dark as well as photoheterotrophic (light fermentation) microorganisms can convert carbohydrate-rich biomass into combustible fuels such as hydrogen or biogas. The primary source for biogas in biohydrogen generation is animal manure, which delivers the necessary microorganisms for anaerobic digestion. Energy crops are also used for biogas production, such as maize, sunflower, and grasses. Landfills are deposits of solid wastes with high content in organic materials and represent a major source of biogas. The first step is the acid or enzymatic hydrolysis of biomass into a highly concentrated sugar solution, which is further fermented by anaerobic organisms to produce volatile fatty acids (VFAs), methane or hydrogen, and CO_2. The organic acids are further fermented by the photoheterotrophic bacteria (*Rhodobacter* sp.) to produce CO_2 and methane or hydrogen, which is known as light fermentation. Combined utilization of dark and photofermentations was reported to improve the yield of hydrogen formation from carbohydrates. Many phototropic organisms, such as purple bacteria, green bacteria, cyanobacteria, and several algae can be used to produce hydrogen with the aid of solar energy. Microalgae, such as green algae and cyanobacteria, absorb light energy and generate electrons. The electrons are then transferred to ferredoxin (FD) using the solar energy absorbed by the photosystem. The mechanism varies from organism to organism, but the main steps are similar.

Other types of fuels from biomass are those based on vegetable oils. They have a different structure than petroleum-based fuels. It appears that some vegetable oils can be used in diesel fuel replacement from both an ecological and economical point of view (see Demirbas 1997). Common vegetable oils and their main properties are listed in Table 6.7.

It can be observed from Table 6.7 that the HHV of all vegetable oil fuels is at about the same value, which is ~39 MJ/kg. The saponification value of oil represents the number of milligrams of sodium or potassium hydroxide required to saponify 1 g of oil, which is a measure of the molecular weight of the fatty acids that compose the oil. The iodine number gives the number of grams of iodine in 100 g of oil. Demirbas (1997) correlated the HHV of vegetable oils with saponification and iodine values:

$$\mathrm{HHV} = 49.43 - 0.041\,\mathrm{SV} - 0.015\,\mathrm{IV}, \tag{6.16}$$

Table 6.7 Technical parameters of main vegetable oil fuels

Oil	Saponification value, mg KOH/g oil	Iodine value, g I/100 g oil	HHV, MJ/kg
Ailanthus	206.34	107.18	39.38
Beech	202.16	105.15	39.59
Castor	202.71	88.72	37.41
Corn	194.14	119.41	39.64
Hazelnut kernel	197.63	98.62	39.83
Laurel	220.78	69.82	39.32
Linseed	188.71	156.74	39.33
Peanut	199.80	119.35	39.45
Poppy seed	196.82	116.83	39.59
Rapeseed	197.07	108.05	39.73
Sesame	210.34	91.76	39.42
Soybean	194.61	120.52	39.63
Spruce	207.09	96.08	39.44
Sunflower seed	191.70	132.32	39.57
Walnut kernel	190.82	135.24	39.56

Data from Demirbas (1997)

where SV and IV represent the saponification and iodine values, respectively; HHV is given in MJ/kg.

Alcohols are probably the most common liquid fuels derived from biomass. Practically, all alcohols can be combusted to generate heat, but only a few are suitable for common motor vehicles: ethanol (C_2H_5OH), methanol (CH_3OH), butanol (C_4H_9OH), and propanol (C_3H_7OH). Ethanol has qualities that makes it a competitor of gasoline in spark ignition engines because it allows for a higher compression ratio, higher flame speed, and leaner operation despite the fact that the energy density of ethanol is lower than that of gasoline and it is more toxic. The general equation for oxidation of alcohol is

$$C_xH_{2x+2}O + 1.5xO_2 \rightarrow xCO_2 + (x+1)H_2O. \tag{6.17}$$

Alcohols can be produced from biomass mainly via fermentation processes. However, it is also possible to synthesize methanol from syngas. Simply, methanol can be produced by hydrogenation of carbon monoxide over a suitable catalyst, usually copper or zinc oxides:

$$CO + 2H_2 \rightarrow CH_3OH, \tag{6.18}$$

which is an exothermic reaction favored by high pressure and low temperature.

Biodiesel is obtained by esterification of vegetable oils; the resulting fuel is clean of sulfur and can be used directly in diesel engines. An alternative route for biodiesel fabrication starts from biosyngas and uses the Fischer–Tropsch method for conversion to diesel fuel. Biodiesel can be used in blends with petroleum diesel to reduce the carbon and sulfur emissions. Also, alcohols such as ethanol can be used to manufacture substitute diesel fuels. As is shown in the next section, ethanol blends can fuel diesel engines.

6.3.2 *Other Synthetic Fuels and Fuel Blends*

We described in the previous section the most common fuels synthesized from biomass. The focus in this section is on additional fuels that can be derived from conventional fossil fuels, and from other fossil fuels such as oil shale, oil sands, or from biomass. Such fuels include urea, ammonia, dimethyl ether, and others. Among possible synthesis methods, the Fischer–Tropsch method, methanol to gasoline conversion, and coal liquefaction can be used to produce synthetic fuels. Nonconventional fossil fuel sources include the following:

- Tar sand bitumen (also called oil sand or bituminous sand) is a sandstone mineral impregnated with heavy bitumen. Special conversion techniques must be applied to extract hydrocarbons from tar sand, as opposed to petroleum and natural gas, which are natural reservoirs of hydrocarbons.
- Oil shale is a sedimentary rock containing a large amount of kerogen (there is no specific chemical formula of kerogen). Petroleum can be produced from kerogen.
- Gas hydrates (mentioned briefly above) are crystalline solids in which methane is trapped in ice lattice.

Synthetic fuels can be produced by general methods, described also in Fig. 6.3 for biomass conversion. In addition, some specific methods are considered in the extraction phase, such as conversion of kerogen into petroleum, extracting bitumen from oil sands, and extracting methane from gas hydrates. These specific processes are not discussed here; rather, we mention a number of important synthetic fuels and fuel blends: hydrogen, ammonia, urea, dimethyl ether, and others.

The use of hydrogen as a synthetic fuel is believed to be a key solution for the future economy. As a transition period, various paths of producing hydrogen from fossil fuel, biomass, renewable resources, and a combination of these are considered. Hydrogen may be produced from many fossil-based sources including coal, natural gas, and hydrocarbons. As shown by Midilli and Dincer (2008), hydrogen is a sustainable solution for reducing fossil fuel consumption. Ammonia and its use as a fuel and hydrogen source are discussed in Chapter 7. Another synthetic fuel is urea, which can act as a hydrogen source. In the case study presented at the end of this chapter, the use of urea as a hydrogen source for cofueling vehicles is analyzed. Dimethyl ether (DME), having the chemical formula CH_3OCH_3, can be used as a fuel in diesel engines, or as a component of fuel blends for gasoline engine. One such fuel blend is formed by combining 30% DME and 70% LPG. Dimethyl ether can be produced from coal, biomass, or natural gas through various methods. The LHV of DME is 28.9 MJ/kg.

One of the known fuel blends is M85, which comprises 85% methanol and 15% gasoline. Because methanol can be derived from biomass sources, M85 can achieve 85% reduction of carbon dioxide reduction with respect to gasoline-only fuel. Pure methanol can be used as a fuel instead of gasoline, in which case it is called M100. Similarly, ethanol E85 fuel blend consisting of 85% ethanol and 15% gasoline is on the market. Since ethanol is derived from biomass, the wheel-to-wheel carbon dioxide reduction is at least 80%. Ethanol also can be used in diesel engines in the form of an ED95 blend, containing 95% ethanol and 5% ignition agent.

6.4 Case Study: Urea for Cofueling Vehicles

Biofuels, being derived from biomass, are considered CO_2-free fuels; thus, in a mixture with gasoline or diesel the carbon dioxide emissions can be reduced. In this case study, we investigate the use of urea as hydrogen source onboard vehicles, where hydrogen is employed as an additive to the primary fuel (gasoline or diesel) to enhance the engine efficiency and to reduce the carbon emissions. The study is based on a previous contribution by Zamfirescu and Dincer (2010). Urea can be synthesized from biomass or other renewable energy sources such that it results in a CO_2-free fuel. Urea, with the chemical formula $CO(NH_2)_2$, is massively produced in industry and is used as a fertilizer. It is considered a nontoxic substance, and several car manufacturers use it on their passenger vehicles for NO_x exhaust reduction. Currently, urea is synthesized from natural gas or petroleum, which is then reformed to produce hydrogen. The hydrogen is therefore combined with nitrogen (taken from air) to obtain ammonia, which will eventually be combined with CO_2 to produce urea. It is simple to produce urea starting only from biomass sources. Another path to synthesize urea is via hydrogen production from renewable sources (e.g., water electrolysis, thermochemical or photocatalytic water splitting, etc.), which is then combined with nitrogen to generate ammonia and with CO_2 to produce urea. The carbon dioxide can originate from various sources: recovered from the cement factories or power plants, taken from biomass combustion, extracted from atmospheric air. In any of these cases, the produced urea will be either a zero-carbon or a low-carbon hydrogen source. H_2 extraction from urea is relatively straightforward, and the following section discusses the involved processes in detail.

Urea is a particulate material delivered in small-size prills. It can be combusted, having a low calorific value comparable to that of wood, that is, about 10 MJ/kg. The average price of urea is $0.3 per kg. In what follows, we introduce the general model regarding the use of urea as a hydrogen source on vehicles to enhance gasoline and diesel fuel efficiency, and analyze the benefits of the method with respect to gasoline and diesel reference cases.

6.4.1 Analysis

Pyrolysis and hydrolysis of urea and ammonia cracking are the key processes for hydrogen generation from urea. All these processes are well studied, but their

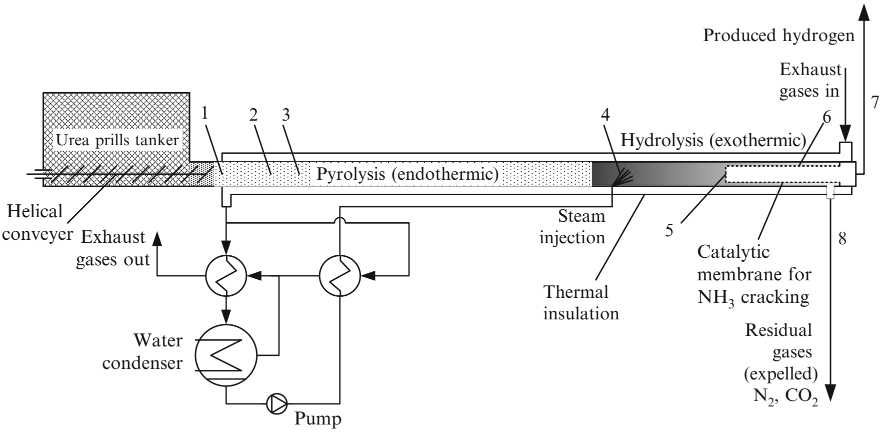

Fig. 6.4 General system layout for hydrogen generation from urea [modified from Zamfirescu and Dincer (2010)]

Table 6.8 Relevant parameters of the fuels included in the case study

Parameter	Urea	Gasoline	Diesel	Hydrogen
Chemical formula	$CO(NH_2)_2$	C_8H_{18}[a]	$C_{12}H_{23}$[a]	H_2
Molecular mass, g/mol	60.5	114.23	167	2
Heating value, MJ/dm^3	14	32	38	10.1[b]
Heating value, MJ/kg	10.5	44	45	142
Heating value, MJ/kmol	635.3	5026	7515	284
Density, kg/dm^3	1.323	0.72	0.85	0.071[b]
Specific cost, \$/kmol	18	158	196	10[b]
CO_2 emitted,[c] $\mathrm{mol_{CO_2}/mol_{fuel}}$	1	8	12	0

[a] Common chemical formula
[b] Cryogenic hydrogen at 20 K
[c] Assumed complete combustion

coupling with the aim to produce hydrogen received limited or no attention. Figure 6.4 introduces the overall system for generating hydrogen from urea.

Pure urea particles are kept in a tank and fed with a helical conveyer in a tubular pyrolysis reactor. The pyrolysis involves heating urea without the presence of oxygen. The general thermodynamic properties of urea and other involved substances are summarized in Table 6.8. Urea melts at 133°C, and after further heating it starts to decompose into ammonia and isocyanic acid according to the reaction (see Schaber et al. 2004)

$$CO(NH_2)_2(l) \rightarrow NH_3(g) + HNCO(g), \tag{6.19}$$

where HNCO(g) is isocyanic acid in gas phase. In a flow pyrolysis reactor, as the one indicated in Fig. 6.4, Eq. (6.19) would occur for the temperature range between 133°C and about 200°C.

After completing the pyrolysis, the hydrolysis of isocyanic acid is initiated by steam injection. This reaction is exothermic and evolves according to this formula:

$$HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g). \tag{6.20}$$

Several other intermediate compounds occur during the hydrolysis of isocyanic acid in the presence of urea, and these are mainly ammelide, ammeline, cyanuric acid, and biuret. All the intermediary products decompose if the temperature becomes high, so that at about 500°C the only products that exist include ammonia and carbon dioxide, according to the complete urea decomposition reaction as follows:

$$CO(NH_2)_2(l) + H_2O(g) \rightarrow 2NH_3(g) + CO_2(g). \tag{6.21}$$

The kinetics of Eqs. (6.19) to (6.21) has been comprehensively studied by Zanoelo (2009), who shows that reactor volumes would result at reasonable sizes for the reaction to be implemented on regular vehicles.

The reaction heat of isocyanic acid hydrolysis covers partially the necessary thermal energy for ammonia cracking, which is conducted in the last reactor shown in Fig. 6.4. This reactor is a catalytic membrane kind possessing a hydrogen-selective membrane impregnated with a ruthenium catalyst, which augments the rate of ammonia decomposition according to the reaction

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g). \tag{6.22}$$

The inner side of the membrane reactor is depressurized, thus allowing for hydrogen diffusion and separation. The residual gases comprising mainly carbon dioxide and nitrogen are expelled with possible heat recovery. The use of ammonia as a hydrogen source for transportation vehicles, according to Eq. (6.22), is discussed in detail in Chapter 7, which is dedicated to ammonia as a fuel, H_2 source, refrigerant, working fluid, and NO_x reduction agent.

The exhaust gases from the engine are used to drive the process of hydrogen production. After delivering heat to the pyrolysis reactor, the exhaust gases are cooled down to condense and separate the water. Once the water is separated, it is heated up and boiled to produce steam, which is injected into the hydrolysis reactor. The modeling assumes that all metallic parts including exhaust pipes and ducts, catalytic bed, and membranes are already at high temperature and that all processes occur at a steady state. The process of hydrogen generation from urea has various steps, explained next with reference to Fig. 6.4.

- State 1: granular urea at ambient temperature is forced into the pyrolysis reactor
- Process 1–2: urea is preheated up to its melting point, which is 133°C
- State 2: the melting temperature is achieved, and the melting process just starts
- Process 2–3: urea melting at quasi-constant temperature

- State 3: all urea is in liquid phase
- Process 3–4: urea pyrolysis according to Eq. (6.19); temperature increases
- State 4: temperature reached ~200°C and mostly ammonia and isocyanic acid remain in the stream (small concentrations of other products are also present)
- Process 4–5: hydrolysis of isocyanic acid (steam is injected); temperature increases
- State 5: temperature reaches 500°C, and Eq. (6.20) is assumed to be completed
- Process 5–6: thermocatalytic ammonia cracking according to Eq. (6.22)
- State 6: ammonia is cracked with a high yield
- State 7: hydrogen is separated through the membrane
- State 8: nitrogen and carbon dioxide remain in the main product stream

Under the assumption that the temperature of the environment is $T_0 = 298.15$ K, the enthalpy in state 1—for 1 mol of urea—is the same as the formation enthalpy; the formation enthalpy of urea is 333.1 kJ/mol. The enthalpy in state 2 is calculated based on urea's specific heat taken from the work by Andersson et al. (1993). On a molar basis,

$$h_2 = h_1 + c_\mathrm{p}(T_2 - T_1). \tag{6.23}$$

where $T_1 = T_0$ and $T_2 = 133$°C and the specific heat is assumed constant. The energy balance per mole of urea during the melting process is

$$h_3 = h_2 + \Delta h_\mathrm{m}. \tag{6.24}$$

where $\Delta h_\mathrm{m} = 13.9\,\mathrm{kJ/mol}$.

At the end of the pyrolysis process it is assumed that the only chemicals present in the stream are isocyanic acid and ammonia; all products are in the gaseous phase. Therefore, the enthalpy at state 4, per mole of urea, is

$$h_4 = h_{\mathrm{NH_3(g)}} + h_{\mathrm{HNCO(g)}}. \tag{6.25}$$

The enthalpies of all chemicals are referenced to the enthalpies of elements at 298.15 K.

At state 5, the urea decomposition is finalized, and the only considered products are 1 mol of carbon dioxide and 2 mol of ammonia; it results in

$$h_5 = 2h_{\mathrm{NH_3(g)}} + h_{\mathrm{CO_2(g)}}. \tag{6.26}$$

At state 6, one retrieves the decomposition products of 2 mol of ammonia and thus the enthalpy is

$$h_6 = 3h_{\mathrm{H_2(g)}} + h_{\mathrm{N_2(g)}} + h_{\mathrm{CO_2(g)}}. \tag{6.27}$$

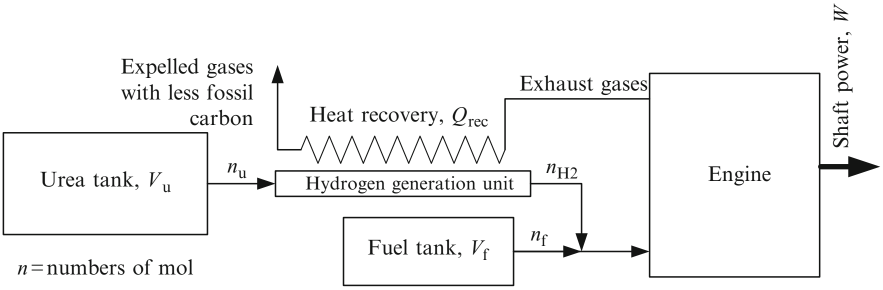

Fig. 6.5 Fueling system for combined urea–conventional fuel engine [modified from Zamfirescu and Dincer (2010)]

The energy balance on the pyrolysis reactor (endothermic) allows for the calculation of the necessary thermal energy input:

$$h_3 + Q_{pyr} = h_4. \tag{6.28}$$

The heat generated during the hydrolysis reaction (exothermic) results from the energy balance:

$$h_4 + h_{H_2O(g)@T_4} = h_5 + Q_{hyd}. \tag{6.29}$$

The necessary heat input to crack the ammonia is given by the balance (written for a mole of urea):

$$h_5 + Q_{crack} = h_6. \tag{6.30}$$

The overall energy balance on the hydrogen production system, for 1 mol of urea, gives the necessary heat input in the system as

$$h_1 + h_{H_2O(g)@T_4} + Q_{input} = h_6. \tag{6.31}$$

According to the system diagram shown in Fig. 6.4, it is assumed that steam is obtained from the exhaust gases by using heat recovery; the exhaust gases are cooled until steam condenses, then the needed quantity of water is extracted from the system and the remaining gases and water vapor are expelled into the environment.

Figure 6.5 shows the fueling system with combined urea–conventional fuel (gasoline or diesel) for an engine delivering exhaust gases at a high temperature (600–800°C). The considered engines may be of the internal combustion kind (conventional gasoline or diesel engine). During the running time, heat is recovered from the exhaust gases (Q_{rec}) and used to generate hydrogen from urea (as explained above). The fuel used to supply the engine is a combination of hydrogen and gasoline or hydrogen and diesel. During the start-up period, when the engine is cold, only gasoline is used as a fuel. Recall that one assumes that urea is synthesized from renewable sources and thus is considered a CO_2-free fuel. Since the running time represents at least 90% of the operation time of an engine, overall the carbon emissions should be smaller with respect to the reference gasoline or diesel cases.

We write c as the concentration of hydrogen in the fuel stream, as given below:

$$c = \frac{n_{\mathrm{H}_2}}{n_{\mathrm{H}_2} + n_{\mathrm{f}}}, \tag{6.32}$$

where $n_{\mathrm{H}_2}, n_{\mathrm{f}}$ represents the number of moles of hydrogen and conventional fuel, respectively, that form the fuel blend delivered to the engine. The HHV of the fuel blend becomes

$$\mathrm{HHV} = [c \times \mathrm{HHV}_{\mathrm{H2}} + (1 - c) \times \mathrm{HHV}_{\mathrm{f}}] \times (n_{\mathrm{H}_2} + n_{\mathrm{f}}). \tag{6.33}$$

The engine delivers shaft power (W) with efficiency, η; therefore,

$$W = \eta \times \mathrm{HHV}, \tag{6.34}$$

and rejects heat amounting to HHV $-$ W; a part $\zeta = 0 - 1$ of the rejected heat is recovered and can be used for hydrogen production from urea. The recovered heat is expressed by

$$Q_{\mathrm{rec}} = \zeta(1 - \eta) \times \mathrm{HHV}. \tag{6.35}$$

The number of moles of produced hydrogen is proportional to the recovered heat, namely,

$$n_{\mathrm{H}_2} = \frac{Q_{\mathrm{rec}}}{\Delta H_{\mathrm{gen}}}, \tag{6.36}$$

where ΔH_{gen} represents the thermal energy to generate 1 mol of hydrogen. From the stoichiometry, the number of moles of urea is

$$n_{\mathrm{u}} = \frac{n_{\mathrm{H}_2}}{3}. \tag{6.37}$$

The above Eqs. (6.19) to (6.37) form a thermodynamic model of the fueling system (Fig. 6.5), which can be exploited to study the feasibility of the solution with respect to energy and cost consumed per unit of power produced.

Table 6.9 State points of the hydrogen generation system from urea (enthalpy given per 1 mol of urea)

State	h, J/mol	T, K	Stream composition
1	−333,100	298.2	1 mol urea granules (compacted)
2	−322,300	406.2	1 mol urea solid at melting point
3	−308,400	406.2	1 mol of liquid urea at melting point
4	−148,563	473.2	1 mol of ammonia + 1 mol of isocyanic acid (both gases)
5	−408,570	773.2	2 mol ammonia + 1 mol carbon dioxide (both gases)
6	−268,381	773.2	3 mol hydrogen + 1 mol nitrogen + 1 mol CO_2 (gases)
7	66,211	773.2	3 mol hydrogen gas at low pressure
8	−334,591	773.2	1 mol nitrogen + 1 mol CO_2 (gases)

6.4.2 Results

The heat input necessary to decompose 1 mol of solid urea has been calculated according to the procedure introduced above. The results, including stream enthalpies, temperatures, and stream composition, are listed in Table 6.9. The associated reaction heats are calculated as follows:

- Pyrolysis heat input $Q_{\text{pyr}} = 160$ kJ/mol of urea.
- Hydrolysis heat output $Q_{\text{hyd}} = 34$ kJ/mol of urea.
- Ammonia cracking heat input $Q_{\text{crack}} = 140$ kJ/mol of urea.
- Total heat input $Q_{\text{input}} = 290$ kJ per mol of urea or ~100 kJ/mol of produced H_2.

In order to compare the novel fueling solution with the conventional ones in terms of energy and cost, it is important to determine the amount of shaft power generated per mole of conventional fuel consumed, denoted here with

$$W_{\text{f}} = W/n_{\text{f}}. \tag{6.38}$$

We introduce the dimensionless ratio of fuels molar content in the fuel blend as

$$\tilde{n} = n_{\text{u}}/n_{\text{f}}, \tag{6.39}$$

representing the number of moles of urea versus the number of moles of conventional fuel. Equation (6.33) becomes

$$\text{HHV} = (3\tilde{n}\,\text{HHV}_{\text{H}_2} + \text{HHV}_{\text{f}})n_{\text{f}}. \tag{6.40}$$

Also Eqs. (6.32), (6.36), and (6.37) result in

$$\text{HHV} = 3\frac{\Delta H_{\text{gen}}}{\zeta(1-\eta)}\tilde{n}n_{\text{f}}. \tag{6.41}$$

For any η and ζ as the parameters, Eqs. (6.40) and (6.41) can be solved simultaneously for $\tilde{n}$ and HHV. The resulting analytical expression for $\tilde{n}$ is

$$\tilde{n} = \left[\frac{1}{\zeta(1-\eta)} \times \frac{\Delta H_{\text{gen}}}{\text{HHV}_{\text{f}}} - \frac{\text{HHV}_{\text{H}_2}}{\text{HHV}_{\text{f}}} \right]^{-1}. \tag{6.42}$$

Assuming in Eq. (6.41) that the number of moles of hydrogen in the fuel blend is $n_{\text{H}_2} > 0$, the solution is feasible only if the recovered heat needed for urea processing is high enough such that

$$\Delta H_{\text{gen}} > \zeta(1-\eta)\,\text{HHV}_{\text{H}_2}. \tag{6.43}$$

The maximum practical value for $\zeta(1-\eta)$ can be estimated for the worst scenario at $0.5 \times (1 - 0.25) = 0.35$; thus, Eq. (6.43) is satisfied: 100 kJ/mol $> 0.35 \times 284 \cong 99$ kJ/mol. Based on Eqs. (6.34), (6.38), (6.41), and (6.42), the specific shaft power (per mole of fuel consumed) is

$$W_{\text{f}} = 3\frac{\eta}{\zeta(1-\eta)} \Delta H_{\text{gen}} \left[\frac{1}{\zeta(1-\eta)} \times \frac{\Delta H_{\text{gen}}}{\text{HHV}_{\text{f}}} - \frac{\text{HHV}_{\text{H}_2}}{\text{HHV}_{\text{f}}} \right]^{-1}. \tag{6.44}$$

Carbon dioxide emitted by the system originates only from the combustion of the conventional fuel and can be estimated based on W_{f} and the number of moles of CO_2 generated per mole of fuel combusted, $\tilde{n}_{\text{CO}_2}$; the mass of emitted carbon dioxide per unit of shaft energy is

$$m_{\text{CO}_2,\text{w}} = \frac{\tilde{n}_{\text{CO}_2}}{W_{\text{f}}}. \tag{6.45}$$

The total cost of fuel and urea per unit of shaft energy is

$$c_{\text{w}} = \frac{c_{\text{f}} + \tilde{n} c_{\text{H}_2}}{W_{\text{f}}}. \tag{6.46}$$

The total mass of fuel and urea per unit of shaft energy is given by

$$m_{\text{w}} = \frac{\tilde{n} M_{\text{u}} + M_{\text{f}}}{W_{\text{f}}}, \tag{6.47}$$

where M_{u}, M_{f} represents the molecular mass of urea and fuel, respectively.

The total volume of fuel and urea per unit of shaft energy is given by

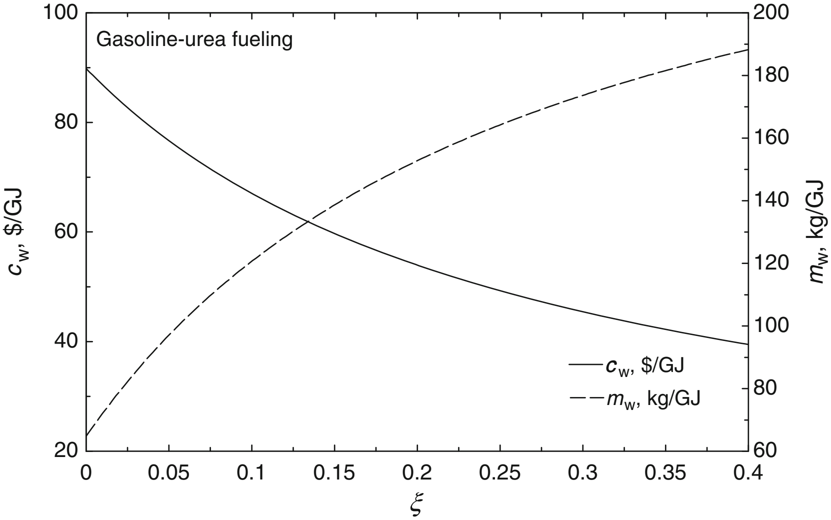

Fig. 6.6 Specific cost and total mass of gasoline + urea fuel per unit of shaft energy [data from Zamfirescu and Dincer (2010)]

$$v_w = \left(\frac{\tilde{n} M_u}{\rho_u} + \frac{M_f}{\rho_f} \right) W_f. \tag{6.48}$$

The mass fraction of urea with respect to conventional fuel $\tilde{m} = m_u / m_f$ is

$$\tilde{m} = \left(\frac{M_u}{M_f} \right) \tilde{m}, \tag{6.49}$$

whereas the volume fraction of urea versus fuel becomes

$$\tilde{v} = \left(\frac{\rho_f}{\rho_u} \right) \tilde{m}. \tag{6.50}$$

The results are presented graphically in Figs. 6.6 through 6.11 as a function of the proportion of heat recovery from the total heat recovered by the engine parameter ζ. We assumed that up to 40% of the rejected heat can be used for hydrogen production from urea, while the rest of the generated heat is lost. Moreover, the typical efficiency of a gasoline engine can be assumed to be 25%, while that of a diesel engine can go to 50%. One can assume, therefore, that the practical achievable efficiency of the engine used for this study is on average 35%.

It is noted that the urea–conventional fuel solution can be regarded as economically and ecologically attractive for specific applications. Figure 6.12 indicates the changes in specific cost, carbon dioxide emission, tank mass, and volume for

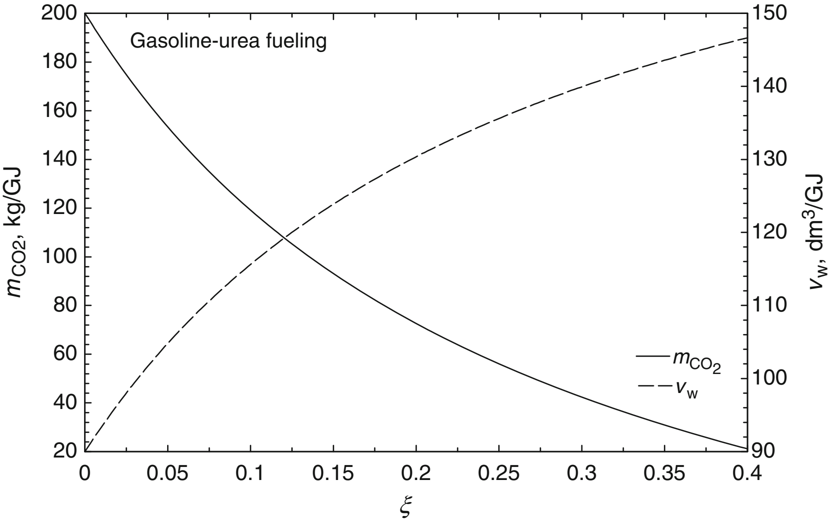

Fig. 6.7 Specific CO_2 emission and volume of gasoline + urea fuel per unit of shaft energy [data from Zamfirescu and Dincer (2010)]

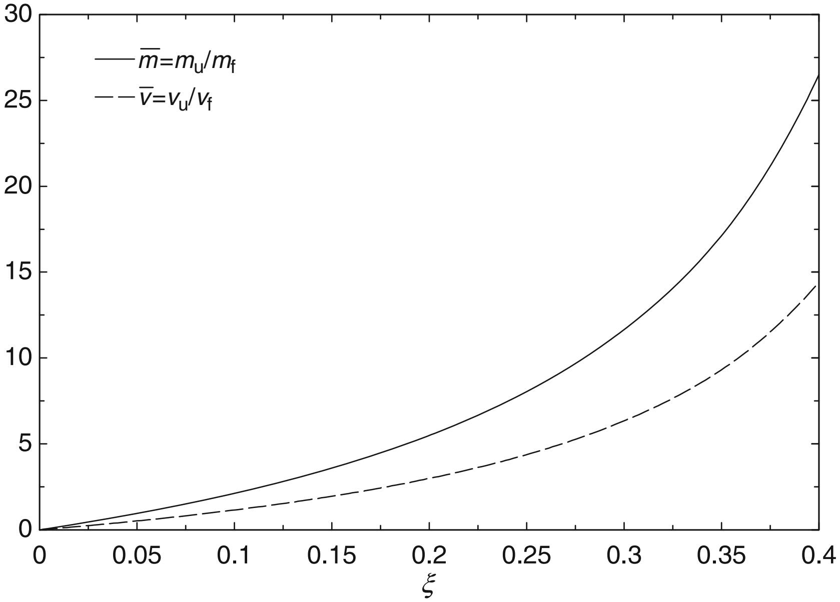

Fig. 6.8 Mass and volume ratio of urea vs. gasoline fuel as functions of the heat recovery factor [data from Zamfirescu and Dincer (2010)]

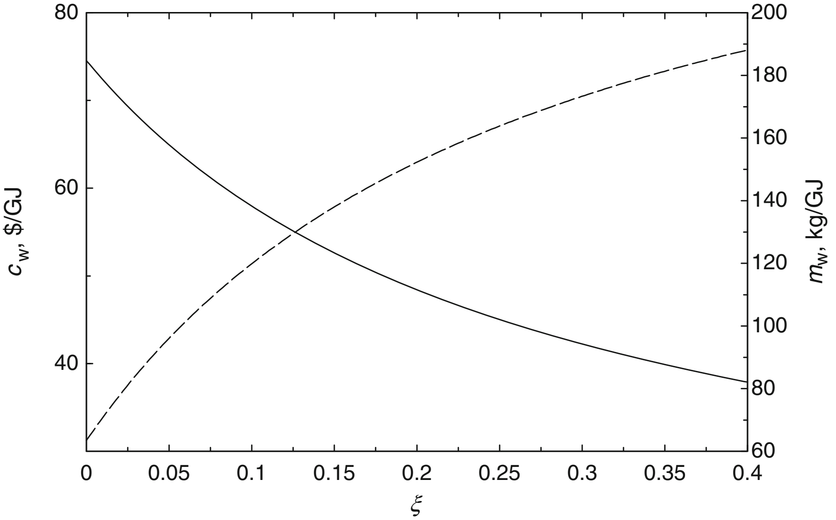

Fig. 6.9 Specific cost and total mass of diesel + urea fuel per unit of shaft energy [data from Zamfirescu and Dincer (2010)]

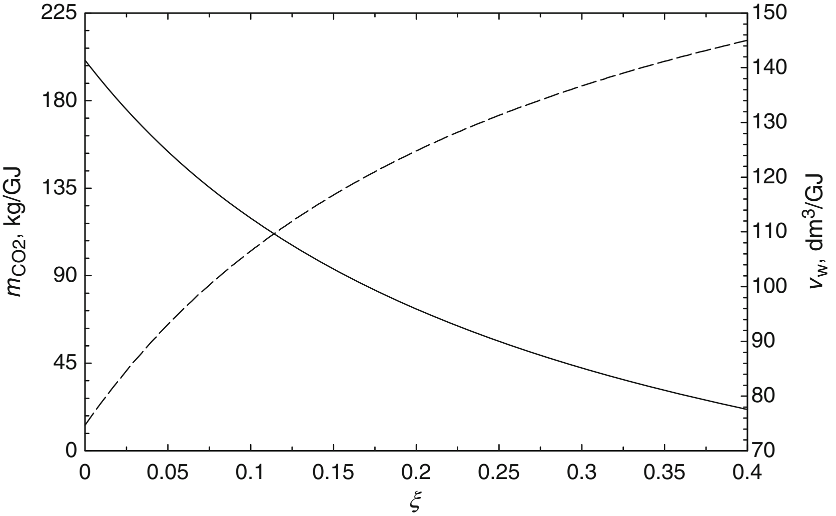

Fig. 6.10 Specific CO_2 emission and total volume of diesel + urea fuel per unit of shaft energy [data from Zamfirescu and Dincer (2010)]

the urea–conventional fuel case with respect to the reference conventional fuel case under the assumption that 10% of the total heat rejected by the engine is recovered and used for hydrogen generation from urea. The percentages in Fig. 6.12 are expressed in relative increments or decrements with respect to the

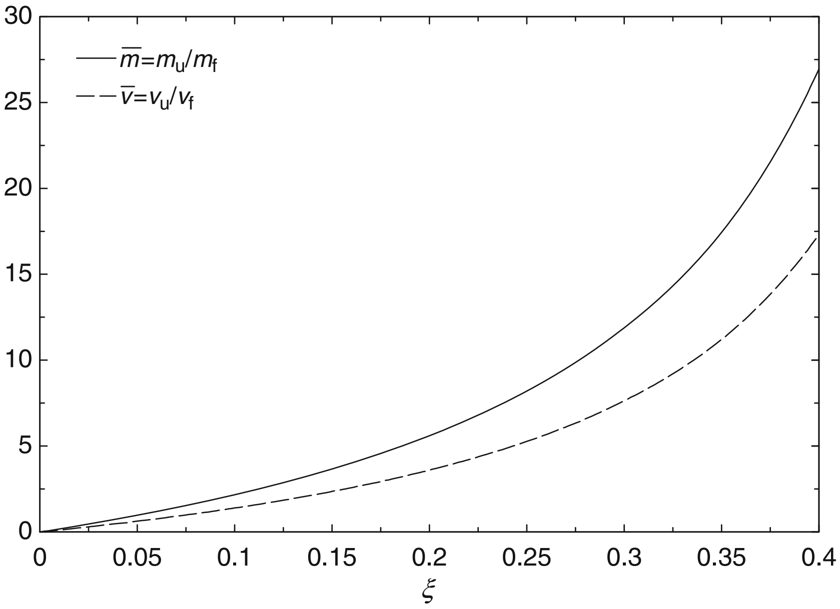

Fig. 6.11 Mass and volume ratio of urea vs. diesel fuel as functions of the heat recovery factor [data from Zamfirescu and Dincer (2010)]

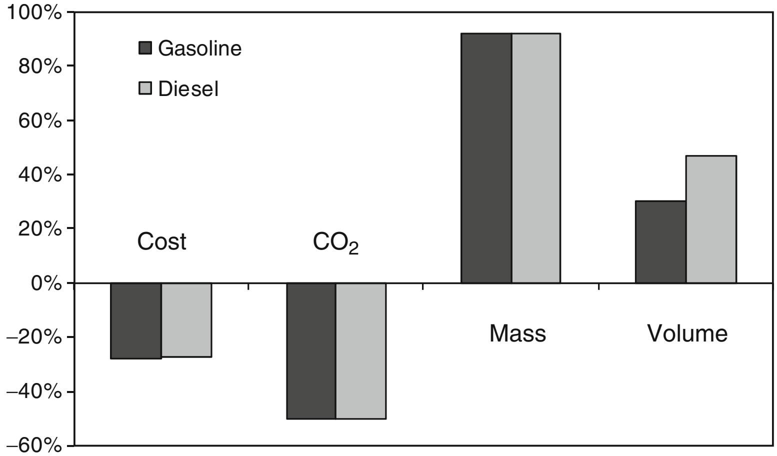

Fig. 6.12 Changes in specific cost, carbon dioxide emission, tank mass, and volume for the urea–conventional fuel case with respect to the reference conventional fuel case [data from Zamfirescu and Dincer (2010)]

reference case, namely, $(x - x_{\mathrm{ref}})/x_{\mathrm{ref}}$, where x represents specific cost, specific carbon dioxide emission, and specific fuel tank mass and volume; the term *specific* here means with respect to produced shaft power energy; the index *ref* represents the reference gasoline or diesel case. It is noted that the cost reduction, carbon mitigation, and mass tank increase for both cases are about the same, namely, 20%, 50%, and 90%, respectively. However, the tank volume increase for gasoline fuel case is about 20% less than in the case of diesel fuel tank, which may represent an advantage.

6.5 Concluding Remarks

Society is in a transition period from fossil fuel–based transportation toward a sustainable transportation sector. In the last century, the sources for transportation fuels and fuels for heating were mainly fossil-based: coal, petroleum, and natural gas. Presently, other fuel sources are considered, with the general aim to achieve cleaner combustion and reduced carbon dioxide emissions. New alternatives to conventional fossil fuels are those including oil sands, oil shale, and carbon hydrates. These fuel sources are considered special in conjunction with the production of synthetic fuels with reduced carbon. Such fuels may be hydrogen, ammonia, urea, methanol, or ethanol. It may be contemplated that carbon dioxide sequestration places can be installed at the extraction sites, where also the synthetic fuel production facility may be placed. Another alternative consists of promoting fuel blends of fossil-based fuel and biofuels. Such blends already exist in the form of ethanol–gasoline, methanol–gasoline, and biodiesel combined with petrodiesel. In this chapter, the fuel sources and the fuel properties, including lower HHV plus fuel's chemical exergy, were discussed in detail. Knowing the chemical exergy of a fuel is of major importance in thermodynamic analysis of processes that use the respective fuel, or in the manufacturing process itself of any specific fuel. Thus, chemical exergy values and formulas were given in the text for the main fuels. Using biofuels is of major importance because this is a real means to reducing carbon dioxide pollution and promoting cleaner options for transportation and energy sector. Many power generation systems—based on fuel combustion—eject heat into the environment. Recovering this heat for local hydrogen generation or cofueling purposes is a way of achieving improved fuel efficiency. The case study in this chapter illustrated the use of urea as a cofuel for diesel and gasoline engines. The advantages of cofueling are extremely relevant, for both mobile and stationary applications. It offers the opportunity to recover heat rejected by engines and upgrade the fuel value and thus improve the overall efficiency. Regarding the results of the case study, it may be shown that for urea + conventional fuel road vehicles, while the onboard fuel storage becomes about 50% larger and 100% heavier than for the conventional vehicle ones, the driving cost is reduced by about 30% and the carbon emissions by about 50%. These figures may be considered attractive enough to encourage further research on this topic.

Nomenclature

c	Molar concentration
ex	Specific exergy, kJ/mol
GCV	Gross calorific value, MJ/mol
h	Specific enthalpy, kJ/mol
H	Total enthalpy, kJ
IV	Iodine value
m	Mass ratio
M	Molecular mass, kg/kmol
$\mathcal{M}$	Specific CO_2 emission, kg/kg or kg/GJ
n	Number of moles
NCV	Net calorific value, MJ/mol
Q	Heat, kJ
s	Specific entropy
SV	Saponification value
T	Temperature, K
w	Moisture content, kg/kg
W	Work, kJ
X	Molar fraction

Greek Letters

η	Efficiency
v	Specific volume, kg/kmol
ρ	Density, kg/m^3
ζ	Heat recovery factor

Subscripts

0	Reference state
DAF	Dry and ash-free
f	Fuel
gen	Generated
rec	Recovery
w	Water

Superscripts

ch	Chemical
$(\sim)$	Dimensionless value

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Study Questions/Problems

6.1 Explain the difference between conventional fuels and alternative fuels.

6.2 Can sulfur be considered a fuel?

6.3 What is the best kind of coal with respect to emission per unit of energy embedded?

6.4 Explain the process of pyrolysis.

6.5 Based on Eq. (6.1) and Table 6.2, calculate the range of gross calorific values for anthracite.

6.6 Determine the range of carbon dioxide emission from lignite and compare your results with those shown in Fig. 6.2.

6.7 From which petroleum-derived fuel can one expect the minimum carbon dioxide emission per energy generated by combustion?

6.8 Describe the main features of biofuels.

6.9 Compare wood and olive kernels from the point of view of combustion energy and carbon dioxide emissions.

6.10 Comment on the main routes of biomass energy conversion methods.

6.11 It is given for one kind of vegetable oil fuel a saponification value of 190 mg KOH/g oil and an iodine value of 90 g I/100 g oil. Calculate the higher heating value.

6.12 Perform a case study similar to the one presented in Section 6.4 for the case of ammonia–gasoline cofueling.