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MINERAL PROCESSING TECHNOLOGIES ON BIOMASS PREPARATION FOR BYPRODUCT BENEFIT IN METALLURGY

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AFFIDAVIT

I hereby declare that the submitted thesis entitled

Mineral Processing Technologies on Biomass Preparation for Byproduct Benefit in Metallurgy

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ABSTRACT

The current thesis reviews wood biomass technology emphasizing its preparation with mineral and thermal processing techniques; records experimental work with three biomass types; and covers a thermodynamic model of zinc oxide reduction with biocoal.

The document is divided into Theory, Experiments, and Carbothermic Model of Zinc Oxide Reduction. Theory covers legislation on biomass usage in Austria, biomass as technical material, and biocoal production. It presents the Austrian legal framework for forestry and its implications on harvesting and material supply. It also describes biomass from a physicochemical viewpoint, mainly its carbonization. Additionally, several topics on biomass economy are discussed: biomass trade, resources, prices, and logistics. Finally, pelleting, or biomass densification, is presented.

Experiments, on the other hand, covers studies on raw and processed biomass, and pellet production with thermally processed biomass and electric arc furnace dust (EAFD). Bark, saw dust, and wood chips from were studied as potential materials to be used in engineering. The analyses emphasized the material physicothermal properties: particle size distribution, bulk density, proximate, elementary, and thermal analyses. From the studied biomass types, wood chips were selected for further study. The material was carbonized under inert atmosphere to release moisture and volatile matter, leaving behind its (fixed) carbon content alone; *i.e.*, turning raw biomass into biocoal. The biocoal thereof produced was pelleted with EAFD containing zinc oxide. Unfortunately, resource and equipment constraints rendered impossible to measure experimentally the actual reduction. Nevertheless, it is expected that the theoretical amount of carbon in biocoal be sufficient to reduce the zinc oxide contained in EAFD into zinc, which could then be recovered.

Finally, the carbothermic reduction of zinc oxide was analyzed by thermodynamic principles and methods. Hence, first principles such as the laws of thermodynamics served for the deduction of relations between temperature, pressure, further process parameters, and material properties. The results thus obtained coincide with experimental findings, as well as current operating conditions of industrial processes.

KEYWORDS biomass, Austrian biomass legislation, biomass economics, biomass thermal conversion, carbonisation, biocoal, pelleting, zinc oxide reduction

ZUSAMMENFASSUNG

Die vorliegende Dissertation beinhaltet einen Überblick über Biomasse mit dem Schwerpunkt auf Waldprodukte, vorwiegend Holz, und dessen Vorbereitung mittels mechanischer und thermischer Verarbeitungstechnologien. Außerdem wird eine Reihe von Experimenten mit drei spezifischen Biomassetypen beschrieben, nämlich mit Baumrinde, Waldresten und Holzspänen. Weiters wird ein thermodynamisches Model der Zinkoxid-Reduktion durch aus Biomasse hergestellte Biokohle vorgestellt.

Die Arbeit ist in drei Teile eingeteilt, Theorie, Experimente und Carbothermisches Modell der Zinkreduktion. Im theoretischen Teil werden die Gesetzgebung über die Verwendung von Biomasse in Österreich und der Stand der Technik bei der Produktion von Biokohle aus Biomasse behandelt. Zusätzlich wird der rechtliche Rahmen für die Forstwirtschaft in Österreich vorgestellt und dessen Implikationen in der Holzgewinnung und -versorgung. Biomasse wird auch von einem physikochemischen Standpunkt beschrieben, insbesondere die Holzverkohlung. Außerdem werden unterschiedlichen wirtschaftlichen Aspekte der Biomasse diskutiert: Handel, Ressourcen, Preisgestaltung und Logistik. Zum Schluss wird die Pelletierung am Beispiel von kompaktierter Biomasse vorgestellt.

Der experimentelle Teil umfasst Studien über unbehandelte und vorbehandelte Biomasse und die Produktion von Pellets mit thermisch vorbehandelter Biomasse und Lichtbogenofen-Staub. Baumrinde, Sägespäne und Holzspäne wurden als potentielle Ausgangsstoffe für den technischen Einsatz untersucht. Die Analyse setzte den Schwerpunkt auf die physikothermischen Eigenschaften: Partikelgrößenverteilung, Schüttdichte, Immediatanalyse, elementare und thermische Analyse. Holzspäne wurden für weiterführende Studien ausgesucht. Dabei wurden die Holzspäne unter inerter Atmosphäre verkohlt, vorbei Feuchte und flüchtige Bestandteile entweichen. Die auf diese Weise gewonnene Biokohle wurde mit Zinkoxid-haltigem Lichtbogenofen-Staub pelletiert. Aufgrund von Ressourcen- und Anlagen-Engpässen war die Bestimmung der Zinkoxid-Reduktion nicht möglich. Die Ergebnisse lassen erwarten, dass der theoretische Kohlenstoffgehalt in der Biokohle ausreicht, um Zink aus dem Zinkoxid-haltigen Lichtbogenofen-Staub zu reduzieren und wiederzugewinnen.

Schließlich wurde die karbothermische Zinkoxid-Reduktion mittels thermodynamischer Grundlagen und Methoden analysiert. Dazu erfolgte die Ableitung der Beziehungen zwischen Temperatur, Druck und weiteren Prozessparametern sowie von Materialeigenschaften aus Grundprinzipien wie den Hauptsätzen der Thermodynamik. Die daraus erhal-

tenen Ergebnisse stimmen mit den experimentellen Ergebnissen und Betriebsbedingungen aktueller industrieller Prozesse überein.

SUMMARY

The current thesis consists of a bibliographical review on biomass, with emphasis on forest-derived products, specially wood, and with emphasis in its preparation, using Mineral Processing Technologies. It also records a series of experiments performed with three specific biomass types: bark, forest residues, and wood chips. Such experiments were carried out using mineral processing as well as thermal processing techniques. Additionally, it presents a thermodynamic model of zinc oxide reduction by coal (carbon) produced with biomass (biocoal).

The document is hence divided into three main parts: Theory, Experiments, and Carbothermic Model of Zinc Oxide Reduction. In the theoretical part, legislation on the usage of biomass in Austria, the state-of-the-art on the usage of biomass as technical material, and biocoal production are treated. Chapter 3 begins presenting the Austrian legal framework for forestry and its implications on tree harvesting, basically showing that strict environmental regulations guarantee future material supply. Then, Chapter 4 describes biomass as used in energy-related sciences from a physical, chemical and thermal viewpoints. In Chapter 5, biomass thermal conversion routes are briefly reviewed with an emphasis on carbonization. Then, from Chapter 6 to Chapter 9, several topics on biomass economy are discussed, such as biomass trade, resources, prices, and logistics. From Chapter 10 to 13, engineering related subjects are presented; for instance, forest harvesting, biomass conditioning, storage, and transportation of raw material at a technical level, giving data on methodologies, performances, yields and energy consumption. Finally, Chapter 14 treats biomass densification, *aka* pelleting.

It is worth mentioning that the information on prices, trade, availabilities and technical information was gathered from the sources presented in the references. However, for establishing the costs analysis of logistics, many site- and project-specific information is required, such as salaries of personnel, prices of electricity, performance and energy consumption of specific machinery, and on so forth. This in-depth, case-sensitive analysis is beyond the scope of the present document. Due to this fact, information on logistics was taken directly from a technical report written by Roald Suurs, [125], considered as representative. Nevertheless, the figures therein were updated when pertinent and compared with other relevant sources of information.

On the other hand, the experimental part was divided into three main areas of study: raw biomass, thermally processed biomass, and pellet production with thermally processed biomass and electric arc furnace dust. Three types of raw biomass (bark, saw dust, and wood chips) from four lo-

cations in the province of Styria, Austria, were studied as potential materials to be used in mineral processing. The analyses emphasized the physicothermal properties of biomass: particle size distribution, bulk density, proximate analyses (moisture, volatile matter, ash yield, and fixed carbon contents), elementary analyses (CHNSO), and thermal analyses (enthalpy change of combustion, *aka* higher heating value). From the three types, one was selected to further study, wood chips, as it shows the most suitable engineering properties. Then, wood chips were carbonized under inert atmosphere to release moisture and volatile matter, leaving behind its (fixed) carbon content alone, turning thus raw biomass into biocoal. The biocoal thus produced was then pelleted with electric arc furnace dust containing zinc oxide. Unfortunately, resource and equipment constraints rendered impossible to measure experimentally the actual reduction. It is expected, however, that the theoretical amount of carbon in biocoal be sufficient to reduce the zinc oxide into zinc, which could then be collected and hence recovered.

As for the carbothermic model, a modern approach to thermodynamics was used to study zinc oxide reduction. Traditionally, thermodynamics is based on « four laws », expressed in terms of heat and temperature. Then, the « fundamental equation » is derived and used as the main analytical tool. This traditional approach has some shortcomings, such as inconsistencies, somehow ad-hoc extensions of the fundamental equation, and so forth. Herein, on the other hand, we follow modern treatments on the subject, particularly [43] and [25]. Such an updated approach is based on energy and entropy local conservation and para-conservation laws, macrostates, and parameter spaces, wherefrom temperature, pressure, and other process parameters and material properties are defined and their interrelations derived. The advantage of this modern view of thermodynamics is a great gain in generality, consistency, and coherence. Moreover, the results thus obtained are in full agreement with those produced following tradition.

Finally, the information herein given was gathered and extended from a series of reports presented to the Chair of Thermal Processing and on technical reports, laboratory reports, and presentations of work done at the Chair of Mineral Processing. In all cases, the relevant information, data and figures were updated as of October, 2016, and more bibliographical research was added, as well as the experimental research.

CONTENTS

Part I

THEORY

1

PRELIMINARIES

1.1 RESEARCH TOPIC

The main topic of the current thesis is the

Usage of Mineral Processing Technologies on Biomass Preparation for Byproduct Benefit in Metallurgy.

1.2 JUSTIFICATION OF THE RESEARCH

The interest on biomass in current research has been growing over the last years, because it is a versatile resource that has been used in both fuel and chemical reagent production. For instance, one of the most attractive products derivable from biomass is *syngas*: a mixture of CO, H_2, CO_2 and CH_4 resulting from the thermal decomposition (*thermolysis*) of solid biomass and subsequent gasification of the volatiles, tars and char that is being used in the production of electric current, to heat homes and industrial processes and of a wide range of chemicals, such as bioethanol, biogas, coal (biocoal), tar, synthesis gas (syngas), alcohols (ethly-, butyl-, isopropyl-), polyols (glyceral, ethylene gycal), ketones (acetone), acids (acetic, lactic, butyric), yeast, glucose, ammonia, acetic acid, synthetic gasoline and many others.

Additionally, besides the industrial, technical and scientific interest in biomass, there are also other incentives for its usage. In Austria, the political driving force for using renewable materials, such as biomass, comes from the country's commitment to comply with the EU Energy Directive with the major objectives of releasing 34 % of the final energy consumption from renewable sources until 2020, reducing the green-house gases emissions and increasing energy efficiency.

However, despite the intense research in this wide field, there are some topics that are seen as crucial in a successful large-scale implementation of biomass:

1. optimization (cost minimization) of biomass logistics, primary of efficient biomass collection and transport chains;
2. efficient and cost effective drying of biomaterial as a key first step in the usage of biomass in technical applications;
3. improvements in the second generation of wood pellets for households or industries as efficient energy carriers;
4. step-wise thermal (mainly pyrolysis) production of fuels, valuable chemical products, oils and lubricants from biomass;
5. microwave induced drying or pyrolysis of biomass.

1.3 RESEARCH OBJECTIVES

The main objective of the present research is to determine the most suitable treatment (including pre- and post-treatments) for the preparation of biomass with the aim of using it in the benefit of metallurgical applications.

Accordingly, the specific research objectives are:

1. to present the state-of-the-art on lignocellulosic (wood) biomass: origin, thermochemical composition, technologies for biomass processing and conversion;
2. to research the current status of wood biomass and forestry in Austria, such as current legislation, standards, and resources;
3. to determine experimentally the most suitable biomass type to be used in metallurgy, along with its pretreatment and treatment by studying their behavior under thermal conversion;
4. to study the products and byproducts released during thermal treatment of biomass and their possible impacts in both industrial processes and environment;
5. to study the optimal process parameters to produce biocoal from various feedstocks;
6. to determine the optimal process parameters for pellet (briquettes) production;
7. to estimate unit costs per pretreatment and treatment that then could be used in detailed cost analysis of different routes on biomass profit; and
8. to determine, as an application, the usage of biocoal in the reduction of ZnO included in dusts from electric arc furnaces.

2

INTRODUCTION

The ever growing worldwide population requires ever growing power to satisfy its needs, such as to generate electric current, to fuel vehicles and to provide heat for homes and industrial processes, [98]. By the end of 2008, the world needed *ca.* 518 EJ largely covered by Non-Renewable Energy Sources (NRES) (85%) – fossil fuels met the 80% alone – and the rest by Renewable Energy Sources (RES), *see* Figure 2.1.

Fossil fuels usage, however, has lead to concerns on their social, environmental and health impacts during their exploration, exploitation, production and consumption – specially the anthropogenic greenhouse gas release, [96, 133]. Additionally, oil prices fluctuations and steady increments during the past few decades have directed scientists, investors, policy- and law-makers and finally governments towards non-fossil energy sources.

Oil prices have been historically tied to the political stability of oil exporting countries, [31].

In this line, Secondary Energy Sources (SES) intend to deal with the problems posed by the fossil fuels usage and are indeed a common alternative in developing countries, [42]. Unfortunately there are still unreliable statistics on their actual consumption and the available data are based rather on estimations and capacities, [31, 61], *see* Figure 2.1.

Rural bioenergy shared the 63 % of the SES in 1995 in developing countries, [42].

Within the SES, RES play an important role, specially solid biomass. It is, in fact, presently under heavily subsidized and intensive research, [58], due to its versatility. It has been utilized as fuel to generate electric current, to heat homes and industrial processes and also to produce a wide range of chemicals, *i.a.* bioethanol, biogas, coal (biocoal), tar, syngas, alcohols (ethly-, butyl-, isopropyl-), polyols (glyceral, ethylene gycal), ketones (acetone), acids (acetic, lactic, butyric), yeast, glocuse and many others, [26, 98, 41, 143]. Thus, not only is biomass intended to replace oil as energy source, but also to invade the petrochemical industry as reactant, [41].

From the myriad of products derivable from biomass, syngas is one of the most adaptable, since it can be employed for chemical synthesis and as a fuel. Technically, syngas is a mixture of CO(g), H_2(g), CO_2(g) and CH_4(g) resulting from the thermolysis of solid biomass and subsequent gasification of the volatiles, tars and char, while leaving behind a coal-like byproduct called biocoal. Raw biomass and biocoal pellets, on the other hand, are the most successful solid biomass based products in the market, mainly because they are being used as energy carriers with the intention to replace coal and other traditional fuels in home and industrial heating. Both of these most interesting biomass derived products, syngas and

SNG, NH_3, CH_3OH and synthetic gasoline are some of the syngas derivable chemicals, [98].

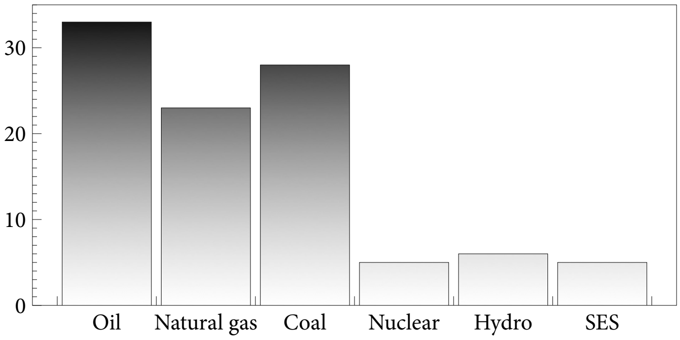

Figure 2.1 In PJ, worldwide energy consumption according to source: i) Non-renewables: fossil fuels (coal, natural gas and oil) and nuclear and ii) renewables: hydro and secondary energy sources, SES, (biomass, solar, tidal and wind). Primary energy sources: fossil fuels, hydro and nuclear. [31, 61].

biocoal, are prepared via thermal decomposition of biomass – thermolysis. Carbonization, a form of thermolysis, is the thermal preparation of biomass at temperatures ranging from 400 °C to 800 °C within an inert atmosphere that leaves condensable, non-condensable volatiles, tars and char, [143].

thermolysis: set of endothermic chemical reactions occurring as a substance breaks up into at least two substances when heated.

Finally, as mentioned before, because of the myriad products converted from and uses of biomass, this documents focuses the topic on the usage of biomass for the production of biocoal.

3

AUSTRIAN LEGAL FRAMEWORK FOR FORESTRY

In Austria, the political driving force for using renewable material comes from the country's commitment to comply with the EU Energy Directive with the major objectives of releasing 34 % of the final energy consumption from renewable sources until 2020, reducing the green-house gases emissions and increasing energy efficiency, [48].

Through the Energy Strategy Austria (*Energiestrategie Österreich*) supported by public and private organizations.

Since biomass is nowadays considered as a renewable source with neutral emissions of CO_2 and low emissions of SOx's and NOx's under controlled combustion, it then offers great technical potential. Thus, to avoid over exploitation, forests – a main biomass resource – are object to regulation. In Austria, the legal framework for forestry is granted by the Austrian Constitution and basically enforced by the Forest Act. The latter provides the legislation for a long-term framework for forestry as it defines its basic goals and management. Additionally, the Act establishes the legal order of governmental action and delegation of authorities and other policies, such as forest grants, [59]. Its implications directly influence any exploitation plan of Austrian forests as it will be discussed throughout this chapter.

NOx's and SOx's are generic terms for nitrogen oxides and sulfur oxides.

3.1 AUSTRIAN FOREST ACT

Originally published in 1975 and amended in 1996, the Austrian Forest Act gives to forests four specific functions, [60]:

1. Production, with priority to a sustainable timber production;
2. Protection, against erosion and natural hazards;
3. Welfare, such as the protection of environmental goods, like drinking water;
4. Recreational.

In order to grant such functions, the Forest Act focuses on the preservation of forests areas, of the productivity of forests sites and of forests yields for future generations by the following principles, [65]:

1. Conservation of woodland and forest soil;
2. Preservation of forests, so that the productive capacity of the forest soil is ensured and the economical as well as the social functions of the forests are guaranteed;
3. Assure potential yields for further generations;

4. Reafforestation and special treatment of protective and protection forests;
5. Forest protection against pests, fires and air pollution;
6. General restrictions related to harvesting;
7. The obligation of forest enterprises to employ trained personnel, and a required standard of education;
8. Governmental support to improve all effects of forests;
9. Forest land use planning and a forest development plan;
10. Tasks and objectives of the Federal Forest Research Institute, Vienna;
11. Rules regulating the use of forest seedlings and forest plants suited to the site for afforestation and reafforestation;
12. Supervision by government forestry authorities of forestry rules and regulations.

Additionally to these principles and the regulations therefrom derived, forests owners have agreed on the regulations of the Pan-European Forest Council, PEFC, – the major certification system to guarantee the sustainability of biomass feedstock from forests. To enter into the program, every company or owner has signed a declaration to sell certified wood. The responsible then commits to fulfill guidelines and specific regional arrangements, [48]. This certification system is also in accordance to the Second Ministerial Conference on the Protection of Forest in Europe, [57].

Finally, the Act also considers forest grants managed by the federal and provincial governments with conservation and improvement of forest conditions as objectives, [65].

3.2 THE AUSTRIAN FOREST PROGRAMME

As depicted in Figure 7.2 and discussed later, forestry is the origin of a wide and complex chain of products involving many different actors: forest owners, wood traders, traditional industries (sawmill and pulp and paper) and recently nontraditional ones (like the energy sector). This complex interaction has resulted in conflicts of interest among all the involved parties. For this reason, a new form of policy making was created: the Forest Dialogue, with the goal on the search for solutions to the various conflicts of interest associated with the forest through the participation of public institutions, interest groups and non-governmental organizations – specifically, according to [55]:

> The concrete target of the Forest Dialogue is to formulate strategies and guidelines for forest-relevant fields of action that can be implemented operationally while safeguarding the property and usufructul rights. The forest programm as an action framework for all forest-related activities will determine the forest policy in Austria in the short, medium and long term.

Since 2003, the Austrian Forest Programme was developed from the Austrian Forest Dialogue to assure forest management. The program is developed in seven areas, [56]:

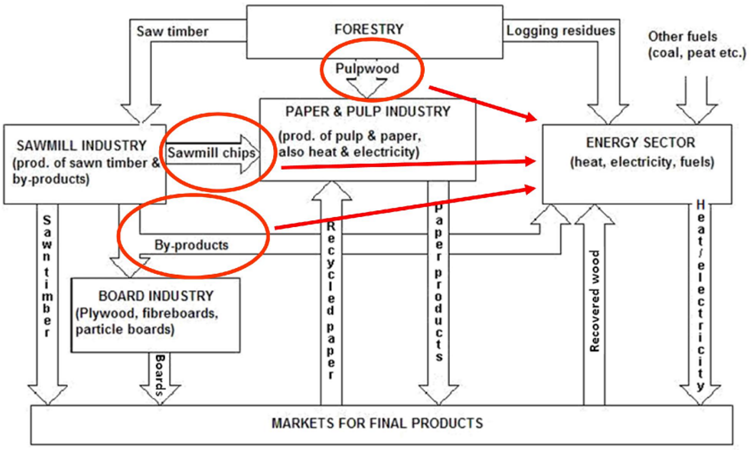

Figure 3.1 Competition for raw materials in the forest industry complex, [104]

1. Contribution of Austrian forests to climate protection;
2. Health and vitality of Austrian forests;
3. Productivity and economic aspects of Austrian forests;
4. Biodiversity in Austrian forests;
5. Protective functions of Austrian forests;
6. Social and economic aspects of Austrian forests;
7. Austria's international responsibility for sustainable forest management.

Since 2006, a permanent body, the Forest Forum, was established to discuss the forest-political developments, to harmonize interests in forest-related subjects, to provide for the controlled implementation and to develop the Work Programme of the Austrian Forest Dialogue. It is also responsible for addressing current important forest-related issues, [136].

3.3 IMPLICATIONS OF THE AUSTRIAN FOREST POLICY AND FORESTRY

The principles of the Austrian Forest Act translate into practice via strict environmental regulations that directly affect forest harvesting and thus the whole chain, as seen in Figure 7.2, [60, 118, 135]. Some relevant operational implications of the law will be treated later. However, it is worth to mention that, while limiting the amount of feedstock that can be harvested, the Policy guarantees its sustainability. This is an important point when developing a long term biomass-based project that should be stressed to and considered by possible industrial partners. For instance, some biomass traders have expressed sustainability concerns and therefore concerns on biomass adoption, *see* Table 3.1, [76].

Additionally, since the whole Austrian forest area is certified by the PEFC and forests owners have agreed on its terms, this enables the Chain of Custody Certification the reproduction of the whole production chain from the PEFC certified forest over wood processing and producing until the finished product, [48]. That is to say, not only is sustainability guaranteed – and thus feedstock supply for the future, but also acquisition of certified material.

Although certification does not imply quality.

On the other hand, even if harvesting is limited, forests companies and subsides are allowed to enhance the forest functions and thus forestry competitiveness and timber production via road constructions, mobility and extension system, but, however, only under regulative terms, like the obligation to employ professional forest personnel and under provincial level supervision by forest authorities on matters as forests, forest management, logging and exterior services, [60]. Moreover, such enhancement can be carried out aided by federal or provincial grants.

Finally, the Forest Dialogue brings an open platform for discussing forest-related issues. It may be interesting to follow the results of the meetings as more industries become interested in the feedstock. Also, it might happen that concerns on using foreign material, and thus on import regulations, arise, so to protect local biomass producers. For instance, some Swedish forestry companies had quited the business, due to a more competitive European wood market, [125].

Country	Raw material supply	Logistics	Sustainability	End-Product quality	Lack of financial support	Unfair competition with fossil fuels
Austria	▓					
Belgium	▓			▓	▓	
Czech Rep.					▓	▓
Denmark				▒		
Finland	▓		░	░	▓	
Germany	▓		▓			
Greece						▓
Italy	▓	▓				
Latvia		▓			▓	
Lithuania	▒					
Netherlands	▓		▓		▓	
Norway						▓
Portugal	▓	▓		▓		▓
Slovenia					▓	
Slovakia		▓			▓	
Spain		▓		▓	▓	
Sweden	▓	▓				▓
UK	▓		▓			▓

Major barrier	Minor barrier	Opportunity
▓	▒	░

Table 3.1 Overview of main barriers for increase utilization and trade of solid biomass as perceived by traders in different EU countries, [76]

4

BIOMASS

In this chapter, the general properties of lignocellulosic (plant-based) biomass are reviewed. It begins with how it is currently understood in energy-related sciences, its origin and taxonomy.

Then, biomass properties regarding its use as fuel are discussed. Such discussion includes current standards to characterize biomass elemental, biochemical and proximate composition and their relationship to standard essays of thermal properties.

Finally, the result of standard procedures collected in a database (Phyllis) were used to find trends among them and relate them to its thermal properties ending with a summary of the findings.

4.1 DEFINITION OF BIOMASS

The definition of biomass has changed in the past few decades from being a material produced by the development of living organisms (microorganisms, plants and animals), [75], to a RES from biological matter [27]. Such a change is mainly due to environmental and socioeconomic concerns translated into changes in governmental policies and legislations, [38].

RES: renewable energy source

Scientifically, on the other hand, the term has a precise, operational definition. Biomass is currently understood as a non-fossil organic, inorganic solid derived from natural and anthropogenic processes. It is naturally formed by material originated from microorganisms and plants via photosynthesis or produced by animal or human digestion and also formed by technogenic products of natural materials processing, [134].

Throughout this document, however, *biomass* will be understood as a non-fossil solid mixture of organic matter, inorganic matter and fluid matter produced by photosynthesis and originated from natural or from technogenic processes; *i.e.*, as a contemporary lignocellulosic biomaterial.

4.2 ORIGIN OF BIOMASS

Contemporary (non-fossil) biomass originates in large quantities by Nature through basically two processes: photosynthesis and animal and human digestion.

It also originates from or is processed in the so-called *technogenic* processes, [8]:

techno-: relating to technology or its use. *genesis*: the origin or mode of formation of something [71]

- industry (food, fibre and wood process residues),
- agriculture (energy and short rotation crops, crop residues and animal wastes),
- forestry (forest harvesting and supply chain; forest and agroforesty residues),

- waste (landfill gas, other biogas, municipal solid waste incineration and other thermal processes) and
- traditional biomass (fuel-wood, charcoal and animal dung from agricultural production).

4.3 TAXONOMY OF BIOMASS

Despite biomass being a « hot research topic », there is a lack of generally accepted terminology, taxonomic systems and standardization, because, perhaps, biomass is a complex material whose constituents depend on several factors as genesis, processing, state, use and so on. However, after having reviewed various arrangements, [73, 74, 45, 134], the usual pattern is to begin with biological information and biomass origin as the base for classification, then a classified material is studied at compositional level and finally at the level of thermal properties.

taxonomy: the branch of science concerned with classification, [71].

Biological information includes sorting biomass according to aquatic or terrestrial species – as algae, grass, straw, husks, wood, *&c.*; biomass origin: manure, municipal solid waste, sludge, *&c.*; compositional information: elemental and proximate analyses and thermal information: hhv .

hhv: higher heating value or heat of combustion

The result of studies on biomass are currently being gathered from scientific and technical publications and then compiled as databases. Biobib and Phyllis are the databases to be reviewed in Section 4.5.

4.4 AUSTRIAN STANDARDS FOR THE ANALYSIS OF BIOMASS

Before detailing the composition of biomass, it is appropriate to briefly discuss the current standards for its physical and chemical analyses.

Under the Austrian legislation, biomass states as an energy source, so there are normed procedures to qualify it and to quantify its properties regarding such utilization.

See, for instance, ÖNORM M 7111, 1996 and 7132, 1998 Appendix B

Table 4.1 partially lists standards for solid biofuels with their status until 12.03.2013. The complete and additional lists of related standards are presented in Appendix B.

It is interesting to notice that, although thermal processing, specially combustion, is used since the antiquity, the field is still under intensive development. For instance, as seen in Table 4.1, more than the half of the documents have the *pre standard* or *draft* status and almost all are at most five years old.

As shown, for example, in the ancient Greek myth of Prometheus who stole fire from Zeus and gave it to humankind.

Finally, the results of similar or equivalent procedures depending on the researcher's choice applied to different types of biomaterials are discussed in Section 4.6.

4.5 BIOBIB AND PHYLLIS BIOMASS DATABASES

Although there is neither an ÖNORM nor a DIN for the classification of biomass, there is an Austrian database for biofuels, BIOBIB, maintained by the Technical University of Vienna, [74]. It summarizes the properties of 331 different fuels classified into 8 groups and 33 sub-groups and varieties, *see* Table 4.2.

Phyllis, on the other hand, is a Dutch database for the composition of biomass and waste [45] based on a Dutch Standard for the classification of biomass, [73], and maintained by the Energy research Centre of the Netherlands.

Phyllis records information about 2946 individual materials sorted into 14 main groups and 101 subgroups. Groups and subgroups contain information not only of natural produced biomass, but also of human-made products and residues. The information about materials is, in its turn, divided into General Information, Material composition and Ash composition briefly summarized in Table 4.4.

The main difference between the two databases is thus the scope: Biobib treats biomass as fuel whereas Phyllis deals with the composition of biomass and wastes and also their thermal properties; that is, the latter's treatment is broader.

Not only is Phyllis a super set of Biobib, it is also more actively maintained: in the Biobib *Literature* section, the newest reference dates 1994. The Dutch database, on the other hand, was updated on 2013-10-14.

Phyllis was, in fact, originally based on Biobib.

Additionally, a key advantage of using Phyllis is the possibility to extract data in multiple ways and its « friendly » user interface. For instance, one can directly gather statistical information about groups, sub-groups and materials, rather than about only single materials – as in Biobib.

Therefore, it is generally advisable to use the Phyllis database over the Biobib one. It this document, thus, the Dutch information will be used, unless otherwise is specified.

Finally, it is worth to mention that Biobib contains information about the thermal ash behavior of materials determined as given by the DIN 51730 (DIN 51730, 1976). This piece of information is absent in Phyllis records. Additionally, energy crops are a separate category in the Biobib database.

Now replaced by the ÖNORM CEN/TS 15370, 2006, *see* Table 4.1

4.6 BIOMASS COMPOSITION

After having classified a biomaterial and gathered the pertinent standards, the second step is to research its composition. In thermal applications, specifically, it falls into two categories: material composition and ash composition.

Material composition usually contains information on proximate, ultimate, elemental analyses, thermal properties and biochemical composition. Ash composition includes the analysis of several elements and inorganic compounds in ash.

This section heavily relies on the work of the Energy Research Centre of the Netherlands and Vassilev et al., [45, 134], since they summarize the present understanding of the composition of « biomass as fuel ».

Alternatively, biomass could be regarded as a fuel; *i.e.*, a mixture of moisture, an active phase and an inert phase. This view and its relationship with its composition will be explained in Section 4.6.4.

Finally, despite biomass being defined in this document as a lignocellulosic material, researchers treat it in a broader sense: as being a complex substance consisting of organic and inorganic materials in variable proportion; *i.e.*, not only does the term include plant material, but also terrestrial and aquatic plant material, chars, manure, biofuels, refuse derived fuels, wood and so on. Thus, information is usually published in a such wider scope. It is, nonetheless, possible to find trends among such compounds.

The following subsections deal with the composition trends of various biomass groups rather than focus on a specific material or a specific group.

4.6.1 *Elemental and ultimate analyses trends*

In biomass-as-fuel technology, ultimate analysis is often used as a synonym of elemental analysis, but not always. For the purpose of this section, however, this differentiation is unnecessary and so the terms are used interchangeably.

For instance, in Phyllis: elemental analysis: quantification of 8 elements and ultimate analysis: 28

As shown in Table 4.5, biomass is composed by major, minor and trace elements, according to their concentration that varies among different biomass types. However, C, O, H, N, Ca and K predominate, regardless the biomaterial type, [134].

Major elements are mainly found in biochemical plant compounds as structural plant materials (cellulose, hemicellulose and lignin) and non-structural ones (extractives) and come into plants due to its metabolism, *see* Section 4.6.2.

Minor elements are present as inorganic compounds proceeding from plant growing and normally end up as gases or in ash after thermal processing. Examples are CO_2, SO_3, Cl, P_2O_5, SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, Na_2O, K_2O and TiO_2, [74, 45, 134].

Trace elements are present as elements, rather than compounds, and, since mostly metals, are generally regarded as toxic. Like derived species of minor elements, after processing, trace elements are found in ash. Some of them are Pb, Cd, Cu, Hg, Mn and Cr, [74, 45, 134].

It can be seen an important trend: C and H compounds are not present in ash; that is, they volatilize after combustion or thermolysis. This is the so-called active phase of biomass. Conversely, minor, their compounds and trace elements are mostly present in ash; so they do not volatilize either during combustion or thermolysis; *i.e.*, they form the inert phase of biomass.

On the other hand, based on elemental analyses of different biomass types, researchers, [35, 134], realized that as received (ar) biomass composition widely varies depending on the biological species or origin of a biomass sample, but dry biomass elemental composition lies between closed ranges regardless its diversity. Table 4.6 and Table 4.7 show the major biomass elements for several biomass types in daf basis.

daf: dry and ash free

In Table 4.7, the main elements of biomass are basically C, O and H for all the biomass types, then, depending on the type, Ca, N, K and Si are also included. Minor and trace elements also vary depending on the biomass types, but usually include Cl, P and S.

Among all the reviewed types, straw is the most heterogenous (14 different major and minor elements in total) whereas untreated wood is the most homogeneous (7). Perhaps, that is why wood has been used more confidently in thermal conversion processes, since it is the least complex material.

Additionally, since N and S are two elements, besides C, posing environmental concerns (*viz.* NOx and acid rain production), they should also be taken into account when choosing feedstock. It is interesting to notice that all the biomass types contain N, but in grass/plant it is a major element. On the S side, grass, plant, husk, shell, pit and straw contain it, but in small fractions, even behind, for instance, Ca or Cl. However, it does not appear as either major or minor element in untreated wood.

feedstock: raw material to supply or fuel a machine or industrial process

Finally, using published data, it is possible to represent the « average elemental (lignocellulosic) biomass composition » as

$$CH_{1.44}O_{0.647}N_{0.0136}Ca_{0.0055}K_{0.0054}\,. \qquad [4.1]$$

4.6.2 *Biochemical analysis trends*

Biochemical material consists of cellulose, hemicellulose, lignin, extractives, other compounds and yields ash when burnt, [86, 45].

Cellulose, hemicellulose and lignin are collectively called lignocellulose. Thus, since plant biomass is mostly formed by this triad, it is also known as lignocellulosic biomass.

Lignocellulose also gives structure to cell walls in plants, it is thus known as *structural material.*

Cellulose is a glucose linear polymer linked by β-1,4 glycoside bonds basically formed by cellobiose (glucose-glucose dimer). When it is hydrolyzed, cellobiose turns into individual glucose monomers (saccharification). Its thermal decomposition ranges from *ca.* 300 °C to 400 °C, [40, 86].

Hemicellulose is a short, highly branched polymer of five-carbons (C_5) and six-carbons (C_6). It contains xylose and arabinose (C_5 sugars) and galactose, glucose, mannose and rhamnose (C_6 sugars). It hydrolyzes more readily than cellulose yielding then mostly xylose and it thermally decomposes from approx. 200 °C to 300 °C, [40, 86].

Lignin is the major polyphenolic structural constituent of plants and the largest non-carbohydrate. It does not ferment but does thermally degrade, yet over a large temperature range: *ca.* 250 °C to 500 °C, [40, 86].

Extractives are materials that do not give structure to plants. They are washed out from them by using EtOH-toluene, 95% EtOH or hot water.

EtOH-toluene: shorthand for ethanol

When combusted, biomass yields ash: a solid material composed of Si, Al, Ca, Mg, K and Na. It will be discussed in more detail in Section 4.6.3.

« Other compounds » are resins, fats and fatty acids, proteins, pectin, starch and other non-structural carbohydrates.

Figure 4.1 presents the average composition of different types of biomass with values extracted from the Phyllis database. It is seen that the structural fractions (lignocellulose) vary for every biomass type while the fraction of non-structural material (other compounds) remains almost constant.

On the other hand, Figure 4.2 depicts the decomposition temperature ranges of lignocellulosic material when undergoing pyrolysis. It is seen that its thermal decomposition begins with that of hemicellulose and ends with that of lignin. Hemicellulose and extractives decomposition takes place faster in a low and narrow temperature range. For hemicellulose, this is due to its branched, amorphous arrange, [86]. Cellulose follows in the decomposition chain over a higher temperature range than that of hemicellulose that is also narrow. Lignin, finally, decomposes over a relatively large range (250 °C) that occurs in parallel to the thermolysis of hemicellulose and cellulose, [40].

The relationship between biomass composition and its thermal stability will be discussed in Section 4.6.4.

Hemicellulose is thus the most unstable polymer of lignocellulose as seen by its ability to readily hydrolyze and its shorter thermal decomposition range, whereas lignin is the opposite: unable to ferment and the most thermally stable. Then thermal processing of biomass is limited by the content of lignin: the lower its content, the easier to process. Moreover, the greater the content of hemicellulose, the better. Straws, grass

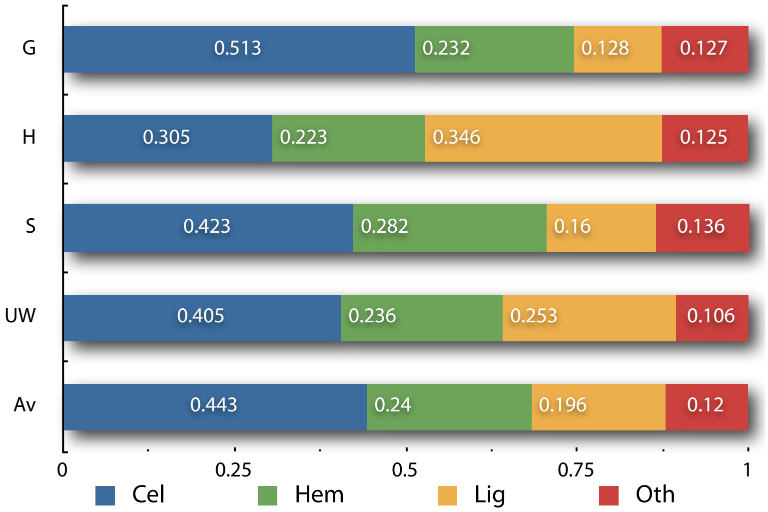

Figure 4.1 Average biochemical composition of various types of biomass. Cel: cellulose, Hem: hemicellulose, Lig: lignin, Oth: others, Av: average, G: grass/plant, H: husk/shell/pit, S: straw and UW: untreated wood mass fractions (kg kg^{-1}) in dry basis, [45]

and plant materials are thus the most suitable, while husk, shell, pits and untreated wood fall in the opposite category.

Finally, although the lignin content is a factor that influences thermal conversion, other ones should additionally be considered such as moisture content, ash yield and enthalpy of combustion (*see* Section 4.6.3 and Section 4.6.4).

4.6.3
Proximate analysis trends

Proximate analysis is rather a set of four analyses: ash yield (A), fixed carbon (FC), moisture (M) and volatile matter (VM). They are intimately related to thermal processing of fuels, specially coal, but currently are also being applied to biomass. Some of the discoveries by means of these techniques to biomass are presented in this subsection.

w_A: ash yield, w_{FC}: fixed carbon, w_M: moisture and w_{VM}: volatile matter mass fractions

Moisture includes water and other compounds that volatilize below 105 °C. It is evaluated by measuring the mass losses in air at 107(2) °C for 1 h, [91]. In biomass, w_M widely varies depending on the species and its origin. For instance, in husk, shell and pit, it ranges from 0. to 0.478 while for grass and plants from 0. to 0.950. In average, w_M equals 0.200.

107(2) °C: value and its uncertainty; *i.e.*, 107 ± 2 °C

Ash is the solid material that remains after combustion and ash yield represents its amount. It is regarded as the residual of the FC test and also a parameter whose value strongly depends on the biomass species and origin. For example, in husk, shell and pit, the $w(A, dry)$ ranges from 0.001 to 0.234. For grass and plants, from 0. to 0.458. In average, it equals 0.049.

Moisture and ash yield are parameters to consider not only due to their influence on the thermal behavior of the material, but also due to their influence on the economy of the process itself. For instance, to heat a wood sample from 25 °C to 105 °C, *ca.* 20% less energy is required when its w_M equals 0.0050 than when 0.155, [39, 64, 121].

$w_{H_2O} = 0.155$ (average moisture of untreated wood as received, *see* Figure 4.3).

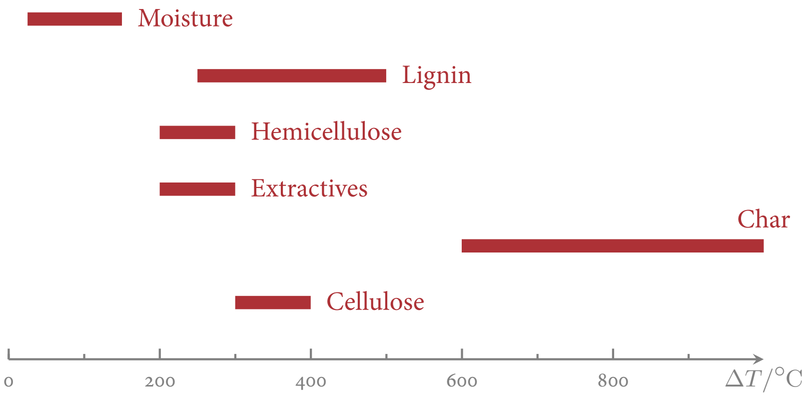

Figure 4.2 Volatilization temperature ranges of biomass main constituents during pyrolysis: M: moisture (drying), (volatilization of) Ext: extractives, Cel: cellulose, Hem: hemicellulose, Lig: lignin and Char: charcoal (carbonization), [40, 91]

In addition, due to the strict interpretation of the ASTM C618, ashes coming from biomass conversion processes – even those produced in the co-combustion with coal – are not accepted for cement manufacture, [143]. Hence, they become disposition problems: *viz.* collection, storage, transport and final disposition in landfills. On top of that, during combustion, inorganic material in biomass could damage burners and affect heat transfer elements, *see* Section 5.2.

On the other hand, VM includes the material that volatilizes at temperatures above 105 °C. It is evaluated by measuring the mass losses in an inert gas at 900(20) °C for 7 min, [91]. Again, w_{VM} ranges depend on the biomass type, lying between 0.200 and 1.00 in natural biomass samples with an average of 0.811.

FC is the solid combustible residue, part of C, that remains after biomass is heated and the volatile matter is expelled. It is determined by subtracting the w_{M}, w_{VM} and w_{A} from a sample or evaluated by measuring the mass losses in air at 815(10) °C for 1 h, [91] and regarded to be either graphite after pyrolysis, [21], or amorphous C after combustion, [75]. w_{FC} values range from 0.123 to 0.379 for natural biomass.

FC differs from elemental C content, because some C is lost during volatilization.

FC ignition temperature: 672 K to 755.4 K

As mentioned in Section 4.6.1, researches, [35, 45, 134], found out that, in a dry basis, proximate analysis ranges also narrow for biomass. For instance, for natural biomass, the w_{FC} range sizes 0.288 in ar basis vs. 0.256 in dry basis.

It can be seen that, since moisture leaves when biomass is dried and since ash remains after combustion, then the active, or usable, part of biomass should be the w_{FC} and w_{VM}.

For thermal applications, finally, the most profitable material is, therefore, the one having the lowest $w(M, ar)$ and w_{A} and, simultaneously, the highest w_{FC} and w_{VM}. Thus, comparing various biomass types, as shown in Figure 4.3, it seems that husk, shell and pit are the most desirable materials to work with – based on proximate analyses –, due to its low w_{M}, the lowest w_{A}, high w_{VM} and the highest w_{FC} among plant material.

$w(M, ar)$: mass fraction of moisture in a as-received basis

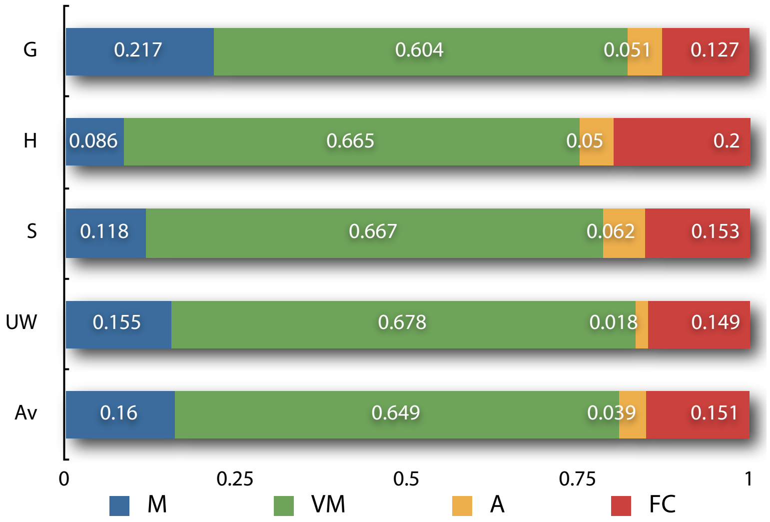

Figure 4.3 Proximate analyses of various types of biomass as received. Proximate analysis: ash yield (A), fixed carbon (FC), moisture (M) and volatile matter (VM) mass fractions ($\mathrm{kg\,kg^{-1}}$). Types of biomass: G: grass/plant, H: husk/shell/pit, S: straw, UW: untreated wood and Av: average, [45]

4.6.4 Thermal analysis trends

In general, the standard enthalpy change of combustion (Δh_c°) of a fuel gives an idea of its chemical energy content or, more properly, the energy released when it is burnt.

The ÖNORM EN 14918, 2010 standardizes this evaluation for biofuels.

In thermal analysis, however, it precisely means the quantification of the Δh_c° of a fuel under predefined conditions of temperature and pressure per unit mass; *i.e.*, the quantification of its Δh_c°.

It is usually called *heating value*, *calorific value* or *higher heating value*, *lower heating value* or *gross heating value* depending on the chosen temperature and pressure.

Higher heating value

The higher heating value (HHV) is the Δh_c° determined at standard atmospheric temperature and pressure (SATP) conditions before and after combustion; that is, by returning all the combustion products to 25 °C (condensing any vapor). Since it refers to an enthalpy, its unit is the joule, J. HHV is also known as gross calorific value, gross energy, upper heating value and mislabeled as specific HHV, hhv, heat of combustion, heating value or calorific value.

Absolute pressure: $p = 100\,\mathrm{kPa}$ (0.986 atm). Thermodynamic temperature: $t = 298.15\,\mathrm{K}$. Celsius temperature: $\theta = 25\,^\circ\mathrm{C}$

On the other hand, the specific higher heating value is the HHV per unit mass of fuel in $\mathrm{J\,kg^{-1}}$ or $\mathrm{MJ\,kg^{-1}}$.

In this document, the symbol $h^\circ(c, hhv)$ is used to represent the specific HHV; so it reads: the enthalpy of combustion at SATP conditions per unit mass of fuel. Variations of such a symbol are also used, for instance, $\Delta h_c(hhv, dry, \mathrm{MJ\,kg^{-1}})$ denotes the (specific) enthalpy of combustion as HHV (SATP) per unit of mass of dry fuel expressed in $\mathrm{MJ\,kg^{-1}}$. Moreover, to denote the molar enthalpy of combustion, $\Delta h_\mathrm{m}(c, hhv)$ will be used.

Entering into matter: given a fuel, its taxonomy and characterization come first, then its thermal properties are analyzed. So one ends up with pairs of composition and thermal analyses

Channiwala and Parikh, [35], studied peer-reviewed data on various fuels: elemental composition, hhv and 22 mathematical models proposed by earlier researchers based on experiments or statistics with the aim of compiling the whole information in one procrastinating tool. The developed correlation between the elemental analysis and ash yield of fuels and their $\Delta h_c(hhv, dry, \mathrm{MJ\,kg^{-1}})$ is:

$$\begin{aligned} h^\circ(c, hhv) \;&=\; + 34.91 w_\mathrm{C} + 117.83 w_\mathrm{H} + 10.05 w_\mathrm{S} - \\ &\quad - 10.34 w_\mathrm{O} - 1.510\, w_\mathrm{N} - 2.110 w_\mathrm{A}\,, \end{aligned} \tag{4.2}$$

where w_C represents the mass fraction of C; w_H of H; w_S of S; w_O of O; w_N of N and w_A of the ash yield – all in a dry basis.

The validity ranges for the parameters in Equation 4.2 are given in Table 4.8.

It can be seen in Equation 4.2 that $h^\circ(c, hhv)$ increases with the contents of C, H and S and decreases with the contents of O, N and with the ash yield.

On the other hand, while Equation 4.2 gives a general expression for different fuels, it is desirable to have one exclusive for biomass. In this line, Sheng and Azevedo, [120], realized that equations based on ultimate analysis give the best accuracy with experimental values and proposed their own for estimating the $\Delta h_c(hhv, daf, \mathrm{MJ\,kg^{-1}})$ of biomass:

$$h^\circ(c, hhv, daf) = -1.3675 + 31.37 w_\mathrm{C} + 70.09 w_\mathrm{H} + 3.18 w_{\mathrm{O}^*}\,, \tag{4.3}$$

where w_C represents the mass fraction of C; w_H of H; w_{O^*} of O and other elements, as S, N, Cl, *&c.*, and A; that is,

$$w_{\mathrm{O}^*} = 1 - w_\mathrm{C} - w_\mathrm{H} - w_\mathrm{A}\,, \tag{4.4}$$

where $w(A, \mathrm{kg\,kg^{-1}})$ represents the ash yield of the material. All the parameters in Equation 4.3 and Equation 4.4 are to be expressed in a daf basis.

Equation 4.3 has an average absolute error of 2.59%, an average bias error of 0.07% and a correlation coefficient, R^2, of 0.834 between experimental and calculated values. It is valid for $\Delta h_c(hhv, dry, \mathrm{MJ\,kg^{-1}})$ between [14.0 ; 22.5] and $\Delta h_c(hhv, daf, \mathrm{MJ\,kg^{-1}})$ within [16.0 ; 23.0].

Finally, the utility of $h^\circ(c, hhv)$ became broader, since it can also be used to establish the elemental composition of fuels. It was mentioned that sometimes ultimate analyses data are unavailable due to time or economical constraints, thus, in an interesting study, Bech et al., [24], developed a procedure to find the elemental composition of fuels based solely on Equation 4.2 and bomb calorimetry. Such a procedure with Equation 4.2, Equation 4.3 or Equation 4.5 – *see* Section 4.6.4 – could be used as a raw estimation of the composition of a fuel, for instance, in field applications.

Lower heating value

The LHV is the Δh_c° determined at SATP conditions before combustion, but at 150 °C after it; that is, by leaving all the combustion products to

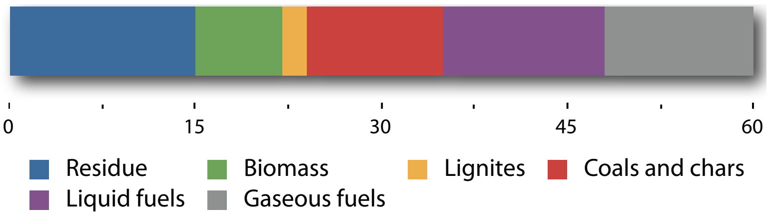

Figure 4.4 $\Delta h_c(hhv, dry, \mathrm{MJ\,kg^{-1}})$ spectrum of several fuels. i) Residue: refuse, municipal sewage water and sludge, waste; ii) biomass: mainly woods and straws; iii) liquid fuels: several hydrocarbons, oils and wood tar; iv) gaseous fuels: several hydrocarbons, [35], *see* Equation 4.2.

150 °C (not condensing any vapor). Since it refers to an enthalpy, its unit is the joule, J. Finally, it is also known as net calorific value or net heating value.

Alternatively, the LHV is the HHV minus the enthalpy of vaporization of water vapor (2260 $\mathrm{kJ\,kg^{-1}}$, [64]); *i.e.*, treating any water formed as vapor, thus releasing the energy to vaporize water as heat.

On the other hand, the specific lower heating value is the LHV per unit mass of fuel in $\mathrm{J\,kg^{-1}}$ or $\mathrm{MJ\,kg^{-1}}$.

In this document, the symbol $h^\circ(c, lhv)$ is used to represent the specific LHV; so it reads: the enthalpy of combustion at LHV conditions per unit mass of fuel. Variations of such a symbol are also used, for instance, $\Delta h_c(lhv, dry, \mathrm{MJ\,kg^{-1}})$ denotes the (specific) enthalpy of combustion as LHV per unit of mass of dry fuel expressed in $\mathrm{MJ\,kg^{-1}}$.

In matter: although in Section 4.6.4 it was mentioned that elemental analysis data give the best approximations for a fuel's chemical energy content, [120], yet they are not always available or consume time and resources. For these reasons, a mathematical expression relating proximate analysis and the energy content of a fuel has been recently developed by Erol et al., [47], for the $\Delta h_c(lhv, dry, \mathrm{MJ\,kg^{-1}})$ of biomass (Equation 4.5):

$$h^\circ(c, lhv) = -5.9 + 83.6 w_{\mathrm{FC}} - 116.\,(w_{\mathrm{FC}})^2 + 20.91\,(w_{\mathrm{VM}})^2 + 325.\,(w_{\mathrm{A}})^2 \,, \tag{4.5}$$

where w_{FC} represents the mass fraction of FC; w_{VM} of VM and w_{A} the ash yield of a biomaterial.

Finally, since the $h^\circ(c, hhv)$ and the $h^\circ(c, lhv)$ are expressions of the same thermochemical property, Δh_c, but in different conditions, all the discussion and results in Section 4.6.4 also hold here.

4.6.5 Biomass vs. other fuels: specific higher heating value

It is interesting to compare the specific higher heating value of biomass to that of other fuels, in order to have a wider perspective on their chemical energetic content and possible areas of application.

Channiwala and Parikh, [35], grouped the $h^\circ(c, hhv)$ values for several fuels into six categories: residues, biomass, lignites, coals and chars, liquid and gaseous fuels. With the result, it is possible to plot an spectrum of their thermochemical energy, *see* Figure 4.4.

In Figure 4.4: biomass $\Delta h_C(hhv, dry, \mathrm{MJ\,kg^{-1}})$ ranges from *ca.* 15 to 22 [35] whereas for plant biomass it lies in the higher, and also narrower, range: 19.3 - 20.4 with husk, shell and pit on top: 20.4, *see* Table 4.9.

Conversely, the $h^\circ(c, hhv, dry)$ of coals and charcoals (the other solid fuels that biomass tries to partially or totally replace) is at worst almost equal than that of husk, shell and pit. Its HHV ranges from $25\,\mathrm{MJ\,kg^{-1}}$ to $37\,\mathrm{MJ\,kg^{-1}}$, [45]. That is to say, at the present state-of-art, biomass could coexist with coal rather than totally replace it at the energetic level.

Such a difference is mainly due to the C:H:O ratios: coal: 1:0.17:0.064, [45] vs 1:0.12:0.843 (*see* Table 4.9) of husk, shell and pit – the biomaterial with the highest enthalpy. It is to be seen that while the C:H is almost the same for both materials; whereas the C:O is *ca.* 13.2 times that of biomass, hence the lower $h^\circ(c, hhv)$ – a difference of more than $10\,\mathrm{MJ\,kg^{-1}}$ between the best cases.

Nevertheless, by means of techniques other than combustion – *viz.* gasification, liquefaction or pyrolysis –, medium and high energetic gases, such as CH_4 or H_2, can be directly extracted from biomass and be used in heating, as fuels or as reactants, increasing, then, the range of applicability of biomass, [26, 41, 98, 143]. For further details, *see* Chapter 5.

Finally, the only fuel above which biomass lies is residues. Residues normally present unfavorable conditions for thermal processing like low $h^\circ(c, hhv)$, high w_M and high w_A and thus are processed by other techniques like fermentation or anaerobic digestion. The only case in which residues are combusted is when having high content of organic, toxic material, [26, 41, 98, 143].

4.6.6 Summary

The relationships among elemental, biochemical, proximate and thermal analyses of various types of biomass are summarized in Table 4.9. Firstly, it can be seen that the value of the $\Delta h_C(hhv, \mathrm{MJ\,kg^{-1}})$ lies in a narrow range: 19.3 - 20.4. That is mainly because the ratio C:H is practically the same for the presented biomass types. However, the enthalpy of combustion increases slightly for hush, shell, pit and untreated wood, for which the ratio C:O is the lowest.

Secondly, the C:N:S relationship varies according to the biomass type, being the highest for grass and plant material and the lowest for untreated wood. Nevertheless, in comparison with coal (1:0.019:0.021), untreated wood offers advantages regarding NOx production and acid rain pollution: $w(N, UW)$ is 4.2 times lower than that of coal while $w(S, UW)$ is 28.8 times lower.

$w(N, UW)$: mass fraction of N in untreated wood

The relationship between lignocellulose content and $h^\circ(c, hhv)$ follows an inverse trend. For instance, for husk, shell, pit and untreated wood, the ratio Cel:Hem:Lig is the lowest whereas the enthalpy the highest. For grass, plant and straw, the opposite is true. However, grass and plant materials have the lowest lignin content and, since it is the most thermal stable, such materials should be more amendable to process. On the downside, grass and plants have the highest w_M and w_A.

Additionally, proximate analysis seems to be crucial to choose the best biomass type regarding thermal processing. For example, although moisture and ash yield are not immediately represented in either elemental or biochemical analyses, they play a key role: drying (moisture removal) is a process that consumes energy and ash possess deposition problems that might negatively affect the economy of a thermochemical process. Husk, shell and pit are thus the best choices in here.

Regarding all the analyses, on the one hand, husk, shell and pit contain the lowest w_{M} and an average w_{A} as received. Untreated wood, on the other hand, has an average w_{M} but the lowest w_{A} as received. Both, nevertheless, have the highest $h^{\circ}(c, hhv)$ among the reviewed biomass types. So they (H and UW) seem to be the best choice for dry thermal processing (combustion or pyrolysis) whereas grass and straws – having high w_{M} and high w_{A} – might be more suitable to wet techniques, like anaerobic gasification or fermentation – *see* Chapter 5.

Finally, in general, it seems that untreated wood presents the greatest advantages for thermal processing among other biomass types: it has i) the most homogeneous composition (7 major and minor elements), making it less complex to study, ii) the highest w_{C}, iii) the lowest w_{N} and w_{S}, iv) low w_{O} (C:O:H:N:S=0.498:0.420:0.0595:0.00353:0.000589), v) an average w_{M} (0.149), vi) the highest w_{VM} (0.678) and finally vii) a high $h^{\circ}(c, hhv)$ (ca. $20\,\mathrm{MJ\,kg^{-1}}$).

Table 4.1 Partial list of the Austrian standards (ÖNORMs) for solid biofuels [72, accessed online on 12.03.2013]

CONTENT	STANDARD	NUMBER	STATUS
Determination of ash content	ÖNORM EN	14775:2009.12.15	standard
Determination of calorific value	ÖNORM EN	14918:2010.02.15	standard
Determination of major elements	ÖNORM CEN/TS	15290:2006.05.01	pre standard
Determination of minor elements	ÖNORM CEN/TS	15297:2006.05.01	pre standard
Determination of moisture content - Oven dry method - Part 1: Total moisture - Reference method	ÖNORM EN	14774-1:2009.12.01	standard
Determination of the content of volatile matter	ÖNORM EN	15148:2009.12.15	standard
Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods	ÖNORM CEN/TS	15014:2005.10.01	pre standard
Fuel specifications and classes	ÖNORM CEN/TS	14961:2005.05.01	pre standard
Fuel specifications and classes - Part 1: General requirements	ÖNORM EN	14961-1:2009.06.01	draft
Method for the determination of ash melting behavior - Part 1: Characteristic temperatures method	ÖNORM CEN/TS	15370-1:2006.12.01	pre standard
Methods for sample preparation	ÖNORM CEN/TS	14780:2005.11.01	pre standard
Solid biofuels	ON-HB	17:2006.01.01	tech. lit.
Terminology, definitions and descriptions	ÖNORM CEN/TS	14588:2004.05.01	pre standard

Table 4.2 Groups and sub-groups of the BIOBIB database [74]

GROUPS	SUB-GROUPS AND VARIETIES
Bark	different trees, not specified
Biomass waste	demolition wood, collar, paper, particle boards, pulp/paper, waste wood, others
Energy crops	miscanthus, others
Husks/shells	almond, olive, walnut, others
Wood	beech, birch, different trees, hard wood, spruce, oak, pine, not specified, others
Others	different crops, others
Straw	barky, rice, wheat, other crops
Grass	different crops, not specified

Table 4.3 Groups and subgroups of the Phyllis database, [45]

GROUP	SUBGROUP
Algae	others
Char	grass, husk/shell/pit, municipal solid waste, non-organic residue, organic residue, refuse derived fuel, sludge, straw, wood
Fossil fuel	coal, natural gas, oil, peat
Grass/plant	alfalfa, cattle feed, cotton, flax, flower/garden plants, fruit, hemp, jute, kenaf, miscanthus, other grass, other plants, reed,
Husk/shell/pit	almond, cacao, coconut, hazelnut, olive, others, peanut, potato, rice, sunflower, walnut
Manure	cow, horse, others, pig, poultry
Non-organic residue	cables, carpet waste, car-shredder, electronic scrap, others, plastics
Organic residue/product agricultural/horticultural	waste, bagasse, black liquor, food industry product, food industry waste, organic domestic waste, paper, paper pulp
Others	non-fossil oil, others, standard import
RDF and MSW (municipal solid waste)	MSW, RDF unknown, RDF (refuse derived fuel) with plastic, RDF without plastic
Sludge	drainage culvert, food industry, industrial waste water treatment, others, paper sludge, sewage
Straw	barley, maize/corn, others, rape, rice, rye, sorghum, sunflower, wheat
Treated wood	composted wood, demolition wood, organic impregnated, others, particle board, salt impregnated
Untreated wood	bark, beech, birch, cork, fir/pine/spruce, leaves, needles, oak, other hard wood, other soft wood, others, park waste wood, poplar

Table 4.4 Typical information of the *Composition of a single material* in the Phyllis database, [45]

CATEGORY	CONTENT
General information	Sample information
Material composition	Proximate analysis, ultimate analysis, elemental analysis, calorific value, biochemical composition
Ash composition	Ash production method, ash composition, bulk density

Table 4.5 Mass fractions of the major, minor and trace elements present in various types of daf biomass (in descendent order). Major: > 0.01, minor: $0.001 - 0.01$ and trace: < 0.001, [45, 134]

TYPE	FRACTION	ELEMENTS
Grass/plant	Major	C, O, H, N and K
	Minor	Si, Ca, Cl, P, S and Mg
Husk/shell/pit	Major	C, O, H, K and N
	Minor	Si, Ca, Mg, P, S and Al
Straw	Major	C, O, H, Si and K
	Minor	N, Cl, Ca, Al, Mg, S, Na, Fe and P
Untreated wood	Major	C, O, H and Ca
	Minor	N, Si and K
Average	Major	C, O and H
	Minor	Ca, K, N, Si, Cl, S, Mg and P
	Trace	Na, Al, Fe, Mn, Ba, Zn, Ti, F, Sr, Ni, B, Cu, Pb, Cr, Mo, Te, V, Sb, Co, Sn, Se, As, Cd, Hg and Br

ELEMENT	AV	G	H	S	UW
w_{C}	0.485	0.473	0.483	0.470	0.498
w_{O}	0.418	0.419	0.407	0.420	0.420
w_{H}	0.0588	0.0576	0.0599	0.0577	0.0595
w_{Ca}	0.00898	0.00820	0.00461	0.00431	0.0110
w_{K}	0.00855	0.0117	0.0152	0.0111	0.00179
w_{N}	0.00768	0.0120	0.0113	0.00871	0.00353
w_{Si}	0.00559	0.00887	0.00548	0.0134	0.00232
w_{Cl}	0.00224	0.00343	0.000797	0.00466	0.000530
w_{S}	0.00117	0.00164	0.00144	0.00155	0.000589
w_{Mg}	0.00106	0.00101	0.00378	0.00176	0.000747
w_{P}	0.00106	0.00173	0.00350	0.00103	0.000442
w_{Na}	0.000698	0.000684	0.000518	0.00137	0.000347
w_{Al}	0.000542	0.000242	0.00107	0.00292	0.000362
w_{Fe}	0.000377	0.000277	0.000970	0.00105	0.000261
Others	0.000439	0.000188	0.00106	0.000499	0.000526

Table 4.6 Average mass fractions of the major and minor elements present in different types of dry and ash free (daf) biomass. Av: average, G: grass/plant, H: husk/shell/pit, S: straw and UW: untreated wood, [45, 137]

Table 4.7 Major elements present in daf biomass in molar fractions normalized (relative) to that of C, [45, 134, 137]

TYPE	w_{C}	w_{H}	w_{O}	w_{N}	w_{Ca}	w_{K}
Grass/plant	1	1.45	0.665	0.0217	0.0052	0.0076
Husk/shell/pit	1	1.48	0.633	0.0201	0.0029	0.0097
Straw	1	1.46	0.670	0.0159	0.0028	0.0073
Untreated wood	1	1.42	0.634	0.0061	0.0066	0.0011
Average	1	1.44	0.647	0.0136	0.0055	0.0054

Table 4.8 Validity ranges for the parameters in Equation 4.2. AAE: Average absolute error and ABE: Average bias error, [35]

PARAMETER	UNIT	VALUE
w_{C}	1	[0 ; 0.9225]
w_{H}	1	[0.0043 ; 0.2515]
w_{O}	1	[0.00 ; 0.5000]
w_{N}	1	[0.00 ; 0.0560]
w_{S}	1	[0.00 ; 0.9408]
w_{A}	1	[0.00 ; 0.714]
$h^{\circ}(c, hhv)$	1	[4.745 ; 55.345]
AAE	%	1.45
ABE	%	0.00

PARAMETER	BASE	G	H	S	UW
C:H:O	daf	1:0.12:0.89	1:0.12:0.84	1:0.12:0.89	1:0.12:0.84
C:N:S	daf	1:0.025:0.0035	1:0.023:0.0030	1:0.019:0.0033	1:0.0071:0.0012
Cel:Hem:Lig	dry	4.01:1.82:1	0.88:0.65:1	2.65:1.76:1	1.6:0.93:1
w_{A}	ar	0.051	0.050	0.062	0.018
w_{FC}	ar	0.127	0.200	0.153	0.149
w_{M}	ar	0.217	0.086	0.118	0.155
w_{VM}	ar	0.604	0.665	0.667	0.678
$h^{\circ}(c, hhv)$	daf	19.605	20.387	19.331	20.118

Table 4.9 Thermal energy of different biomass types as a function of their elemental, biochemical and proximate analyses. $h^{\circ}(c, hhv)$ in $\mathrm{MJ\,kg^{-1}}$, Cel: cellulose, Hem: hemicellulose, Lig: lignin, M: moisture, VM: volatile matter, A: ash yield, FC: fixed carbon, daf: dry and ash free, ar: as received, G: grass/plants, H: husk, shell, pit, S: straw and UW: untreated wood

5

BIOMASS CONVERSION

In thermochemical processing, biomass is mostly regarded, treated and standardized as a fuel. According to this vision, it is useful to sort the biomaterial composition into moisture, active and inert phases. Table 5.1 shows such an equivalence.

In biomass, moisture mainly consists of water and less of other fluids that also volatilize below 105 °C. This is the w_{biomass} that changes the most, because its material is present due to plant growing, exclusion or inclusion during handling, processing, storage or transport, [86, 134].

The active phase is composed by organic matter that volatilizes above 105 °C. It is mainly formed by lignocellulose or extractive materials (fat, proteins, sugars and so on) included into it due to plant growing. At atomic level, it is composed by C, O and H as major elements and Ca, K, N, Si, Cl, S, Mg and P as minor elements that vary according to the biomass type. Additionally, according to the proximate analysis, the active phase corresponds to the volatile matter and FC, since their compounds burn or are released to the gaseous state of aggregation and then, either preserved like gases or condensed as liquids, be used as fuels or chemical precursors.

Finally, the inert phase is formed by the rest of the constituents that do not volatilize or react during thermal processing, such as Ca, K, Si and so on. They are present as an amorphous phase, mineraloids or minerals – included into the biomaterial mainly due to plant growing – and are responsible for some disadvantages of using biomass, *see* Section 5.2.

The following sections discuss some information about biomass as fuel.

5.1 BIOMASS CONVERSION

Biomass conversion means its transformation into:

- a fuel: to generate electric current, to heat homes and industrial processes, or
- a reagent: to produce a wide range of chemicals, such as bioethanol, biogas, coal (biocoal), tar, syngas, alcohols (ethly-, butyl-, isopropyl-), polyols (glyceral, ethylene glycal), ketones (acetone), acids (acetic, lactic, butyric), glucose and many others, [26, 41, 95, 98, 143].

There are three processes to carry out such conversions: physicochemical, biochemical or thermochemical. Physicochemical methods are used to produce biodiesel; biochemical methods include anaerobic digestion and hydrolysis/fermentation to produce biogas; and combustion, distillation, pyrolysis, gasification and liquefaction (hydro-gasification) are thermochemical techniques to yield not only fuels but also reagents [95, 98].

Table 5.1 Biomass composition vs. biomass as a fuel, [21, 93, 134]

	BIOMASS AS FUEL		BIOMASS COMPOSITION	
moisture	fluid matter (volatiles $< 105\,^\circ\mathrm{C}$)	water, gas, gas-liquid phase	mostly water	fluid matter
active phase	volatiles $> 105\,^\circ\mathrm{C}$ Fixed C	structural material (lignocellulose) non-structural material (extractives)	mainly C, O, H, N and S compounds	organic matter
inert phase	ash	amorphous phase mineraloids minerals	Ca, K, Si, Mg, Al, Fe, P, Cl, Na, Mn, Ti and other elements	inorganic matter

Thermochemical conversion of biomass proceeds by combustion, gasification, pyrolysis and liquefaction-hydrothermal upgrading. Combustion yields hot gases that can be used to produce steam, heat processes or drive electric current. Gasification and pyrolysis yield low or medium energy gases. Low energy gases can be used like combustion gases or to fuel internal combustion engines. Medium energy gases may be used as combustion or low energy gases plus to produce fuel gases or methane. Additionally, pyrolysis medium energy gases could be used to produce synthetic liquids, methanol or gasoline produces. Moreover, it yields char or hydrocarbons precursors of fuel oil and distillates. Finally, liquefaction-hydrothermal upgrading results into hydrocarbons like pyrolysis, [95, 98].

Among the aforementioned processes gasification and pyrolysis are the most versatile techniques, specially the latter. Furthermore, pyrolysis and gasification could be used in conjunction to extract the most of a given type of biomaterial, [40, 108].

Alternatively, processes can also be categorized as dry or wet depending not only on the moisture of the material they can convert but also on its ash yield. Wet techniques, on the one hand, are mainly biochemical and more suitable for material that has a high moisture content and yields high amounts of ash. On the other hand, the rest of the materials could be economically processed via dry techniques including thermochemical processes, [108].

What is left is to have a criterion to help in the decision of processing it via dry or wet techniques. Thus, feedstock of materials can be also defined as dry and wet: dry feedstock are those having $w(M, ar)$ equal or less than 0.1 and $w(A, dry)$ equal or less than 0.2 and wet feedstock are those having $w(M, ar)$ greater than 0.1 and $w(A, dry)$ greater than 0.2. Finally, dry feedstocks are thus more suitable to be processed by dry techniques and wet ones by wet processes, [108], *see* Figure 5.1. In Figure 5.1, it can be seen that grass and plant biomaterial are the only wet lignocellulosic feedstocks, so it could be more profitable to process them via biochemical techniques rather than via the thermal ones due to their high moisture content and ash yield. All the other types of lignocellulosic materials can be processed using dry techniques, specially husks, shell and pits due to their low moisture and ash yield.

5.2 ADVANTAGES AND DISADVANTAGES OF USING BIOMASS AS FUEL

The major advantages and disadvantages of using biomass as fuel are gathered in Table 5.2. There are also some specific benefits or hindrances depending on the biomaterial and process to be used. For instance, herbaceous materials (straws and grass) contain higher portions of alkali metals, Si, S, Cl, Ca and Fe than woody biomass. Thus herbaceous material utilization is more likely to deposit ash (ash fouling) onto combustors and to corrode not only them, but also heat transfer elements, reducing their useful life and heat transfer capacity, [41].

Fouling: deposition of unwanted material on solid surfaces

As seen in Table 5.2, the main reasons to use biomass are its great availability, low exploiting costs and environmental benefits. That is why it is being used worldwide, specially in developing countries. On the contrary, it has a relatively low energetic content, high contents of moisture and

Table 5.2 The major advantages and disadvantages of using biomass as fuel. RES: renewable energy source, [134]

ADVANTAGES	DISADVANTAGES
RES for natural biomass	Incomplete RES as fuel regarding its life cycle assessment
Environmental friendly (CO_2 neutral conversion)	Lack of common terminology, classification and standards
Normally, low ash yields, C, S, N and trace elements	Variability of composition, properties and qualities
Commonly, high concentration of volatile matter, Ca, H, Mg, O and P	High contents of moisture, Cl, K, Na, Mn and some toxic trace elements
Great reactivity during conversion	Low energy density
Capture of some hazardous compounds by ash during conversion	Potential competition with food and feed production
High availability and relatively low resource	Possible soil damage and loss of biodiversity
Diversification of fuel supply and energy security	Possible hazardous emissions during thermal treatment

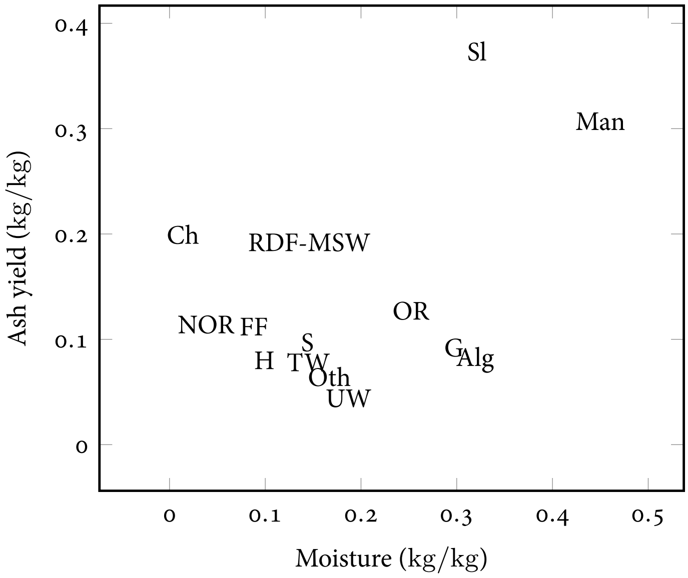

Figure 5.1 Moisture and ash yield mass fractions for different materials used as fuels. Alg: algae, Ch: char, FF: fossil fuels, G: grass/plant, H: husk, shell, pit, Man: manure, NOR: non-organic residue, OR: organic residue-product, Oth: others, RDF-MSW: refuse derived fuel, Sl: sludge, S: straw, TW: treated wood and UW: untreated wood

high yielding of ash. The latter factors imply high costs to industrialize the process, due to drying and ash deposition.

5.3 CURRENT TECHNOLOGIES

As seen in Appendix C, there are several available technologies to thermally convert biomass. Each of them could cover a report unto itself. Thus, as stated in Chapter 2, we devote the rest of this section to deepen into carbonization – a form of pyrolysis.

5.3.1 Biomass carbonization

Biomass carbonization is the process of heating biomass at high temperatures under inert conditions with the intention of producing biocoal. Thus, thermal biocoal production is a form of pyrolysis.

The process begins when biomass is fed into a thermal reactor. There, it is gradually heated from 200 °C to 900 °C for a couple of hours while moving from the reactor feeder to its outlets. The reactor inlet is normally sealed to prevent the inclusion of O_2 that, otherwise, would burn biomass, thus yielding ash.

During heating, biomass undergoes (thermal) decomposition that forces it to release gases (moisture and volatile matter content) leaving behind biocoal: a black, coal-like solid mostly composed of the initial material's fixed carbon content.

The two reaction products (gases and biocoal) are separately redirected: gases go to two outlets (one for combustion before atmospheric release; another one for analyzing its composition). Biocoal, on the other hand, goes to a collecting unit.

Finally, during thermal conversion more than 50 gases and vapors are released, leaving behind a C-based solid (assumed to be graphite), [21].

Table 5.4. However, only the major gases are analyzed, CO(g), CO_2(g), H_2(g), N_2(g), SOx(g) and NOx(g), and the solids, biocoal, are also sent to research for composition and thermal properties (proximate and ultimate analysis and higher and lower heating values, respectively).

There are two important requirements for heat transfer in a carbonizer – a pyrolysis reactor, [20]:

1. to the reactor heat transfer medium (solid reactor wall in ablative reactors, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors);
2. from the heat transfer medium to the pyrolyzing biomass.

5.3.2 *Biocoal*

Biocoal is the main product of biomass pyrolysis with the purpose of increasing its energy content. Thermal treatments are regularly applied in the range of 200 °C to 300 °C under atmospheric pressure and in the absence of oxygen. However, thermal treatments at higher temperatures, 900 °C, such as carbonization, are also used.

During the thermal treatment, the water contained in the biomass as well as superfluous volatiles are released, and the biopolymers (cellulose, hemicellulose and lignin) partly decompose giving off various types of volatiles. The final product is the remaining solid, dry, blackened material which is referred to as *biocoal*. During the process, the biomass typically loses 20% of its mass (dry basis) and 10% of its heating value, with no appreciable change in volume.

After the biomass is treated it can be densified, usually into briquettes or pellets using conventional densification equipment, to increase its mass and energy density and to improve its hydrophobic properties. The final product may repel water and thus can be stored in moist air or rain without appreciable change in moisture content or heating value, unlike the original biomass from which it is made.

5.3.3 *Added value of biocoal*

Biocoal and biocoal pellets have several advantages over raw biomass:

- High energy density: An energy density of 18 GJ/m^3 to 20 GJ/m^3 can be achieved when combined with densification (pelletizing or briquetting) compared to values of 10 GJ/m^3 to 11 GJ/m^3 for raw biomass, driving a reduction in transportation costs. Importantly, pelletizing or briquetting primarily increases energy density.
- More homogeneous composition: biocoal can be produced from a wide variety of raw biomass feedstocks while yielding similar product properties. Most woody and herbaceous biomass consists of three main polymeric structures: cellulose, hemicellulose and lignin – together called lignocellulose. Thermal treatment primarily drives moisture and oxygen-rich and hydrogen-rich functional groups from these structures, resulting in similar char-like structures in all three cases. Therefore, most biomass fuels, regardless of origin, produce thermally treated products with similar properties with the exception of the *as received* properties, which largely reflect the original fuel ash content and composition.

Table 5.3 Range of the main operating parameters for pyrolysis processes. SRT: solid residence time, [20]

TECHNOLOGY	SRT	HEATING RATE	PARTICLE SIZE	TEMPERATURE
	s	$K\,s^{-1}$	mm	K
Conventional	450–550	0.1–1	5–50	550–950
Fast	0.5–10	10–200	<1	850–1250
Flash	<0.5	>1000	<0.2	1050–1300

Table 5.4 The most important by-products of biomass pyrolysis, [21]. All of them are gases with the exception of graphite: C(s).

GROUP	COMPOUND
Inorganic carbon compounds	C(g), CO, CO_2
Hydrogen compounds	H, H_2, OH, H_2O, HO_2, H_2O_2, HCO
Oxygen compounds	O, O_2
Nitrogen compounds	N, N_2, NH, NH_2, NH_3, NNH, NO, NO_2, N_2O, HNO, CN, HCN, H_2CN, HCNN, HCNO, HOCN, HNCO, NCO
Sulfur compounds	S, SO_2, SO_3, H_2S, COS, CS_2
Hydrocarbons	CH, CH_2, CH_3, CH_4, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_3H_7, C_3H_8, C_6H_6, $C_{10}H_8$, $C_{12}H_{10}$
Other organic compounds	CH_2O, CH_2OH, CH_3O, CH_3OH, HCCO, CH_2CO, HCCOH, CH_2CHO, CH_3CHO
Carbon (graphite)	C(s)

- Hydrophobic behavior: biocoal has hydrophobic properties and when combined with densification makes bulk storage in open air feasible.
- Elimination of biological activity: All biological activity is stopped, reducing the risk of fire and stopping biological decomposition like rotting.
- Improved grindability: biocoal has better grindability than biomass. This leads to more efficient co-firing in existing coal fired power stations or entrained-flow gasification for the production of chemicals and transportation fuels.

6
BIOMASS TRADE

The European biomass market has grown in the past years not only in import and export quantities, but also in the number of actors. However, this growth has also come with reserves from non traditional industries. In this chapter, the current trade of biomass within Europe, its market integration and the perception on the usage of biomass as feedstock by the industry and proposals to overcome them will be also presented and discussed.

6.1 BIOMASS TRADE

The increasing European demand for renewable sources has been growing in the last decade as the result of environmental awareness and policy. In 1990 the share of *Biomass and Waste* in the energy consumption of the EU-27 was 2.7 %. By 2007, this share has doubled to 5.4 %. This demand is expected to increase due to political and legislative motivations and to become more independent of foreign energy sources, [104, 110].

The increment on the use of biomass lies in its flexibility. Not only is it currently used as a fuel in a large variation of scales: from domestic heating or combustion in stoves with outputs below 10 kW to district heating and combined heat and power plants with outputs of several hundred MW, [94], but also, more recently, as a reactant for the production of a myriad of other products, [41, 143]. Its adaptability and policy changes affected the biomass trade as seen by the internationalization of its market. Wood, for example, was once a local or regional fuel, but now it has become a more internationally traded commodity.

Now, it is difficult to present precise figures due to the youth and volatility of the market. Figure 6.1 depicts only rough estimating figures on the import/export of solid biomass to/from several European countries. Despite this limitation, it could be noticed therein that Denmark and Italy are the largest consumers of biomass whereas Austria, Finland and Latvia the main contributors. The Netherlands and Sweden are both. Finally, the rest of the countries only export feedstock with the exception of Lithuania.

Nevertheless, the current contributions seem not to satisfy the market as more of it is required. For instance, wood pellets, a refined product, is nowadays intensely being traded in Europe, even with material from overseas. Figure 6.2 shows the trading routes for pellets where, besides trades among European countries, pellets are entering to the continent from Canada, Russia, South Africa and USA. This foreign amount mainly goes to Denmark, the Netherlands and Sweden; loosely in accordance with Figure 6.1 where these actors also appear as major consumers.

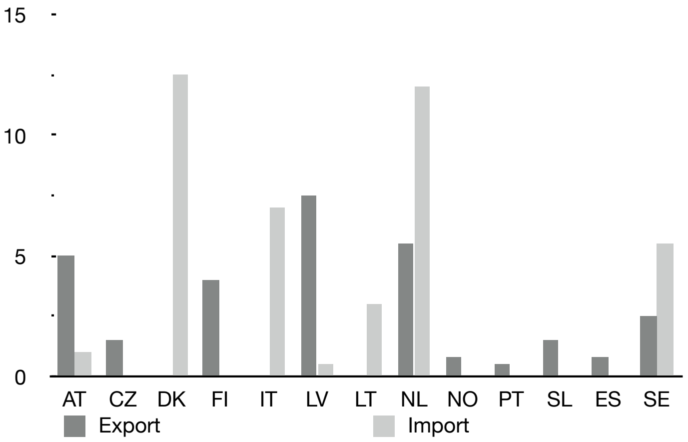

Figure 6.1 Rough estimations on solid biomass trade in selected European countries in 2006, [76]. Values in PJ. AT: Austria, CZ: Czech Republic, DK: Denmark, FI: Finland, IT: Italy, LV: Latvia, LT: Lithuania, NL: Netherlands, NO: Norway, PT: Portugal, SL: Slovenia, ES: Spain, SE: Sweden

In particular, Austria has a long record of exporting coniferous saw wood: a total of *ca.* $7 \times 10^6\,\mathrm{m}^3$ during 2008, [14]. As seen in Table 6.1, the major volumes have been going steadily to Croatia, Germany, Italy, Japan and Switzerland and unsteadily to the rest of the counties, notably Slovenia.

Finally, in a market integration study, [103], Olsson reports mixed results: the market for unrefined wood fuels among Estonia, Finland and Sweden could not be considered as integrated, despite a decrease in price differences, while the Austrian, German and Swede biomass wood pellet markets could be considered as integrated. Based in these different submarkets, he postulates that, even though there has been progress towards market integration, Europe has « still a way to go until there is a common European bioenergy market ».

6.2 BARRIERS TO BIOMASS ADOPTION

It seems obvious that the biomass usage directly influences its trade, price and availability. This relationship, though, is very unstable as revealed by official figures: wood harvest in Austria had its highest peak in 2007 and then declined by 23.3 % from 2008 to 2009 as the result of, among others, a decrease in demand and high wood prices, ending in a 24.2 % drop in the output value of forestry goods, [16], *see* Table 6.1.

Resource reserves do not imply market availability. Specially in the forest sector: if prices are high, it is profitable to harvest.

For this and other reasons, biomass adoption arises concerns among non traditional industries regardless of the sector and geographical location. Junginer, [76], recapitulates a series of interviews, summarized in Table 3.1 by country, to representatives of various European companies in various European countries on their worries on using biomass, whereas Ileleji, [70], reports almost the same issues, but in the USA. The main results of such studies are summarized as follows:

Country	1990	1995	2000	2004	2005	2006	2007	2008
Total (1000 m^3)	4176.196	4561.383	6016.379	7245.662	7119.66	6693.958	7637.474	7012.832
Major destinations								
Croatia		96.912	62.643	85.04	101.412	102.439	142.79	104.106
Germany	708.078	612.256	626.412	652.616	643.173	645.957	624.794	530.212
Italy	2679.84	2911.03	3888.551	4452.535	4371.679	4408.835	4482.628	4073.11
Japan		176.374	505.449	463.38	367.38	371.289	355.11	285.289
Libya	49.978	147.468	987	4.889	3.638	4.773	4.843	38.595
Saudi-Arabia	46.371	103.092	157.286	43.668	16.803	11.061	18.839	57.757
Slovenia		168.004	262.487	172.888	24.54	44.452	473.536	553.533
Switzerland	190.114	138.571	122.939	95.502	93.226	92.785	96.789	112.745
UK		28.709	12.128	45.98	97.109	94.065	208.394	79.746

Table 6.1 Export of coniferous saw wood from Austria (in 1000 m^3), [14]

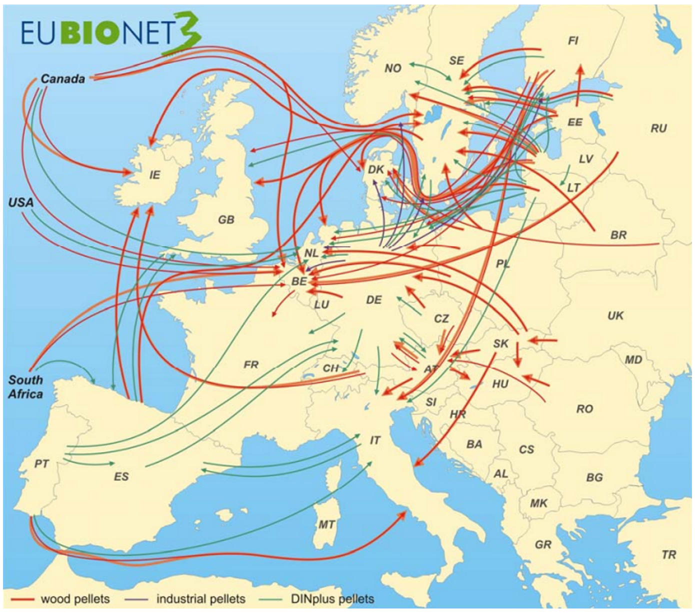

Figure 6.2 Trading routes for pellets, [76]

- Raw material supply: not only do forest products have to be shared with traditional industries – chiefly with the sawmill and the pulp and paper industries, but also non traditional industries depend on the traditional ones to get material; *e.g.*, the sawmill industry supplies the raw material, residues, for pellet makers. On the other hand, the pulp industry dictates wood prices and thus material availability on the market: if prices are high, it is profitable even for small forest owners to lumber or deforest and the supply of raw material, for the whole chain, increases. *See* Figure 7.2 depicting the forest industry complex.

- Costs: one of the most influencing factors for the production, export and import, and consumption of biomass. Interviewees mentioned high investments costs for biomass conversion installations and for insufficient or non-existing biomass supply infrastructure leading towards a high risk of large capital investment.

- Lack of infrastructure throughout the supply chain: logistical issues, such as bad roads, are a major barrier affecting low-density biomass types. Besides, even in places where transport does not pose issues, biomass storage does, such as location and material preservation.

Including production, harvesting, transport, storage and material preprocessing, as size reduction, densification, drying and so forth

- Natural phenomena: biomass growth depends on natural phenomena.

- Sustainability: some actors see sustainability as potential obstacles. An additional preoccupation is the agricultural sector-wide paradigm shift; *i.e.*, to replace traditional crops – food crops – for energy crops.

- Quality of the biomass-based end-products: end-product quality is a requirement to increase confidence on the industry.

- Standardization: lack of industry standards and regulations; that is, industries should provide the quality of biomass-based products required by their processes.
- Technology: technology still remains unproven at commercial scale.
- Acceptance: industry and consumers acceptance and awareness.

To the aforementioned barriers, Rathbauer, [110], adds some more as perceived by the Austrian industrial sector:

- Strict regulations and additional requirements in Austria by the Austrian State;
- Influence of foreign distributors. Some of them try to lower price down to production costs, creating pressure on local biomass producers;
- The Austrian forest ownership model which is perceived as very structured and managed by countless private persons probably resulting in multiple contractual arrangements for raw material supply.

6.3 PROPOSALS TO OVERCOME THE BARRIERS TO BIOMASS ADOPTION

Some proposals to overcome the barriers to biomass adoption are the following, [70, 76, 103, 104, 110, 125]:

- Enhancement of ecological and environmental objectives: cost saving should not be an argument for the decision on biomass usage;
- Direct negotiation: producers may also act as distributors, so to avoid market trades in the supply chain;
- Secure long-term feedstock delivery contracts to edging against risks;
- Higher wood prices negotiation: if prices increase, so does the supply of raw material;
- Optimized feedstock logistics: transportation logistics is key to developing a successful biomass-based project. This includes pre-processing of material and a comprehensive feedstock in-storage quality monitoring plan;
- Non-local unrefined or refined biomass: import of raw material to cover the European shortage or to save costs. Some considered locations were Canada, USA, North-West Russia, South Africa, Central and South America. See, for example, Figure 6.2 that shows the trade of wood pellets;
- End-product quality: providing satisfactory end-product quality increases confidence on biomass usage;
- Research: more research will arise as long as industry adopts biomass feedstock as major components of their feedstock needs;
- Creation of biomass aid packages.

Unrefined biomass refers to raw biomass whereas refined biomass usually denotes pellets and briquettes.

An important conclusion of a study published by Junginer, [76], is that refined biomass had overcome many of such barriers due to their high energy density, policy support and abundant feedstock supply. It could be added that in the case of Austria there are standards to test for pellet quality and safety, [17, 18].

6.4 DISCUSSION

The biomass trade is difficult to follow mainly because of a lack of common terminology. Some information sources treat biomass as coming from forestry and agricultural residues, municipal waste, used wood and so on, all under the label *biomass for energy* or *biomass fuel*. Besides, even when available, figures should be regarded as estimations. There are, however, two exceptions: wood biomass and biomass pellets. It is possible to find official statistics for the former, due to the necessity to report the number of tree fellings and to its interaction with traditional industries. The latter, pellets, has become traceable because of its adoption in Europe and imports from overseas. Moreover, there is an own category for both in the Statistics Yearbook, [14], just next to fossil fuels, for instance, in the report on the Overall Consumption of Fuels 2007/2008.

Due to its flexibility and policy, there is a European trend to increasingly embrace biomass as a material for different purposes, chiefly as energy *source*. However, industries still hesitate on its adoption at large scale, mainly because of material supply: other industrial materials are regularly transported, stored, preserved and homogenized before usage, but biomass feedstock poses a rather challenging task: to gather the unrefined material from different sources in a stable flow under an unstable market where many unrelated industries dictate prices and availability. This opens a door for the consideration of refined biomass, specially with a more stable trade and the possibility to import biomass from outside Europe in the case of shortages.

In either case, unrefined or refined biomass usage, a key factor to guarantee supply is to directly agree with producers in long feedstock delivery contracts with high enough prices so material is always available. It seems that material reserves would pose no problems, because of a guarantee sustainability, at least in Austria. In the case of refined biomass, only transport and storage will constitute an addition to the material cost. In the case of the unrefined one, there will be more considerations to make besides logistics, namely preservation and conditioning – discussed in the following chapters.

Finally, another crucial step in the adoption of biomass comes at the technological level. Biomass from different sources is under research for many purposes. Nonetheless, refined biomass is principally used for energetic reasons. Due to the advantages that it presents as a commodity and also to some technical reasons that will be presented in the next chapters, it would be interesting to look for uses of pellets within industrial processes, besides energy, to test its performance and to establish a quality control and monitoring program.

7

BIOMASS RESOURCES AND MARKET AVAILABILITY

In this chapter, biomass availability focused on alternative uses is discussed. It begins with a review of the fate of forest products and their interaction with the so-called forestry chain complex. This interaction is very important, since it decides the shift between resource and market availability of wood-based materials. For these reasons, the next sections treat biomass resources rather than availabilities in some European countries and in Austria.

7.1 THE FATE OF FOREST PRODUCTS AND THE FOREST INDUSTRY COMPLEX

To better understand wood biomass availability, it is useful to review the fate of forest products during and after harvesting (Figure 7.1) and the industries behind them (Figure 7.2), collectively named the forest industry complex, or product chain. According to [118] and [125], forest harvest begins with tree cutting. While cutting trees, harvesters sort out logs and branches on different piles. In some countries, much of these processes are currently fully mechanized, while, in Austria, are done manually. The materials are then recovered in three ways: logs, chips and bales:

This fact directly impacts on wood prices, as discussed later.

1. Logs: logs are mainly redirected to valuable applications, like construction, furniture making, musical instrument manufacture and so on, via lumber production, *see* Figure 7.1. The lower part of the tree stem is sent to the timber industry whereas the next tree meters are normally destined to the pulp industry. Only athe top part of the tree stem and the branches are available for alternative uses.

2. Chips: branches are then collected and piled. Residues are left drying during summer and then gradually chipped or flaked locally and finally transported directly to conversion plants – alternative sector.

3. Bales: sometimes, composite residue bales, a new material compression technology, is used to compress forest residues into log-shaped bales with the objective to increase its bulk density. Then, they are sent to alternative industries.

Additionally, byproducts or residues coming from traditional industries are also available to alternative applications, named as the *Energy Sector* in Figure 7.2. Nevertheless, Suurs, [125], noted that more of the trees could be used for non traditional purposes, due to a rise in energy prices: since they are close to paper prices, the part of the tree destined to the pulp industry could also be used for alternative purposes.

It can be seen, although not directly, that forest material – and, therefore, biomass feedstock – depends on market prices: much of the trees

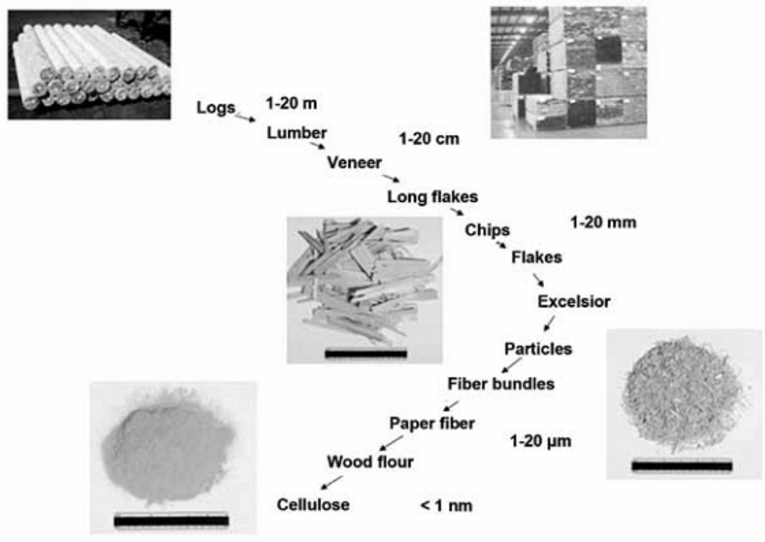

Figure 7.1 Basic wood products, from largest to smallest, [62]

goes to valuable applications, which pay high prices, whereas residues go to the alternative sector; *i.e.*, if wood prices are high, it becomes profitable for producers to harvest entire tree stands and, thus, directly or indirectly, they pour material for the whole chain. This is due to the very nature of the raw material, trees: unlike crops or other agricultural products, trees could be kept alive for a period of years and felled only when prices are good for producers. Furthermore, it is to be noticed that, if a factor affects forestry, like a natural disaster, policy changes, taxation and so forth, it will affect the whole chain. This is also true for traditional industries. If they are affected, then forestry is also affected – less demand, less felling, and thus there is a decline of material for the whole chain. In any of these cases, supply for the alternative industries is always affected since it is a function of the traditional ones. Finally, the opposite is not true: if a factor affects alternative industries, it will have no substantial impact on forestry, since they pay the lowest prices for wood.

For these reasons, it is difficult to follow the forest biomass market, since it results from a complex interaction of several directly-related actors. On top of that, it will be seen that other factors also influence this market, as oil prices.

7.2 BIOMASS RESOURCES IN EUROPE

Several materials are labeled as *biomass for energy* or *biomass fuel* making it difficult to gather its trade, prices and amount. Additionally, in some countries, official statistics are not yearly collected and published, but rather biennial or in longer periods, because of the youth and volatility of the market. On the other hand, information on material feeding traditional industries is up-to-date. On top of that, as shown in the previous section, tree harvesting depends on market prices, rather than on biological considerations – trees are kept as resources for years. Due to these difficulties, technical or scientific reports or collections of statistics

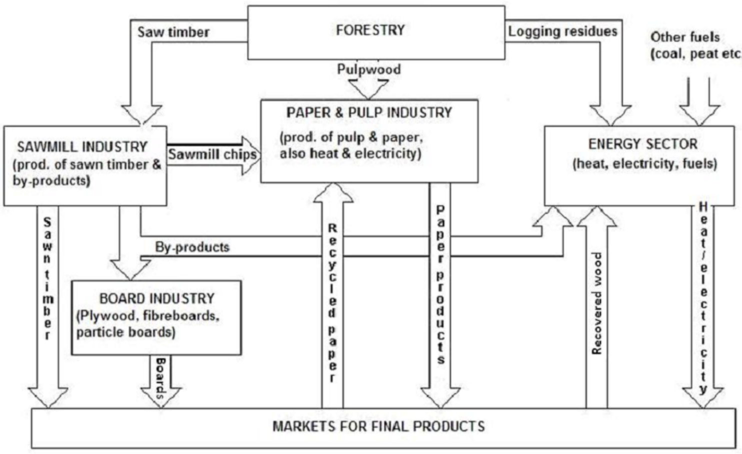

Figure 7.2 Competition for raw materials in the forest industry complex, [104]

usually present the potential of resources rather than the material availability on the market. So, even if biomass resources do not imply market availability, data on European and Austrian resources are presented and discussed.

In general, the total annual amount of biomass resources in the EU24 and Norway is approximately 6577 PJ (157 Mtoe). As shown in Figure 7.3, from this amount, 48 % are currently exploited, leaving *ca.* 3385 PJ in reserves. The biomass type in balance is the spent liquors (0 % in reserves) whereas the largest reserve is in the herbaceous and fruit biomass type (1355 PJ), closely followed only by forest residues (1080 PJ). Additionally, it is to be noticed that refined biomass is the only one showing over exploitation; *i.e.*, negative reserve, −50 PJ. This explains the foreign import of the material, as shown in Figure 6.2.

Mtoe: millions of tons of oil equivalent

The biomass potential by country is presented in Figure 7.4. Germany is the country with the largest amount of resources (> 1000 PJ) – mainly herbaceous and fruit biomass and forest residues – followed by France – forest residues and firewood, Spain – forest residues and solid industrial wood residues – and Sweden – herbaceous and fruit biomass, forest residues and other biomass; each country with resources ranging from 1000 − 500PJ, then by Austria – used wood, Finland – spent liquors and forest residues, Italy – herbaceous and fruit biomass and forest residues, Poland – forest residues – and the UK with country's resources ranging from 500 − 300PJ and finally the rest of countries. Nevertheless, not all of this potential is used, but rather kept as resources – Figure 7.5. Germany is still the country with the largest amount of reserves, but then followed by Spain, Italy, Sweden and the UK.

7.3 BIOMASS RESOURCES IN AUSTRIA

The Austrian biomass resources are presented in Figure 7.4, Figure 7.5 and in more detail in Figure 7.6, joined with the consumption and reserves. With a total annual stock of 175 PJ, used wood, 87.5 PJ/y, solid

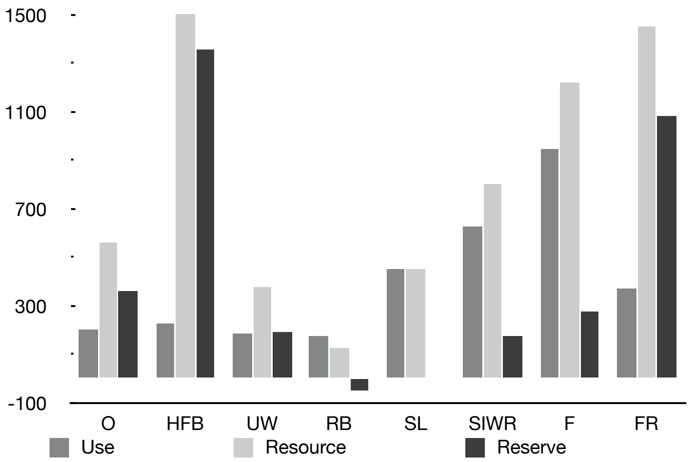

Figure 7.3 Biomass use, resources and reserves in 2006 in EU-24 and Norway, [76]. Values in PJ. FR: forest residues, SIWR: solid industrial wood residues, F: firewood, UW: used wood, HFB: herbaceous and fruit biomass, SL: spent liquors, O: other biomass, RB: refined biomass

industrial wood residues, 62.5 PJ/y, and herbaceous and fruit biomass, 25 PJ/y, constitute the largest part of the reserves.

Since it exhibits the greatest potential, it would be advantageous to know where all of the used wood material goes, to whom it belongs, what are its properties and how to collect it. It may pose logistical problems to use this resource, but its outstanding amount shows great potential.

The case of herbaceous and fruit biomass is rather interesting, because their reserves equal their potential, that is, all of this biomass type is not consumed at all, or perhaps in little amounts. This is maybe due to two factors: its poor physicochemical properties regarding combustion and the fact that it is produced all over the country and belongs to many agriculturists making it, therefore, difficult or not profitable to gather and use it in industrial scales. *See* Figure 7.7.

The case of residues is also interesting. It can be seen that forest residues potential equals the reserve, that is, it is not consumed. Again, logistical issues and multiple ownerships may be the reason, *see* Figure 7.7. However, residues coming from wood-based industries, timber and pulp and paper, are consumed in at least 25 % of the potential. This consumption may be explained by the fact that traditional industries have fixed locations, stable material flows and the output material (residues) has been already pre-processed. So it may be favorable to research the output per industries, the physicochemical properties of the material and how much it will cost to buy, transport and pre-process it.

Finally, in an opposite direction of the European trend, Austria does have reserves of refined biomass, $<$ 6 PJ.

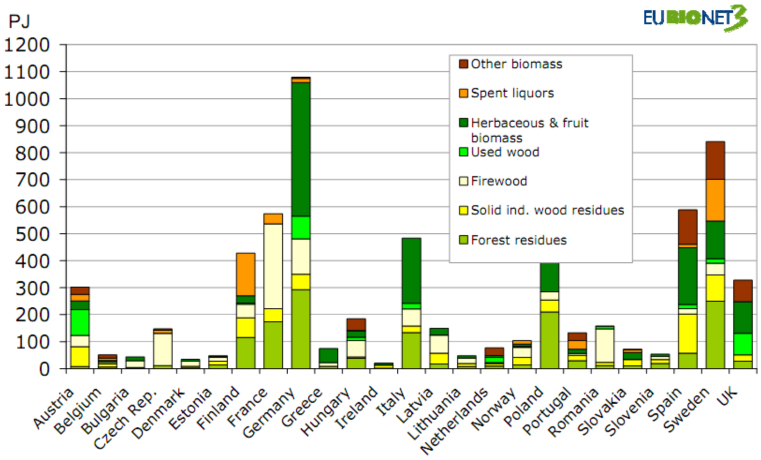

Figure 7.4 Biomass resources by type in EU24 and Norway, [76]. Values in PJ

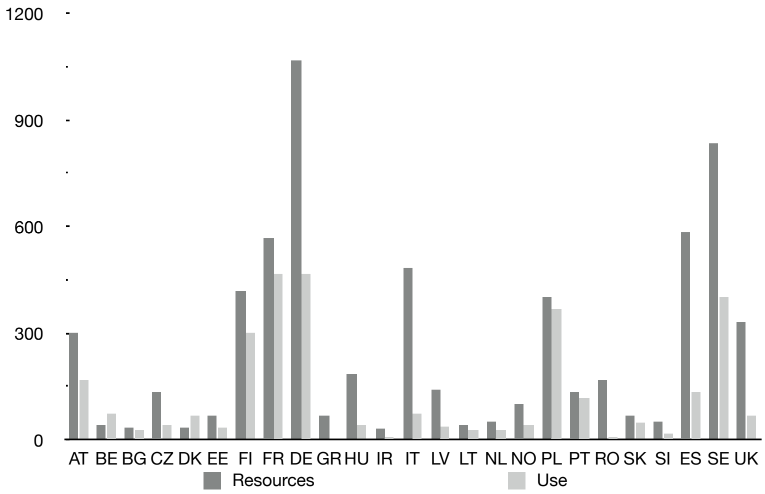

Figure 7.5 Biomass use compared to resources by country in 2006, [76]. Values in PJ

7.4 WOOD BIOMASS IN AUSTRIA

Official information on wood biomass is relatively easy to find, because fellings have to be reported and because of its long interaction with traditional industries. In this section, some figures are presented and discussed.

Nearly 47.2 % of the Austrian territory is covered by forests. According to the Austrian Forest Inventory (2002), the forested area has been increasing steadily. The average growing stock of the productive forests is $292\,\mathrm{m}^3/\mathrm{ha}$ and the total growing stock is $972 \times 10^6\,\mathrm{m}^3$. The yearly increment in productive stands is $31.4 \times 10^6\,\mathrm{m}^3$ and the yearly amount of felling is $19.8 \times 10^6\,\mathrm{m}^3$. Additionally, this increment is thought to increase to 85 %, representing $25 \times 10^6\,\mathrm{m}^3$, [65]. These figures agree with those reported by Rathbauer, [110], who gives numbers for the timber production.

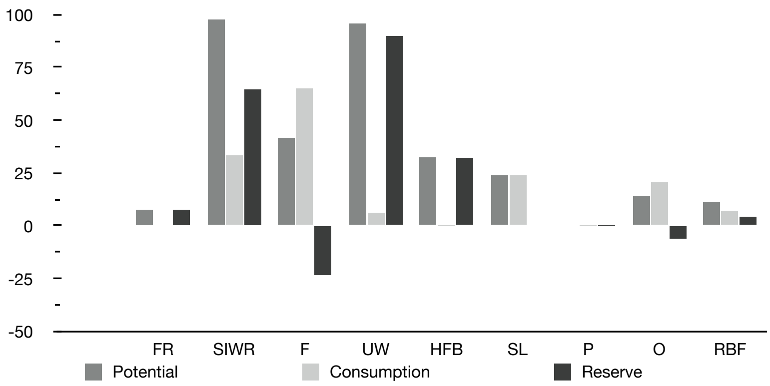

Figure 7.6 Potential, consumption and reserves of various biomass types in Austria during 2006, [110]. Values in PJ. FR: forest residues, SIWR: solid industrial wood residues, F: firewood, UW: used wood, HFB: herbaceous and fruit biomass, SL: spent liquors, P: peat, O: other biomass, RBF: refined biomass fuels

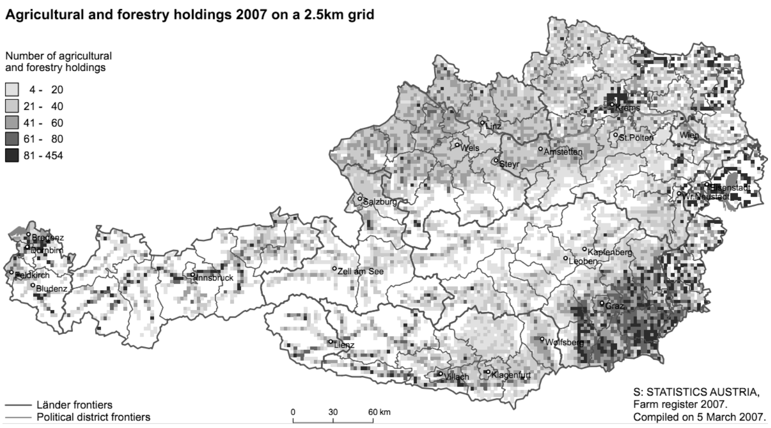

Figure 7.7 Austrian agricultural and forestry holdings, [15]

During 2008, 21.8×10^6 m^3 of wood were cut in Austria. From them, 72.1 % was accounted as softwood, 23.0 % as hardwood and the rest, 4.81 %, as firewood and wood chips, [14]. This is in accordance with the composition of the Austrian forests whose main species Norway spruces – coniferous softwood – accounts for more than the half of the Austrian forested surface, *see* Table D.1 in Appendix D.

Table 7.1 shows the type of wood that was cut during 2008 per *Länder*. The numbers presented therein agree with Figure 7.7 picturing resources. *Steiermark* leads the total cut of woods with 33.4 % of the total. This is remarkable, because of the topography of the region and of the numerous environmental regulations on forest harvesting in mountainous zones.

Type	Burgen.	Kärten	NiederÖst.	OberÖst.	Salzburg	Steier.	Tirol	Vorarl.	Wien	Austria
Hardwood	54.4	21.6	404.3	262.6	66.8	188.7	10.6	14.6	25.8	1049.4
Softwood	317	2291.8	2354	2539.6	991.3	5978.4	1020.6	228.9	1	15722.6
Firewood and Wood chips	294.5	486.4	1358.1	1041	308.7	1164.4	268.3	94.8	7.6	5023.8
Total	665.9	2799.8	4116.4	3843.2	1366.8	7331.5	1299.5	338.3	34.4	21795.8

Table 7.1 Total cut of wood (without bark) by *Länder* in 1000 m^3, 2009, [14]

8

BIOMASS PRICES

The factors establishing biomass prices can be distinguished between long and short run, [104]. The dominant factor for short-term prices has been raw material costs, especially in forest derived products. Not only do they vary intensely due to the fluctuating demand, but also due to other fluctuating factors. For instance, biomass prices rise because of higher oil prices, since the latter are used throughout raw material production: harvesting, collection, transport and so on. However, this effect is to be seen in a period of over one year. For longer periods, there is little connection between them. On the other hand, investments in new equipment and other long term decisions affect the long run prices of biomass. They are difficult to estimate, because they are case-based.

Finally, as reported in [125], the increasing demand for and prices of forest biomass has led to import the material in some countries. Due to this competition, some producers had to lower prices even near production costs. Then, production costs seem to be a reasonable way to follow the biomass market as a rough approximation to the material prices. These will be the figures shown and discussed in this chapter.

8.1 BIOMASS PRICES IN EUROPE

As mentioned, gathering information on biomass is not an easy task, prices are not exception, especially at the European scale. However, information is increasingly surfacing to cover this hindrance. For this reason, it is useful to rely on statistics from comparative studies, but with the drawback of having figures of early years.

Table 8.1 and Table 8.2 show the average supply costs of biomass originated in several European countries and Latin America. At the EU15 level, recent prices vary from 1.6 €/GJ to 5.4 €/GJ depending on the biomass type. Higher costs correspond to dedicated crops, since they need dedicated cultivation, whereas lower prices are related to byproducts or residues from other industries. One of the lowest prices is that of solid industrial residues, which also correspond to the second major biomass reserve in Austria – Figure 7.6. However, during two years residues prices increased in a factor of 2.6, from 0.93 €/GJ in 2002 to 2.4 €/GJ in 2004. Similar tendencies were reported until 2008, when prices decreased due to the economic crisis. Additionally, within the EU15, where prices vary considerably among residues and wood fuels.

In the NMS-10, on the other side, price differences among products are lower averaging 2.35 €/GJ, with the exception of energy crops.

Table 8.1 Average supply costs of tradable biomass and crops in 2004, [44, 51]. EU-15: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden and the United Kingdom. NMS-10: Poland, Czech Republic, Slovakia, Hungary, Slovenia, Estonia, Latvia, Lithuania, and the island nations of Cyprus and Malta. BG: Bulgaria. RO: Romania. toe: tons of oil equivalent

Tradable	EU-15		NMS-10, BG, RO	
	€/GJ	€/toe	€/GJ	€/toe
Forestry byproducts	2.4	100	2.1	88
Wood fuels	4.3	180	2.7	113
Dry agricultural residues	3.0	126	2.1	88
Solid industrial residues	1.6	67	2.5	105
Solid energy crops	5.4	226	4.4	184
Imported biofuels	6	251	6	251

Table 8.2 Costs ranges of different biomass forms excluding off-site transport, 2002, [125]. LA: Latin America. Conversion factor: enthalpy of reaction of Norway spruce: $hhv = 20.0987\,\mathrm{GJ/t}$.

Biomass form	Production costs					
	Range				Average	
	€/t_{dm}		€/GJ		€/t_{dm}	€/GJ
Residue logs	13.64	15.49	0.68	0.77	18.62	0.93
Residue chips	28.7	30.55	1.43	1.52	42.96	2.14
Residue bales	20.99	28.26	1.04	1.41	24.3	1.21
Salix chips/bundles	58.7	125	2.92	6.22	89.14	4.43
Eucalyptus chips (LA)	4.7	43.5	0.23	2.16	24.1	1.20
Eucalyptus bundles (LA)	3	4.5	0.15	0.23	3.8	0.19

Finally, overseas prices appear cheaper, but conditioning and transport costs should be added to such figures. Besides, there is an uncertainty about their trade, amount and yielding.

8.2 RAW MATERIAL PRICES IN AUSTRIA

As mentioned, statistics from Austria are readily available, those on prices are not the exception. The main source for wood biomass prices constitutes the Economic Accounts for Forestry maintained by Statistics Austria and published annually, [16]. The FAO website, [53], on the other hand, presents export prices of other products, chiefly residues.

In general lines, according to [16], during 2009, there was a steep decrease in forestry value added [1] and factor income, [2] despite that in 2006 and 2007 these values experienced a strong increase. This is consistent with the timber felling report of the Federal Ministry of Agriculture, Forestry, Environment and Water Management: in 2009 the quantity of wood felled accounted for 16.7×10^6 m^3 under bark. Compared to 2008 (year of highest value), wood harvest declined by 23.3 % mainly due to a significant reduction in the quantities of damaged wood, a decrease in demand as a consequence of the economic crisis and low timber prices. As a result, the output value of forestry goods dropped by 24.2 % to around 1×10^9 €, [16]. Again, these facts show the volatility of the biomass market and trade prices and also gives a foundation to the industrial reluctance to embrace biomass as a feedstock.

On the other hand, the output value of the forestry industry as a whole, which besides the output of forestry goods, reached about 1.3×10^9 € (-22.8 % compared with 2008). Of this, the output accounted for about 79.7 % and the non-timber sector, for about 20.3 %. The main item, with a share of about 54.8 % of the total output value, was coniferous timber for industrial uses, consisting of both sawable stem wood and undressed timber for the pulp, paper and board industry. Comparatively high proportions were also recorded for firewood (19.2 %) and forestry services (16.6 %), [16].

Coniferous timber for industrial uses, non-coniferous timber for industrial uses, firewood and other products including the non-timber sector.

As seen in Table 8.3 showing unit producer prices, higher prices correspond to valuable material; *i.e.*, saw logs, whereas lower ones correspond to material used by the pulp and paper industry and industrial wood. So, if the lower figures – around 30 €/m^3 – are proposed by alternative industries, it may be profitable for producers to harvest forest in a regular basis as it is currently done to feed the pulp and paper industry, making thus alternative industries regular and profitable costumers.

On the other hand, the FAO, [53], reports overall values for various wood-based materials exported from Austria during the year 2009, presented in Table 8.4. Chips and particles seem to offer the best deal with a low price. Nevertheless, logistics, densification and, more importantly, material preservation may increase the final price. Moreover, security concerns may arise in the handling of such materials.

It will be seen in the following chapters that finely chipped and moist material decays rapidly if not well preserved.

Wood residues have a price rather high, similar to that of saw logs class B 1a, but this is as an export price and not a producer one, so it includes trade fees and taxes. Besides, it was not mentioned its exact nature, therefore, logistics and conditioning costs may increase the final prices.

The export prices of coniferous saw wood is *ca.* 1.5 times greater compared to the producer price of spruce saw log class B, 1b. As mentioned, this increment accounts not only for taxes, which are unavoidable, but also traders fees. For this reason, one of the recommendations to overcome the use of biomass at industrial level was to deal directly with producers, eliminating, thus, trading from the chain, *see* Section 6.3.

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[1] The difference between the sale price of a product and the cost of materials to produce it.

[2] The returns received on factors of production, *aka* Net Factor Payments.

Finally, the high export price of non-coniferous saw wood may be explained because of its low coverage in Austrian forests and perhaps its quality and, therefore, use in specialized industries.

Type	€/m^3	€/GJ	Type	€/m^3	€/GJ
Round wood - Saw logs over 10m			Pulp wood		
Spruce/Fir, class B, 1b	60.52	6.69	Spruce/Fir	28.82	3.19
Spruce/Fir, class B, 2b	73.88	8.17	Pine	29.65	3.28
Spruce/Fir, class B, 3a	75.79	8.38	Beech	37.01	4.09
Spruce/Fir, class B, media 2b	74.76	8.27			
Round wood - Saw logs under 10m			Fire wood		
Spruce/Fir, class B, 1a	38.92	4.30	Softwood	36.44	4.03
Spruce/Fir, class B, 1b	57.53	6.36	Hardwood	54.26	6.0
Spruce/Fir, class B, 2b	72.16	7.98			
Spruce/Fir, class B, 3a	74.48	8.23			
Spruce/Fir, class B, media 2b	72.12	7.97			
Pine, class B, 2a+	57.36	6.34			
Beech, class B, 3	73.93	8.17			
Industrial wood			Pulp wood (grinding)		
Spruce/Fir	30.93	3.42	Spruce/Fir	35.26	3.90

Table 8.3 Producer prices for Austrian forestry products in 2009, [15]. (Unit conversion based on spruce properties: mass density $\varrho_{\mathrm{dry}} = 450\,\mathrm{kg/m^3}$ and enthalpy of reaction: $hhv = 20.0987\,\mathrm{GJ/t}$.[44, 46, 14])

Table 8.4 Unit prices for some forest products traded during 2009 from Austria, [53]. Figures calculated using price export value with a currency conversion of 1 € = 1 $ and the properties of Norway spruce. *See* caption of Table 8.3.

Product	Unit price	
	€/m^3	€/GJ
Chips and particles	3.33	0.41
Saw wood (coniferous)	119.42	9.90
Saw wood (non-coniferous)	408.43	33.87
Wood residues	38.59	3.20

9

LOGISTICS

Logistics is rather a set of activities ranging from production sites to end-user plants. This includes production of dedicated material (if decided) and residues, harvesting, collection, transport, in-line storage, end-user storage, conditioning, safety plans and monitoring throughout the chain. In this chapter, an overview of the process will be given, leaving the specifics to the following parts of the document.

In general, there are several major logistical questions that must be clearly determined when considering biomass as a potential feedstock: which biomass from what sources? Where and what type of pretreatment, *aka* conditioning or conversion? What is the best location for the conversion plant, if required? What is the optimal scale of such a plant? What are the chain costs (transport, storage, conditioning)? What are the material balances, including moisture, in chain? What are the potential losses of dry material during harvesting, collection, storage and transportation? What is its energy consumption? To aid in the decision making process, all of them can be organized in a so-called logistic chain. An example of such a chain is given in Table 9.2.

Practically, on the other hand, these logistical questions may be broken down according to the characteristics of biomass under consideration. As seen in Table 9.1, for each characteristic, an action plan can be assigned. Of them, however, collection and transport are the most important and should be optimized, because they play a crucial role in determining the economic feasibility of a project: such costs are often rather high in comparison of material costs, for example. Nevertheless, specific details are often complex, because chains can be set up in many different ways, making thus difficult to estimate the logistical costs and energy consumption. For instance, many field sources of biomass are remote from the final destination; thus, there is the alternative of moving the biomass to a plant near the consumer or moving the product from a remote biomass processing plant. The factors affecting the location of biomass plants are both non-economic and economic. Non-economic factors include the community concerns about traffic congestion and possible emissions such as dust or odors. Economic factors include the relative transportation cost of biomass vs product rather than near population centers and the potential benefit from large-scale integrated processing of biomass, for instance, a multi-product biomass refinery. Modeling the logistics of a design can, therefore, become very useful, [11, 127, 125].

Table 9.1 Biomass characteristics and proposed actions, [11]

Characteristic	Action
Small quantities scattered over many sources	Collection and transport
Heterogeneous quality	Pretreatment
Relatively high moisture content	Drying
Different types	Pretreatment
Different types	Flexible end-user plants
Seasonal patterns	Storage
Lower energy content than fossil fuels	Pretreatment

Finally, feedstock material is rather a mixture of materials with different physicochemical properties: branches and leaves with high moisture content and low density values, pines and bark with low moisture content and medium densities and trunks with medium moisture content, medium densities and relatively high resistance to stress forces. Moisture content and densities are the parameters that directly influence transportation logistics and transportation costs, whereas stress forces and proximate analyzes influence processing costs and disposition costs; *e.g.*, ash disposition. Since material density plays an important role during the whole logistics, it is thus advisable to increase it by compressing the material, in analogy at what is done with municipal residues when collecting them from houses and commerces to landfills. Compacting residues increases its density and, therefore, trucks are filled not only by volume but by weight. The result is that less travels are needed translating into monetary savings.

Production system Chain structure	Logs		Chips		Bales/Bundles				MeOH		Pyrolysis oil	
					Bales		Pellets					
	S	L	S	L	S	L	S	L	S	L	S	L
Harvesting and forwarding	●	●	●	●	●	●	●	●	●	●	●	●
Storage in pile												
Bailing					●	●	●	●	●	●	●	●
Chipping			●	●								
Storage in pile			●	●	●	●	●	●	●	●	●	●
Storage at roadside	●	●										
Pyrolysis oil synthesis											●	●
Local transport	●	●	●	●	●	●	●	●	●	●		
Central storage			●	●			●	●	●	●	●	●
Central chipping							●	●	●	●	●	●
Central drying			●	●			●	●	●	●	●	●
Central pelleting							●	●				
Methanol synthesis									●	●		
Central transport	●		●		●		●		●		●	
Storage at export terminal	●	●	●	●	●	●	●	●	●	●	●	●
Train transport		●		●		●		●		●		●
Ship transport	●		●		●		●		●		●	
Transport to conversion unit	●		●		●		●		●		●	
Storage at conversion unit	●	●	●	●	●	●	●	●	●	●	●	●
Chipping	●	●		●	●							
Drying chips	●	●		●	●							
Power conversion	●	●	●	●	●	●	●	●			●	●

Table 9.2 Example of a logistic chain. S: International Sea Transport, L: International Overland Transport, MeOH: methanol, [125]

10

FOREST HARVESTING

Forest harvesting may refer to thinning or felling. Thinning is the cut and collection of branches, leaves, pines and bark. Felling, on the other hand, is the process of cutting the tree stand(s) as a whole and the collection of all of its (their) products: the same as the thinning materials plus the trunk(s). Both processes are different in the techniques used, harvesting times, product yields, regulations and so on, but are similar in other ones: collection, chipping of residues, transport and so forth. Thus, throughout this chapter, both methods will be treated as harvesting, with special emphasis in felling, due to its complexity. The distinction will be done in the last section.

Given this remark on terminology, this chapter begins with a brief discussing of the processes and techniques used to harvest forests and the products therefrom derived. Then, pertinent regulations that directly affect forest harvesting will be analyzed. Finally, some production costs as a function of the whole process are given.

10.1 PROCESS

Harvesting is done during the winter to dry the wood over the summer. The cutting area comprises from 0.5 ha to 1 ha. Next, the trees covering such surface are harvested using one of the methods given below, [128] – the actual method to be used depends on the stand age and environmental regulations:

- Pole-length harvesting: The tree is delimbed at the stump, then the whole stem is extracted in one piece to be cut into various products (saw logs, pulpwood, fencing, wood fuel) at the roadside. The stem only is used, leaving crown and branch residues.
- Part pole-length harvesting: Similar to pole-length, but saw logs are removed from the main stem at the stump.
- Short wood harvesting: The tree is delimbed and crosscut into different products at the stump with saleable product (including wood fuel) extracted. The stem, crown and branch wood down to a specified size are used with unusable residues left in the wood.
- Terrain chipping: Chipping takes place at the stump as part of the harvesting process using a self-propelled chipper. The whole tree is used.
- Whole-tree harvesting: The whole tree is used, leaving few or no residues. It can combine elements of other harvesting systems, with conventional

round wood products extracted and residues chipped either in the wood or at the roadside, or the whole tree chipped.

These methods can be carried out at different mechanization levels. In Finland and Sweden, the process is fully mechanized whereas in Austria some tasks are carried out manually. While harvesting, harvesters sort out the logs and the branches on different piles. Then the materials are recovered in different ways, [65, 118, 125]:

1. Residue log: logs are mainly used in valuable applications like timber and paper. The lower part of the tree stem is used for the timber industry whereas the next tree meters are normally destined for the pulp industry. The top part of the tree stem and the branches can be available for non traditional industries as well if price arraignments are done. The bulk density of logs is assumed as $0.3\ \mathrm{t_{dm}/m^3}$ having a moisture content of about 50 %, whereas the density for Norway Spruce logs varies from $450\ \mathrm{kg/m^3}$ to $700\ \mathrm{kg/m^3}$ depending on the water content.
2. Residue chips: branches are scooped up by machines and formed into piles, typically about $4 \times (25 - 50) \times 4\mathrm{m}$ in size. Residues are left drying for the summer and, after about 6 mo, their moisture content decreases to between 30 % and 40 % during outside storage. Then, gradually, parts of the pile are chipped locally and transported directly to the conversion plant. Chips have a relatively low bulk density of about $0.15\ \mathrm{t_{dm}/m^3}$ with a moisture content at the moment of harvest of 50 %.
3. Composite residue bales: a new harvesting technology is the compression of forest residues into log-shaped compressed bales or compressed-residue-bales (CRBs). These CRBs have a diameter of about 75 cm and 3 m length. Their bulk density is $0.15\ \mathrm{t_{dm}/m^3}$ to $0.23\ \mathrm{t_{dm}/m^3}$ and having normally an initial moisture content of 50 % – this value depends on the humidity of the feedstock material. After in-field drying lower humidity values can be reached: 30 %. CRB can be handled like logs by conventional forestry equipment and therefore no special investments are needed.

10.2 SPECIFIC ENVIRONMENTAL REGULATIONS ON HARVESTING IN AUSTRIA

It was mentioned that the Austrian Forest Act translates into strict regulations on forest harvesting. Some of them, gathered from [60, 118, 135], are

- The need to report any clearings;
- The prohibition to destruct, degrade or damage forest sites and individual stands;
- The obligation to use forests for no other purpose but for forest culture and to ban, through authority, the exploitation of protective or welfare forests.
- Timber production is object to strict control, as being a part of the forest functions: regulations on felling (*e.g.*, immature stands are not to be felled), on production and trading of trees (*e.g.*, Christmas trees clear cuts exceeding 2 ha), on clear cuts exceeding 0.5 ha (they must be approved by authority independently of the forest type in order to limit negative environmental effects or soil and adjacent forest stands) and on special regulations for felling in protective forests;

Individual trees younger than 60 y

- Additionally, there are stricter regulations on forest management on a provincial level in the mountainous parts of Austria. Specifically, strip clear cuts (mainly in mountainous areas) should not exceed 50 −m width, 600 −m length and with a maximum area of 3 ha. Besides, they need to comply with other regulations, such as the Forest Development Plan, the Hazard Zone Plan, the Forest Plan, the Torrent and Avalanche Control Service and so forth.

Clear cut is a forestry practice to harvest most or all trees in a harvest area, [132]. However, a strip clear cut is the harvest of a stand over a period of three to seven years by removing several strips rather than the entire stand at once, [33].

Effectively, then, these regulations limit the amount of feedstock and end in high labor costs, but guarantee material sustainability.

10.3 NORWAY SPRUCE

As it can be seen in Table D.1, the most prominent tree species – and therefore the majority of forest products, byproducts and residues – is the Norway spruce. A very brief description of its biology and uses follows.

Mainly found in temperate and boreal regions, the Norway spruce (*Picea abies* or *Fichte*) is a coniferous evergreen softwood tree that can grow to heights from 20 m to 60 m tall at a rate of 60 cm/y to 90 cm/y their first 25 y under good conditions whereas, in heavy or poor soils, it may average 30 cm/y. Its wood is used in the wooden aircraft, paper, musical instrument industries and as a building wood when properly treated.

The main problem with the wood of this species is that, even its heartwood is prone to decay and does not resist fungal or insect attacks. , For this, it should be carefully stored and preserved, otherwise, for example, if left outside, it lasts no more than 12 mo, [62, 78, 138]. This low resistance is, however, shared with other tree species growing in Austrian soils, notably Alder, Beech, Birches, Firs and Pines.

The very core of a tree

Finally, even though the felling of Norway spruces is limited, not only by its biology, but also by environmental regulations, Norway spruce forest residues are available during the whole year and parts of them can be harvested anytime of the year, normally at rates given in Table 10.1 depending on the tree stand age. In more detail, it can be seen that timber is available after the 15th, in average, stand age, and that yielding increases with time: from an average of 55 m^3/ha to 275 m^3/ha at the final harvest. However, during their lifespan, trees yearly produce residues in a regular basis: approx. 35 m^3/ha.

10.4 COSTS

Forest harvesting costs vary from 17 €/m^3 to 50 €/m^3 depending on the mechanization level of the harvesting method, [50]. This method largely depends on the terrain: not only will steep terrain limit the use of heavy or large forestry equipment, but also the construction of roads – essential for the procurement process. In Austria, for instance, forest owners are responsible for building access roads. Table 10.2 shows some values obtained by the Austrian Chamber of Forestry and Agriculture, through [50].

Since in Austria harvesting is mostly done in mountainous regions (*Steiermark*) where roading is expensive and regulated, some tasks are manually done, thus increasing costs. The numbers in Table 10.2 explain why the producer prices are never below 28 €/m^3 for pulp wood and wood residues and 60 €/m^3 for large saw logs; *cf.* Table 8.3 against Table 10.2.

Table 10.1 Biomass residues under a typical management regime of a southern Finnish forest stand, [50]. toe: tons of oil equivalent

Treatment	Stand age	Timber yield	Biomass residues yield		
	y	m^3/ha	m^3/ha	toe/ha	GJ/ha
Pre-commercial thinning	10-20	-	15-50	3-9	125-375
1st commercial thinning	25-40	30-80	30-50	6-9	250-375
2nd commercial thinning	40-60	50-90	20-40	4-8	165-335
3rd commercial thinning	50-70	60-100	20-40	4-8	165-335
Final harvest	70-100	220-330	70-130	13-24	545-1005
Total during rotation	-	360-600	155-310	30-58	1255-2430

Finally, Table 10.2 shows an inverse relation between harvesting type and harvesting capacity vs. harvesting costs: manual cutting exhibits the least capacity, but the highest costs. Full mechanization of the process, on the other hand, ends in a three-time performance gain at half price. However, equipment, road construction, qualified personnel and M&O costs should be added.

Type of harvesting	Equipment	Harvesting capacity m^3/d	Harvesting cost €/m^3
Manual cutting	Chainsaw, extraction by hand	3-40	36-50
Partially mechanized	Chainsaw, extraction by tractor, winch or skidder	30-97	16-35
Highly mechanized	processing using a processor, extraction by cables	60-129	21-36
Fully mechanized	processing by harvester, extraction by forwarder	59-120	17-25

Table 10.2 Harvest performance with the differing levels of mechanization in Austria, [50]

11

BIOMASS CONDITIONING

Biomass conditioning has two major technical and economical purposes: to improve the efficiency of the transport chain by reducing the material size and humidity, thus reducing volume and finally increasing transport weight and to upgrade the material quality, mainly humidity reduction, therefore, making it less prone to fungal and insects attacks. Such tasks could be carried out by size reduction, drying and densification. In this chapter, the former are presented, leaving the latter – pelleting – for another part, Chapter 14.

11.1 SIZING

As local chipping is considered to be included in the harvesting operation, this section exclusively discusses central biomass chipping at large scale.

To facilitate handling, a shredder can be used to chip the wood down to 5 −mm to 50 −mm length. As mentioned, commonly, forestry residues are chipped locally and then transported directly to the end-user, like a conversion plant. An added advantage is the efficiency gain of the chain due to positive scale effects. However, because of their small size and high moisture content, chips are highly susceptible to fungal growth and tend to decompose when kept for long periods. To avoid it and dry matter losses, chips should be artificially dried or chipped as late as possible in the transport chain. , [50, 62, 125].

The practical load factor for central chipping equipment is typically 1500 h/y. This number must be corrected for the width of the operation window. The processing capacities depend on the type of chipper. Some large scale chipping installations are presented in Table 11.1. Capacities range from 5 t_{fw} to 80 t_{fw}.

tfw: tonne fresh weight

Table 11.1 Characteristics of different chipping installations, [125]

Type	Roll crusher	Hammer-mill	MP Bolagen
Capacity (t_{dm}/h)	1-10	25-50	80
Power consumption (kW)	65	240	1320
Capital costs (1000 €)	137.32	358.22	529.07
Maintenance (% inv.)	20	20	20
Lifetime (y)	15	15	15

Table 11.2 Total specific costs of chipping woody biomass for three chipping machines, [125]

Operation window (mo)	Roll crusher €/t_{dm}	Hammer-mill €/t_{dm}	MP Bolagen €/t_{dm}
12	6.5	3.5	2.0
9	8.7	4.7	2.7
6	13.0	7.0	4.1

11.1.1 *Costs*

Chipping costs presented in Table 11.2 were based on annualized capital costs, maintenance and energy costs, [125]. It was assumed a feedstock material with a moisture content of 50 %. All figures were corrected in order to make the operation speed independent of the material's moisture content.

11.1.2 *Energy*

For calculations, the total power consumption can be assumed to be linearly dependent on the installed capacity and therefore the specific energy consumption is independent of the scale of operation. Table 11.3 gives the calculated total specific power consumption for the machines considered in Table 11.1, [125]:

11.2 FORCED DRYING

Three different reasons exists for the artificial drying of woody biomass. After felling, biomass has a moisture content of typically 50 %. Depending on the feedstock criteria of the conditioning plant, this value might be too high. A solution to this is to upgrade the material quality by drying it. A second reason is the decomposition of wet biomass. Some biomass types quickly start to decompose, resulting in dry matter losses in a period of weeks. Another risk is the fire and health hazards caused by the rotting material. Finally, the third reason to facilitate transportation: drying reduces the mass of the material bringing down transport costs in the chain. However, drying does not greatly affect the material volume; so it is important to know the factors determining the transport costs, mass or volume. Additionally, all dryers demand chipped feedstock material, so sizing will always precede drying.

Different types of dryers are available. The simplest and commonest drying technology is the rotary drum dryer (RDD). Biomass is dried by bringing it in direct contact with a continuous flow of air or flue gas while rotating it around in a drum. Another equipment is the fluidized bed dryer (FBD), which uses a continuous flow of gas, passing through a bed of biomass particles and inert material, normally sand. The hot gas enters the bed at the bottom and leaves at the top of the dryer. Finally, a third newer technology is the re-compressive dryer (RD). This machine uses steam heat without any external heating.

Table 11.4 summarizes some relevant information. Equipment capacities range from 15 t_{fw}/h to 100 t_{fw}/h. A large scale operation dries 8500 h/y, working practically 24 h/d.

Table 11.3 Total primary energy consumption of chipping woody biomass for three chipping machines, [125]

Type	Roll crusher	Hammer-mill	MP Bolagen
Primary energy consumption (GJ/t_{dm})	0.18	0.13	0.23

Table 11.4 Characteristics of different drying installations. RDD: rotary drum dryer, FBD: fluidized bed dryer, RD: re-compressive dryer

Type	RDD					FBD	RD
Brand	A	B	C	D	F	G	H
Capacity ($t_{fw/h}$)	100	36	17.8	33.48	25-45	14.57	38.2
Heat consump. (MW)	12.5	?	10	?	20.47	4.9	-
Elect. consump. (kW)	2000	750	180	180	50	294	3629
Moisture input (%)	70-80	50	50	50	60	50	?
Moisture output (%)	7-10	10	10	15	15	15	?
Capital costs (1×10^6 €)	5.0	4.1	1.6	6.5	0.61	1.4	5.1
Maintenance (% inv.)	3	3	3	3	3	3	?
Lifetime (y)	15	10-15	10-15	10-15	10-15	10-15	?

Table 11.5 Total specific costs for drying chipped biomass from 40% to 10% moisture content, [125]

Operation			RDD			FBD	RD
window (mo)	VdB	VdB	St	Fl/A	Gdk	E W	V, F
12	3.7	7.1	9.1	8.9	4.3	10.6	23.8
9	4.8	8.7	10.6	11.0	4.9	12.2	30.2
6	6.8	11.9	13.5	15.3	6.1	15.5	43.1

11.2.1 *Costs*

Costs in Table 11.5 were calculated by Suurs, [125]:

- Considering capital investment, maintenance, operation, power and heating costs;
- Assuming the lifetime as 15 y for all systems and operation and maintenance as 3 % of the total investment costs;
- A salary of 25 €/h and a two-person crew;
- Power with a cost of 18 €/MWh, 65 €/MWh, and 0.13 €/kWh on heating prices.

The calculated costs for drying range from 3.8 €/t_{dm} to 23.8 €/t_{dm} for a 12 −mo operation window and from 6.1 €/t_{dm} to 43.1 €/t_{dm} for a 6 −mo operation window. If the more expensive alternatives are discarded, it can be seen that biomass can be dried for about 4 €/t_{dm} to 15 €/t_{dm}. Other studies estimates a price range of 1.1 €/t_{dm} to 6.5 €/t_{dm} at $MC = 20\,\%$ to 12.9 €/t_{dm} to 17.3 €/t_{dm} at $MC = 50\,\%$.

11.2.2 *Energy*

The specific energy consumption was calculated with the values presented in Tables Table 11.4 and Table 11.5 and presented in Table 11.6. As done for sizing, the total power consumption was assumed to be linearly dependent on the installed capacity and therefore the specific energy consumption is independent of the scale of operation.

Table 11.6 Total specific primary energy consumption for drying sized biomass, [125]

Type	RDD					FBD	RD
Brand	VdB	VdB	St	Fl/A	Gdk	E W	V, F
Energy consumption (GJ/t_{dm})	1.1	0.3	3.9	0.1	3.9	2.5	2.6

12

BIOMASS STORAGE

During the supply design, two goals are primary to ensure a constant feedstock flow: to lower handling costs and to provide appropriate storage. Specifically, the major challenges to overcome are the biomass susceptibility to decomposition and insect and fungus attacks; the seasonal dependency of the material supply and the lack of methods and standards for monitoring feedstock quality, [34, 62].

As seen in Table 9.2, storage must be created at critical points in the supply chain, not only on production or end-user sites; specially, where cargo is transferred among transport modalities of different scales. For instance, a large ship or train can take more than a thousand times freight than a road truck. Sufficient storage facilities solves this logistic bottleneck.

12.1 STORAGE CAPACITY

To determine the required storage capacity, two situations must be considered. On the one hand, when considering a constant supply of feedstock, it is enough to consider a two-day buffer storage at each transfer point to process the biggest possible shipments. On the other hand, when supply limitations occur, a larger storage capacity is necessary. In this case, large stocks of material must be stored usually at the top of the chain joined with material upgrade – conditioning, when required. This additional capacity is calculated by multiplying the system's scale by the operation window required for the harvesting. In case, for instance, of a six month harvesting window, a supply buffer storage capacity of half the total annual scale is considered necessary, [125].

Table 12.1 and Table 12.2 give examples of the characteristics of different storage facilities. It is to notice that supply restriction drastically increases the storage size in a 100-time factor.

Finally, a large storage also requires proper humidity and ventilation. Table 12.3 gives drying and decomposition of material for two storage types.

12.2 COSTS

Typical costs can be calculated with data presented in Table 12.1 by annualizing capital investments and adding 3 % maintenance, [125]. Land costs, only included in the open air alternative, were assumed as 2.3 €/m^2 – location dependent. Finally, power consumption was assumed to be negligible.

Table 12.1 Characteristics of some storage facilities, [125]

Biomass form	Logs, bales and bundles			Chips and pellets	
Type	Open air	Outdoor uncovered	Outdoor roofed	Bunker	Silo
Size (m^3)	2	3000	3000	25000	5000
Surface (m^2)	1	–	–	–	–
Capital cost (1000 €)	–	27	108	1630-2170	331
Maintenance (% inv.)	3	3	3	3	3
Lifetime (y)	N/A	25	25	25	25
Land costs (€/m^2 y)	2.3	–	–	–	–

Table 12.2 Some typical storage capacities, assuming an annual scale of 10 Mm^3 and a supply harvesting window of 0.5 y/y, [125]

Chain	Ordinary storage (m^3)	Supply storage (m^3)
Harvesting site	50000	0
Central Gathering Point (CGP)	50000	5000000
Export terminal	50000	0
Import terminal	50000	0
End-user plant (Truck)	50000	0
Total	250000	5000000

Table 12.3 Dry matter losses and drying characteristics during storage. MC: moisture content, [125]

Storage operation	Dry matter loss	Moisture content loss
Storage in pile and or at roadside	15 %	results in 35 % to 45 %
Covered storage	3 %/mo (for chips with $MC < 20\,\%$)	decrease of 1.5 %/mo (chips with $MC > 20\,\%$)

Table 12.4 Specific storage costs, depending on average storage time (€/m³), [125]

Biomass type	Logs, bales and bundles			Chips and pellets	
Type	Open air	Outdoor uncovered	Outdoor roofed	Bunker	Silo
Costs (€/m^3)	1.1	1.3	5.0	12.2	9.3

Table 12.5 Range of specific storage costs for different types of biomass, [125]

	Logs	Bales or bundles	Pellets	Chips
Costs (€/m^3)	4(16)	3-7(23-25)	16-20	62-81

Specific costs are presented in Tables Table 12.4 and Table 12.5. From these figures a mass based costs estimates for storage of different types of biomass can be deduced. Depending on the density of the feedstock, costs range from 3 €/t_{dm} to 7 €/t_{dm} for uncovered outdoor storage and 16 €/t_{dm} to 81 €/t_{dm} for roofed or indoor storage.

12.3 ENERGY

Since artificial drying is not considered part of the storage operation, no energy expenses are associated with storing biomass.

13

TRANSPORTATION

The major bottleneck in the success of biomass usage is the spatial distribution of feedstock – material scattering – and the associated costs on collection and transportation. The unit collection cost of biomass depends upon spatial density, biomass recovery cost and unit transport cost of biomass. They will be reviewed in this chapter.

Biomass may be transported in several different forms. The most appropriate option will depend on the biomass type and form, quantity, intended customer and distance to be traveled. Additionally, different transport combinations should also be considered depending on the cargo, as bags, tipper trailer or truck, flat bed trailer, tanker, grain or animal feed vehicle, timber haulage wagon, container and container lorry, walking floor trailer, rail, inland waterway and ship. For forestry products, the most common combination is the vehicle-trailer combination, where vehicle refers to ship, train or truck, [127].

On the costs side, the associated cost components may be divided into distance variable costs (DVC) and distance fixed costs (DFC). DVC depend on the transportation mode and the specific location; for instance, ton kilometer cost of trucking or rail shipment. DFC, on the other hand, depend on the type of biomass, equipment (loading and unloading) and contractual arrangements involved – both case specific. Thus, DFC will vary based on the specific form of biomass (that is, material moisture and density, *see* Table 13.1) to a far greater extent than DVC. Increases in the moisture level of biomass reduce the amount of dry metric tons per load and, as trucking costs are charged per actual metric ton, the calculated transport cost per dry metric ton will vary for every biomass source. For truck, rail and ship transport, mass is the primary factor setting the cost of shipment, although for low density loads volume can become the limiting one, [122].

Some important general characteristics of transportation and its economy are, [122, 117]:

- The economy of scale is negligible for some modes of transport, such as truck, rail and ship: more biomass means more loads at a set per load that depends on the distance traveled. Ship transport has the lowest DVC costs, but the cost of getting biomass onto and off a ship is high relative to the cost of loading a truck.
- In the cases of refined biomass, the transportation cost of the product is lower than that of the raw material. This is attributed to the fact that raw biomass has low energy density, even lower when wet.

Table 13.1 Average air and solid volume fractions for some wood-based materials, [113]

Type	Bundles	Chips	Residues	Round wood
Air:Solid ratio	0.55:0.45	0.60:0.40	0.80:0.20	0.30:0.70

- Distance and mode of transportation also impact the economy of the logistic chain. Normally, cost diminishes with increasing distance. For instance, it was found that above 500 km, the cost of transporting raw biomass by truck is more than that of transporting biomass by train or ship. For loose raw biomass, the cheapest mode of transport up to 30 km distance is tractor-wagon and beyond 30 km, truck. Similar were the results for transportation of bales and biomass briquettes, except that the distance for which tractor is the cheapest is up to 10 km and truck is suitable beyond 10 km. However, truck was the cheapest mode of transport of briquetted biomass for all distances.

Therefore, it could be summarized that transport costs depend on two factors: distance to be traveled and the physicochemical properties of the material to be transported. Factors like economy of scale are not as important.

Finally, transportation should include a comprehensive feedstock in-storage quality monitoring plan throughout the chain and the development of optimized feedstock logistics integrating prepossessing and transport, [70].

13.1 TRUCK TRANSPORT

On relatively short transport distances, truck is normally used for transport. An average allowed gross combination weight in Europe is 40 t and load capacity of 25 t. Table 13.2 shows different characteristics for trucks.

Additionally, it is interesting to notice the effects of material conditioning on transportation. Table 13.3 shows that drying chips has no effect on the total transport costs. This is because chip density is low, even when the material is wet. Hence, the volume determines the amount of transports needed. Transfer costs are dependent on volume as well, so a weight reduction is of no use. The application of densification technologies seems effective, though: transport costs for pellets are much lower than those for chips.

13.1.1 Energy

The energy consumption during truck transport is determined by the total amount of diesel consumption, using for diesel a lower heating value of 35.7 MJ/L. Transfer operations cost about 5 $\mathrm{MJ/t_{dm}}$. These results correspond with a range of 0.6 MJ/t km to 1.0 MJ/t km, including the return trip, Table 13.4.

13.2 TRAIN TRANSPORT

An advantage of using train transport is that it can cover large distances with more cargo and, therefore, less travels than truck. However, according to [125], train logistics in Europe are far from ideal. At some borders, the engine has to be changed or sometimes even the whole train because

Table 13.2 Characteristics of different truck types, [125]

Truck type	Dutch bulk	Swedish bulk	Chemical tanker	Pellets truck
Truck capacity max (t)	25	40	25	35
Truck capacity max (m^3)	120	130	33	80
Average speed (km/h)	65	65	65	65
Fuel use (L_{diesel}/100 km)	34	45	45	45
km-costs (€/km)	1.24	0.85	1.24	1.1

Table 13.3 Specific costs of truck transport of wood biomass (€/t_{dm}) and liquid fuel (€/t) for different cargo types, [125](MC: moisture content)

Distance	MC	Logs	Chips	Bales	Pellets	Pyrolysis oil	Methanol
50 km	45 %	7.9	12.3	9.9			
	<10 %		11.0		4.1	6.5	5.8
200 km	45 %	20.8	24.1	22.9			
	<10 %		24.1		11.1	23.0	20.7

Table 13.4 Specific primary energy consumption during truck transport of woody biomass (GJ/t_{dm}) and liquid fuel (GJ/t) for different cargo types, [125]

Distance (km)	Logs	Chips	Bales	Pellets	Pyrolysis oil	Methanol
50 km	0.10	0.11	0.10	0.07	0.09	0.09
200 km	0.38	0.43	0.38	0.23	0.33	0.33

of a difference in track width. These conditions are partly responsible for the fact that it is difficult to gain insight in the cost determining factors of rail transport.

Typically, trains are considered to carry a volume of 2500 m^3 and 1000 t with an average speed of 75 km/h. The number of trains necessary and the amount of time between two transports can be easily determined. For instance, at a 2-way distance of 3000 km and an annual scale of 20 Mm^3 about 37 trains are needed which travel with 65 min interval schedules. Note, that a load of little less than 2500 m^3 is expected each hour, which is about equal to the amount processed in the truck transport link (a truck load of 130 m^3, every 3.5 min).

13.2.1 Costs

The costs for rail transport are difficult to obtain, but something can be said about prices. The prices are hard to generalize, because they depend on the availability of return-freights, the total volume of transport in the same direction, the transfer terminal policies and the route.

Based on containers of 38 m^3 and 15 t that can be put on a train (three containers per wagon), of 4.7 €/t to 11.7 €/t, transfer costs are assumed to be 1.0 €/t_{dm}. When assuming a 50 % moisture content, 24.4 MJ/t_{dm} to 28.6 MJ/t_{dm}. This implies that train transport costs are assumed to be scale independent. All later calculations are based on values for forest residues (for all woody fuels, except pellets). For pellets it is assumed that train transport costs are cheaper, because of their lower density. A factor of 0.3 is applied, representing the density ratio of the materials, as shown is Table 13.1.

13.2.2 Energy

Energy consumption gives a figure of 0.63 MJ/t km to 0.70 MJ/t km, based on trains of 800 t and 2400 m^3, including the energy embodied in the vehicle and infrastructure. For a distance of 1000 km to 1500 km, this

Table 13.5 Train transport costs, including transfer, for different energy carriers in €/t_{dm} for woody biomass or €/t for liquid biofuels, [125]

Biomass form	500 km	1000 km	1500 km	2000 km
Salix	25.5	36.3	47.2	58.0
Forests residues	28.6	40.8	53.1	65.3
Pellets	9.0	12.8	16.7	20.5
MeOH	31.7	45.2	58.7	72.2

implies and energy expenditure of 630 MJ/t to 1050 MJ/t. Energy consumption as a result of transfer operations amounts to 10 MJ/t_{dm}.

14

DENSIFICATION: REFINED FUELS

Throughout this document, there were references to one of the most sophisticated methods for upgrading woody biomass: dry pellets. Pellets are a high-quality material, regularly used as fuel. They consist of compressed wood and are typically $6 - \mathrm{mm}$ to $12 - \mathrm{mm}$ diameter.

Generally speaking, the reasons behind densification, *aka* pelletization, are several, both technical and economical, [76, 103, 125]:

- The market integration of pellets trade is becoming increasingly stable, not only among European countries, but also overseas – Chapter 7;
- Business may be done directly with providers in an easier fashion, since there are currently associations of pellets producers. For instance, the Biomass Trade Centres, [28], – link redirected from the Styrian Chamber of Agriculture and Forestry, [124], an association of five countries that deal with biomass. Additionally, more links are provided in [106], specially to the Austrian partner, propellet, [109]. Finally, there is the European Biomass Association covering not only pellets, but the rest of biomass types as well, [49];
- They can be stored without risk of self-ignition, decomposition, fungal or insect attacks;
- Their transport is cheaper and safer than with wet or dried bulky biomass – *see* Chapter 13 on the importance of moisture and density in transport and on their influences on transportation costs;
- Direct thermal conversion of pellets has an efficiency level of approximately 80 %, [107], and, when required, they can be immediately substituted for fossil fuels, mainly coal;
- They can be used as a fuel or as a chemical reactant;
- Its energy content does not change during storage so dry matter losses are of no concern. However, they must be protected against rain;
- Pellets conforming to European standards (DIN 51731 or ÖNorm M-7135) have less than 10 % water content, are uniform in density of $1\ \mathrm{t/m^3}$, have good structural strength, and low dust and ash content,[18].

There are two ways of getting pellets: buying them in the market or producing them. Both will be discussed in the following sections.

14.1 PELLET PRODUCTION

Pellet production is done in the so-called densifiers or pelletizers. Densifiers accept nearly all types of biomass with certain degree of conditioning depending on the type of equipment used. However, standard conforming pellets cannot contain any recycled wood or outside contaminants. Recycled materials such particle board, treated or painted wood, melamine resin-coated panels and the like are unsuitable for use in pellets, since they may produce noxious emissions or uncontrolled variations in the burning characteristics of the pellets, [139].

Specifically, pellets are produced by compressing the wood material which has first passed through a hammer mill to provide a uniform mass. This mass is then fed to a press where it is squeezed through a die having holes of the size required (normally 6 −mm diameter). The high pressure of the press causes the temperature of the wood to increase greatly and the lignin, contained in the biomass, plastifies slightly forming a gluing material that holds the pellet together as it cools. Finally, produced pellets have a bulk density of $0.5\ t_{fw}/m^3$ to $0.7\ t_{fw}/m^3$ and a moisture content of 8 %.

Table 14.1 summarizes some key characteristics for different densification machines. As mentioned, for all machine types, the raw material has to be chipped and dried to a moisture content of 10 % before pelleting if possible, that is, a drying step will always precede the pelleting step. Specific investment costs are high so it is important to keep the machinery running continually. It can be assumed that the pelleting machine operates at a practical load-factor of 7300 h/y.

14.1.1 *Costs*

Table 14.2 gives some cost ranges, calculated in [125]. It was assumed that only machinery with the highest capacities would be used. The capital lifetime was assumed to be 10 y for all systems and annual operation and maintenance costs of 49% of the total investments costs. A costs range of 10 €/t_{dm} to 20 €/t_{dm} should be expected.

14.1.2 *Energy*

The primary energy consumption during pelleting was based upon the power characteristics presented in Table 14.1. Energy expenditure was considered to be linearly dependent on production scales. The results are presented in Table 14.3.

In average, however, the energy needed for the production of pellets is generally *ca.* 10 % of their own energy content – consumed in drying the raw material. In case of dry raw material being used, the pellet production consumes only about 1 % to 2 % of their energy content. This implies an energy consumption of about $0.2\ GJ/t_{dm}$ to $0.4\ GJ/t_{dm}$ in magnitude.

14.2 PELLET ACQUISITION

Pellets are available in the market as a final product; that is, there is no need to produce them if so desired. The information of these products (trade, costs, transportation, storage and so on) was already presented in the precedent chapters joined with the information for the other biomass types for the sake of comparison.

Type	Extruder						Roller press
Brand	Valm SRL	ECO Briq.	Fr Hausm	Spaenex	Desmi	M. Wirth	A. Kahl
Capacity (t_{fw}/h)	0.2-3.2	0.8-1.0	0.1-2.0	0.15-3.0	1.1-2.0	0.25-0.46	0.5-5.0
Elect. cons. ($kWh/t_{fw}/m^3$)	34-90	22-28	41-130	36-56	29	30-60	60-70
Capital costs (1000 €)	13.7-271	92.3-115	7.0-140	6.4-366	77.1-129	12.2-22.5	18.3-366

Table 14.1 Characteristics of different densification installations, excluding all pretreatment equipment, [125]

Operation window (mo)	Extruder Valm SRL	ECO Briq.	Fr Hausm	Spaenex	Desmi	M. Wirth	Roller press A. Kahl
12	10.8	10.9	8.2	12.6	6.7	6.6	9.0
9	13.2	14.2	10.2	16.1	8.5	8.0	11.1
6	18.0	20.8	11.2	23.1	12.2	10.9	15.3

Table 14.2 Specific costs of pelleting chipped wood in €/t_{dm},[125]

Type	Extruder						Roller press
Brand	Valm SRL	ECO Briq.	Fr Hausm	Spaenex	Desmi	M. Wirth	A. Kahl
Energy cons. (GJ/t_{dm})	0.84	0.26	0.52	0.52	0.27	0.56	0.65

Table 14.3 Specific costs of pelleting chipped wood in €/t_{dm},[125]

Part II

EXPERIMENTS

15

EXPERIMENTAL RESEARCH OVERVIEW

The experimental research started with the sampling of lignocellulosic biomass (wood-based biomass) from four locations:

- Eppenstein, province of Styria, Austria: bark, saw dust, and wood chips;
- Gaal, Styria: shredded forest residues;
- Leoben, Styria: wood chips; and
- Mautern, Styria: shredded forest residues.

Their geographical locations can be seen in Figure 15.1.

With the samples taken, the research program was divided into three experimental subprograms: one for raw biomass, another for thermally processed biomass (biocoal), and one, finally, for producing pellets with thermally processed biomass and electric arc furnace dust. For the raw biomass, in its turn, the following subprogram was established:

- particle size distribution of the different fractions;
- bulk density;
- proximate analyses: moisture, volatile matter, ash yield, and fixed carbon;
- elementary analyses: carbon, hydrogen, nitrogen, sulfur, and oxygen; and
- thermal analysis: higher heating value.

The analyses were performed at the laboratories of the Chair of Mineral Processing and at the laboratories of the Chair of Thermal Processing Technology, both Chairs belonging to the Montanuniversität Leoben, Austria.

On the other hand, once raw biomass samples were characterized and classified, they were thermally processed, by carbonization under inert atmosphere, to produce biocoal. The produced biocoal was subject to:

- proximate analyses: moisture, volatile matter, ash yield, and fixed carbon;
- elementary analyses: carbon, hydrogen, nitrogen, sulfur, and oxygen; and
- thermal analysis: higher heating value.

Carbonization was performed at the laboratories of the Chair of Non-Ferrous Metallurgy, whereas the analyses, at the laboratories of the Chair of Mineral Processing and of the Chair of Thermal Processing Technology. (All Chairs belonging to the Montanuniversität Leoben, Austria.)

With the results of the raw and carbonized biomass analyses, a wooden material was chosen, wood chips, to undergo the final stage of the research, which comprised:

- sampling of « fresh » raw material;
- air drying;
- proximate analyses, elementary, and thermal analyses;
- carbonization;
- pellet production parameter analysis;
- pelletizing; and
- reduction of ZnO in electric arc furnace dust to Zn.

The three aforementioned chairs provided their equipment for the analyses.

The rest of the present part is thus dedicated to present the methodologies used to perform the different experiments and analyses.

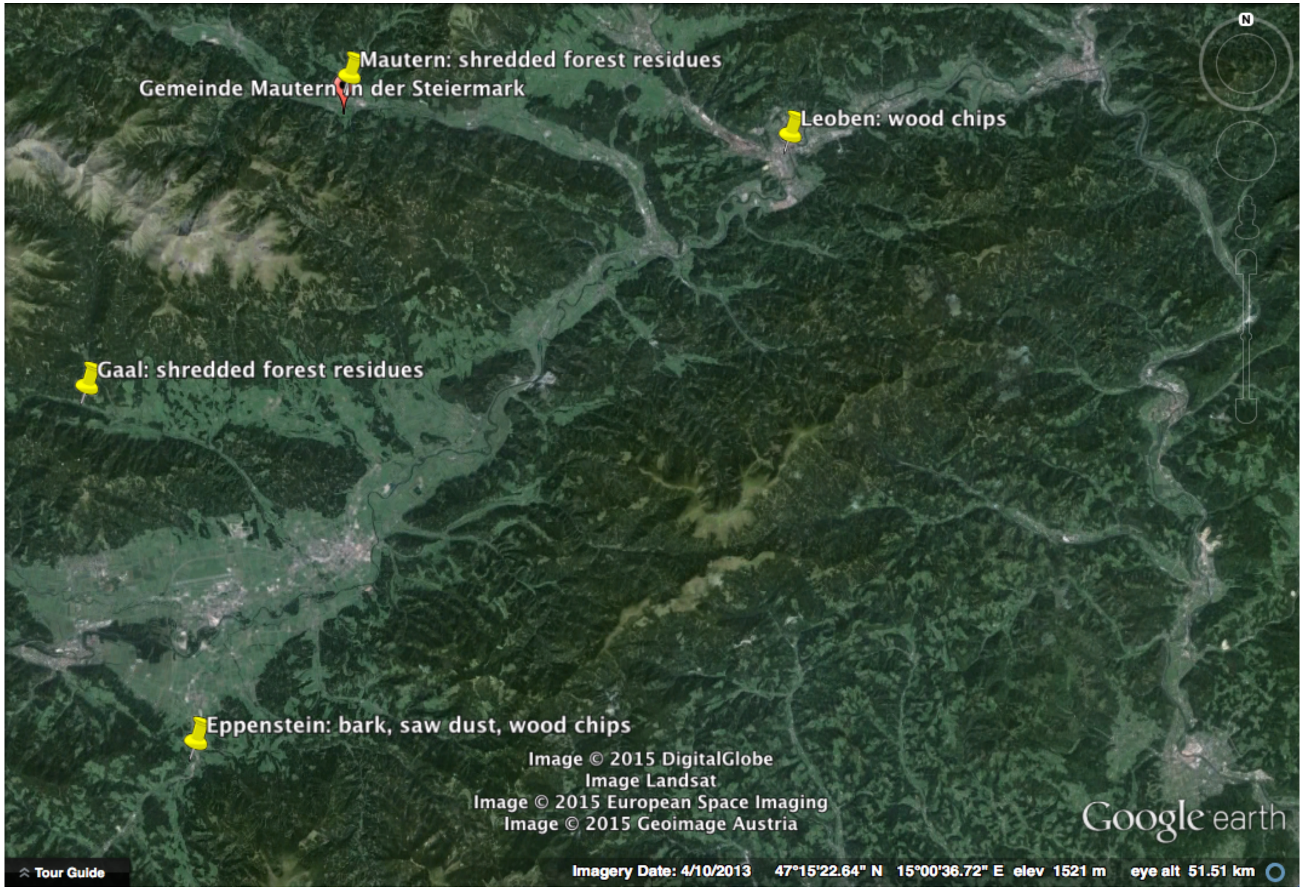

Figure 15.1 The four locations where biomass samples were taken for the current project: Eppenstein (bark, saw dust, wood chips), Gaal (shredded forest residues), Leoben (wood chips), and Mautern (shredded forest residues).

16

PARTICLE SIZE DISTRIBUTION

The present chapter reports the particle size distribution protocol for the concrete case of the material sampled in Eppenstein. However, the same methodology was applied in the other described cases.

16.1 METHODOLOGY

[Sample origin] The material, bark, was sampled in Eppenstein, Styria, AT.

[Sample composition] Mainly shredded bark and dust.

[Sample preparation] The collected material was dried at room conditions for about three weeks. Then, the sample was quartered and one of the quarters was used for the analysis. Additionally, bark from the same origin that had been prepared in the same way was added.

[Mechanical sieve] The sample was mechanically sieved using a Haver UWL 400 sieving machine in three steps, but with the same general procedure. For the first step, the biggest sieves were used: 125, 100, 80, 63, and 50 mm. For the second step, 40, 31.5, 20, 18 and 16 mm. For the third one, 14, 10, 8 and 6.3 mm.

[General procedure] The sieves were mounted onto a collecting tray and then onto the sieving machine. The sample was thus transferred into the sieve set and, finally, the machine was set to work for 7 min.

Once the sieving machine stopped, the material was collected from each tray and placed into previously weighed plastic bags. The *ensembles* were weighed on a balance: Kern TB ($d = 2$ g).

Ensemble: sieve and sample

[Manual sieving] The amount of sample that passed the 6.3 −mm sieve was manually sieved through the 3.15-, 2.5-, 1.6-, 1.0-, 0.5- and 0.25 −mm. The separation was done using two sieves at time, collecting the retained portion into weighed plastic bags and finally weighing them on the scale.

16.2 RESULTS

The data collected during the analysis are presented in Table 16.1. Uncertainty was calculated using the uncertainty of the sample and bag mass (2 g) plus the bag mass uncertainty (2 g); that is, 2 g per sieve.

The initial amount of sample prior to sieving was not measured. However, the total amount of sieved material is shown in Table 16.1: 4.752(84) g.

With the information in Table 16.1, it is possible to depict the particle size distribution diagram for the sample under analysis: Figure 16.1.

Table 16.1 Sieve analysis laboratory data. Sample Origin: Eppenstein. Material: Bark. Analysis dates: 2011-03-07 to 2011-03-09. Responsible: DH

Sieve Aperture mm	Sieving Method	Mass of retained sample kg	Uncertainty g
125	Mechanical	0.000	4
100	Mechanical	0.000	4
80	Mechanical	0.084	4
63	Mechanical	0.184	4
50	Mechanical	0.124	4
40	Mechanical	0.356	4
31.5	Mechanical	0.344	4
20	Mechanical	1.320	4
18	Mechanical	0.264	4
16	Mechanical	0.246	4
14	Mechanical	0.258	4
10	Mechanical	0.482	4
8	Mechanical	0.386	4
6.3	Mechanical	0.142	4
3.15	Manual	0.312	4
2.5	Manual	0.046	4
1.6	Manual	0.072	4
1	Manual	0.044	4
0.5	Manual	0.034	4
0.25	Manual	0.028	4
0	Manual	0.026	4
Total		4.752	84

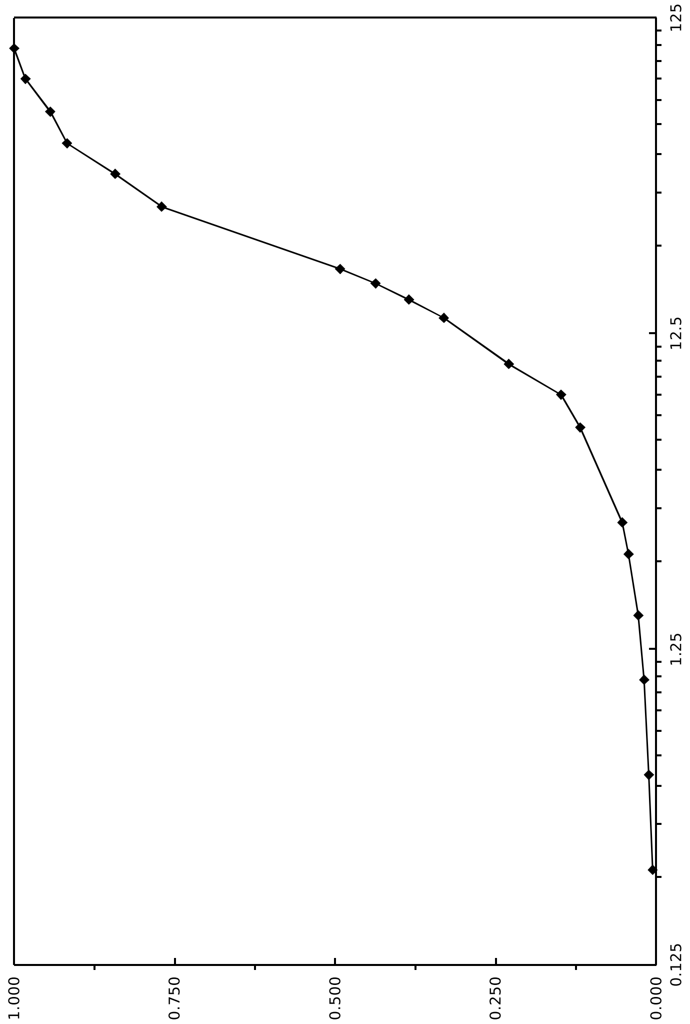

Figure 16.1 Particle size distribution. Sample Origin: Eppenstein. Material: Bark. Analysis dates: 2011-03-07 to 2011-03-09. Responsible: DH

17

BULK DENSITY ANALYSIS

The present chapter reports the bulk density protocol for the concrete case of the material sampled in Eppenstein. However, the same methodology was applied in the other described cases.

17.1 INTRODUCTION

Bulk density refers to the density of a material that comes in large mass or volume. It includes solid, liquid and gaseous phases.

The total mass is commonly accounted for solid and liquid particles, whereas the total volume accounts for all the states of matter.

The procedure is standardized via the ONR CEN/TS 15401:2010.01.01, « Methods for the determination of bulk density » for solid recovered fuels and the ASTM E 873:1982, « Standard Test Method for Bulk Density of Densified Particulate Biomass Fuels (Re-approved 1998) », [18].

17.2 METHODOLOGY

[Sample origin] The material, bark, was sampled in *Eppenstein*, province of Styria, AUT. The forest is populated by two species of coniferous: Spruce and Larch. There, all of the residues are shredded *in situ* to a size between 100 mm and 250 mm and then sieved through 250 mm.

[Sample composition] The sample was composed mostly by bark, shreds and dust.

[Sample preparation] The material was taken from a larger amount that had been previously dried for *ca.* three weeks at room conditions. Then it was partitioned into four. One of the quarters was used for the present assay.

[Bulk density determination] A plastic bucket with a known volume (5.331(1) l) and mass (216(1) g) was filled with sample. Then it was allowed to fall onto a piece of wood from a distance of *ca.* 15 cm. Next it was refilled with sample to compensate for the reduced volume and finally weighed on a scale (Kern TB $d = 2\,\mathrm{g}$).

At the end, the bulk density was calculated and the uncertainties of the measurements estimated.

17.3 RESULTS

The data collected during the analysis is presented in Table 17.1. Uncertainty values were estimated as described in [97].

17.4 DISCUSSION

With the values presented in Table 17.1 it is possible to calculate the value for the bulk density:

$$\gamma_{\text{bulk}} = 158.1(4)\,\mathrm{kg\,m^{-3}}\,. \qquad [17.1]$$

Table 17.1 Bulk density analysis laboratory data (sample mass was determined with the bucket mass tared.). Sample Origin: Eppenstein. Material: Bark. Analysis date: 2011-03-15. Responsible: DH

Parameter	Value	Uncertainty	Unit
Bucket mass	216	1	g
Bucket volume	5.331	0.002	l
Sample mass	0.906	0.002	kg
Sample mass	0.870	0.002	kg
Sample mass	0.794	0.002	kg
Sample mass	0.802	0.002	kg
Average	0.843	0.002	kg

18

THERMAL ANALYSES

The present document reports the analyses performed at the laboratories of the Chair of Thermal Process Technology (TPT) using samples gathered from Eppenstein and Gaal. However, the same methodology was applied in the other described cases. The analyses comprised water content, elemental analyses (carbon, hydrogen, nitrogen, and sulphur), and enthalpy change of combustion, *aka* higher heating value.

18.1 INTRODUCTION AND THEORETICAL BACKGROUND

The set of experiments was carried out at the laboratories of the Chair of Thermal Process Technology (TPT), Montanuniversität Leoben, AT. Since all the equipment used during the analyses is technologically sophisticated, its operation requires more than basic training and, overall, experience; so the major tasks were done by the Chair's personnel.

The analyses carried out were basically the determination of the moisture, ultimate analyses and change in the enthalpy of combustion (aka, higher heating value or hhv), in biomass samples; that is, the measurement of moisture content, C, H, N and hhv. The technical references can be found in [1, 2, 3, 5].

Water content was measured using gravimetry in a balance while the drying process itself was done by means of an autoclave. The water content was then calculated:

$$w_{\mathrm{H_2O}} = \left(1 - \frac{m_S}{m}\right) \times 100\%\,, \qquad [18.1]$$

where $w_{\mathrm{H_2O}}$ is the fraction of water (water content) in the sample, m_S mass of solids in the sample (mass of sample after having been dried) and m is the mass of the sample as received.

On the other hand, CHN analyses were done in a gas analyzer using complete (total) combustion of biomass samples in an reactive atmosphere; that is, allowing the inclusion of O_2. This could be represented as a (unbalanced) symbolic reaction, [102, 108]

$$\mathrm{CHONS(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} + \mathrm{H_2O(g)} + \mathrm{NO_2(g)} + \mathrm{SO_2(g)}, \qquad [18.2]$$

where $\mathrm{CHNS(s)}$ represents biomass composition before combustion. The values for CHNS come from the values of their gaseous phases [CO_2(g), H_2O(g), NO_2(g) and SO_2(g), respectively] by means of calculations done by the equipment using recorded values, calibration values and molecular masses of the different species.

Finally, enthalpy change of combustion corresponds to the hhv. It was measured in a bomb calorimeter tracking the change in enthalpy of water from 22 °C to 23 °C while biomass burns. Again, the process could be represented as a (unbalanced) symbolic reaction:

$$\mathrm{CHONS(s)} + \mathrm{O_2(g)} \xrightarrow{\Delta} \mathrm{CO_2(g)} + \mathrm{H_2O(g)} + \mathrm{NO_2(g)} + \mathrm{SO_2(g)}, \quad [18.3]$$

where the symbol Δ represents heating; that is the hhv.

18.2 METHODOLOGY

In this section, the processes used to analyze the samples are described. [The following description is a product of personal notes [66] while performing the experiments.]

18.2.1 Sample origin and composition

868(2) g of shredded (250 mm), sieved (250 mm) and dry (air-dry for *ca.* 5 weeks) forest residues from the location of Gaal (Styria, AT) prepared during 2011-02-16 were used for the analyses. The sample was labelled with a TPT internal code: lab-24-11.

Similarly, 1.010(2) kg of shredded, sieved and air-dried bark from the location of Eppenstein (Styria, AT) prepared during 2011-03-07 were also used for the analyses. The sample was labelled with a TPT internal code: lab-25-11.

18.2.2 Size reduction and sample preservation

Both materials (forest residues and bark) were shredded twice at the TPT laboratories: the first time down to 4.0 mm and then to 0.75 mm.

Finally, the each shredded material was placed into four labelled recipients (eight in total):

1. a glass bottle hermetically sealed (to guarantee moisture preservation);
2. two plastic bottles (kept as reserve at the TPT labs);
3. and a plastic bag containing the rest of the sample (to be used for further analyses).

18.2.3 Water content

Three samples for each material (six in total) were taken directly from the hermetically sealed glass bottles to perform the water content analyses.

Then, *ca.* 1 g per analysis were weighed using a Mettler Toledo AX 204 ($d = 0.1$ mg) and its value registered.

Next, the materials were placed in plastic recipients and finally in an autoclave at 105 °C for 2.5 h.

After this time, the water-free samples were weighed and then the water content calculated. Finally, the reported values are the average values of the three measurements.

18.2.4 Elemental analyses

The elemental analyses of the samples were done in two stages by means of two different procedures: first, C, H and N were analyzed and then S.

Carbon, hydrogen and nitrogen analyses

Carbon, hydrogen and nitrogen analyses were carried out using one equipment: LECO CHN-1000, Leco Instruments GmbH pre-set with the KOHLE method (internal TPT program).

The calibration of C and H was performed with EDTA (EDTA 1054) ranging from *ca.* 0.1 g to 0.2 g to cover the whole analysis ranges with a Mettler Toledo AT261 scale ($d = 0.1$ mg).

EDTA: Ethylenediaminetetraacetic acid

Nitrogen was calibrated with N-corn (1.69(3) % N content).

For the measurement, approximately 0.08 g of sample were placed into an automatic sampler. Five samples per material were used; *i.e.*, a total of ten samples. From these, four were analysed and one was used as control.

Finally, the resultant C, H and N amounts were calculated as the average value of the measurements and then their bases were changed to dry (reported as dry substance).

Sulfur analysis

Sulfur analysis was carried out using a LECO SC144DR. The oven temperature was kept constant at 1320.52(1) °C and the sample was burnt with O_2(g) at 2.8 bar.

The calibration was performed using Sulfur in coal 502-433 by (LECO) with a S content of 0.24(3) %. The samples for calibration varied from 0.19 g to 0.23 g to cover the whole analysis range with a Mettler Toledo AT261 scale ($d = 0.1$ mg).

During the S determination, C is also recorded, but its value is taken from the CHN measurements.

For the measurement, ten samples (five for each location) with masses ranging from *ca.* 0.19 g to 0.23 g were placed into a ceramic mould and then entered into the oven. Once there, the gas produced during the combustion of the sample with oxygen was analyzed and recorded.

Finally, the average values were taken and their bases changed to dry (using the water content as-received).

18.2.5 Enthalpy change of combustion

aka heating value, energy value, higher heating value

The analysis of the enthalpy changes of combustion was done with samples taken from the glass bottles; *i.e.*, with the as-received water content.

The measurements were carried out on an analytic balance (Mettler Toledo AX 205) $d = 0.01$ mg and in a bomb calorimeter (IKA-Werke C5003) in an adiabatic system that exchanges energy (combustion) to a water pool kept initially at *ca.* 22 °C. Combustion took place with O_2 at 40 bar.

For each measurement, the process was as follows:

1. the sample was weighed to an amount of approximately 0.3 g;
2. then it was soaked (*ca.* 0.1 g) with paraffin oil ($\Delta_c H = 46.300$ kJ/g) used as ignition aid;
3. simultaneously, 5 ml of distilled water was placed into a metallic container;
4. next, the sample and a cotton string ($\Delta_c H = 50$ J/g) – also used as ignition aid – was placed on top of the container;
5. then the container was sealed and placed into the bomb calorimeter;
6. the bomb calorimeter was started, the combustion of the materials took place and finally the results were displayed on the equipment's screen.

18.3 RESULTS

18.3.1 *Water content*

The average water content was 7.63(1) % for the Gaal sample (shredded forest residues) and 7.21(1) % for the Eppenstein sample (bark).

18.3.2 *Elemental analyses: CHNS*

For the sample of Gaal (shredded forest residues), the amounts were carbon 50.84(1)%, hydrogen 5.90(1)%, nitrogen 0.66(1)% and sulphur 0.08(1)%; *i.e.*, a ratio of CHNS: 50.8:5.90:0.66:0.08%. These values were reported in a dry basis.

For the bark (Eppenstein), the amounts were carbon 51.33(1)%, hydrogen 5.64(1)%, nitrogen 0.37(1)% and sulphur 0.03%; *i.e.*, a ratio of CHNS: 51.3:5.6:0.37:0.03%. These values were reported in a dry basis.

18.3.3 *Enthalpy changes of combustion*

For the shredded forest residues (Gaal), the $\Delta_c H_{\text{expt}}(\text{dry}, \text{MJ kg}^{-1}) = 21.484$ (aka, hhv); the $\Delta_c H_{\text{theor}}(\text{dry}, \text{MJ kg}^{-1}) = 20.189$ (aka, lhv).

For the sample of Eppenstein (bark), the $\Delta_c H_{\text{expt}}(\text{dry}, \text{MJ kg}^{-1}) = 20.976$ (aka, hhv); the $\Delta_c H_{\text{theor}}(\text{dry}, \text{MJ kg}^{-1}) = 19.738$ (aka, lhv).

19

PROXIMATE ANALYSES

The present chapter reports the proximate analyses protocol for the concrete case of the material sampled in Eppenstein and Gaal. However, the same methodology was applied in the other described cases.

19.1 INTRODUCTION AND THEORETICAL BACKGROUND

Proximate analysis is a set of thermochemical analyses that measure the water mass fraction, volatile matter mass fraction and ash yield mass fraction of a biomass sample, [102].

All of such analyses are usually based on thermal gravimetry; that is, measuring the mass of a sample as received, then placing it into a thermal reactor (usually an oven) under specific temperature conditions, letting the sample stand in the reactor for a specific retention time and finally measuring the mass left after the thermal treatment, [123].

Water mass fraction is measured by exposing the sample to a temperature of 105(5) °C for 24 h. Then, the water content is calculated by

$$w_{\mathrm{W}} = \left(1 - \frac{ms}{m}\right) \times 100\,\%\,, \qquad [19.1]$$

where w_{W} is the water mass fraction, ms the solid mass measured after 24 h and m is the mass of the sample measured as received; that is, before the thermal exposure, [1].

Volatile matter mass fraction is measured by exposing the sample for 7 min to a temperature of 900(10) °C. Then, it is calculated by

$$w_{\mathrm{vm}} = \left(1 - \frac{ms}{m}\right) \times 100\,\%\,, \qquad [19.2]$$

where w_{vm} is the volatile matter mass fraction, ms the solid mass measured after 7 min and m is the mass of the sample measured as received; that is, before the thermal exposure, [6].

Ash yield mass fraction is measured by exposing the sample to variable temperature according to a defined (heating) temperature profile, *see* Figure 19.1. Then, it is calculated by

$$w_{\mathrm{ay}} = \left(1 - \frac{ms}{m}\right) \times 100\,\%\,, \qquad [19.3]$$

where w_{ay} is the ash yield mass fraction, ms the solid mass measured after heating and m is the mass of the sample measured as received; that is, before the thermal exposure, [4].

Regularly, the values for the moisture content analysis and ash yield analysis are reported in dry basis by means of the following expression:

$$w_{\mathrm{dry}} = w_{\mathrm{ar}} \left(\frac{100}{100 - w_{\mathrm{W}}}\right)\,, \qquad [19.4]$$

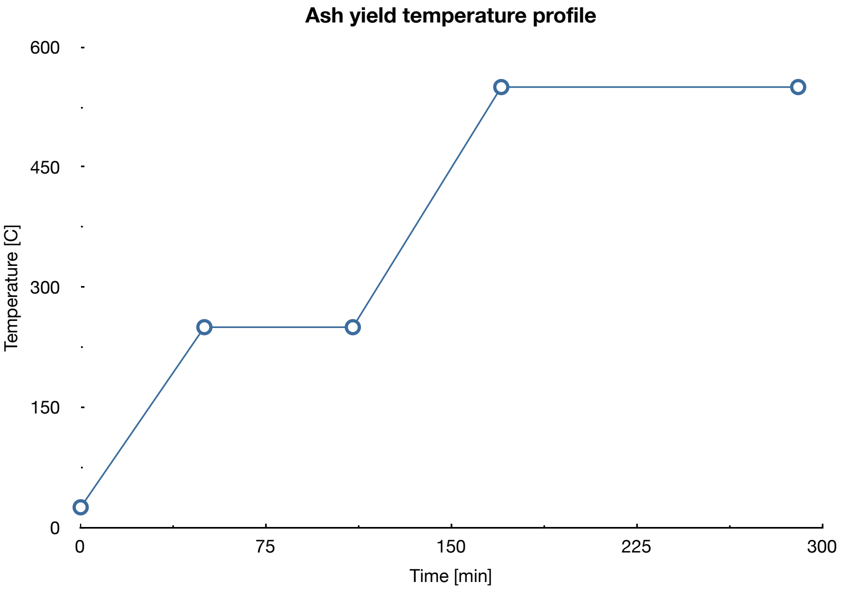

Figure 19.1 Ash yield heating
Ash yield (heating) temperature profile. The initial value for temperature is the Room Temperature at the beginning of the test.

where w_{dry} is either the volatile matter content value or the ash yield value in dry-basis, w_{ar} the parameter value in as-received basis and w_{w} is the moisture content in percentage (%).

19.2 METHODOLOGY

The set of experiments was carried out at the laboratories of the Chair of Mineral Processing (AuV), Montanuniversität Leoben, AT. The samples used during the experimental phase were prepared at the Chair of Thermal Process Technology (TPT), Montanuniversität Leoben, AT.

[The following description is a product of reviewing and applying standard methods of analyses, [1, 4, 6], and personal notes [66].]

Samples were gathered from the locations of Gaal (forest residues) and Eppenstein (wood chips). They were shredded (250 mm), sieved (250 mm) and dried (air-dry for *ca.* 5 weeks). Then, they were sent to the TPT to be shredded by 0.75 mm. Finally, they were labelled with TPT internal codes: lab-TPT-24-11 for Gaal's sample and lab-TPT-25-11 for Eppenstein's sample.

19.2.1 Moisture content analysis

The process used to measure moisture content was as follows:

1. The equipment was set up to operate: an oven (Heraeus Instruments UT 6060) was set to 105 °C and an analytical balance (Mettler Toledo AX 204, $d = 0.1\,\mathrm{mg}$) was tared;
2. a ceramic crucible used to hold the samples during the thermal treatment was tared;
3. into the tared crucible, approx. 1.3 g of sample was placed and then its actual mass was measured;

4. the set crucible-sample was placed into the oven for 24 h;
5. when the retention time was finished, the set was taken out of the oven and placed into a desiccator for few minutes (regularly 10 min) to cool down and facilitate manipulation;
6. finally, the mass of the set was measured again.

[Note: three samples for each location were used during the experiments in order to take into account possible error sources and to have a better statistical significance. The reported values were calculated using the arithmetic mean value if there were not outliers.]

19.2.2 Volatile matter content analysis

The process used to measure volatile matter content was as follows:

1. The equipment was set up to operate: a muffle oven (Nabertherm GmbH, 30 °C to 3000 °C with controller P320MB1) was set to 900 °C and an analytical balance (Mettler Toledo AX 204, $d = 0.1\,\mathrm{mg}$) was tared;
2. a quartz, sealable recipient used to hold the sample during the thermal treatment was tared with its lid (top);
3. into the recipient, approx. 1.3 g of sample was placed, sealed and then its actual mass was measured;
4. the set recipient-sample was placed into the oven for 7 min;
5. when the retention time was finished, the set was taken out of the oven and placed into a desiccator for few minutes (regularly 10 min) to cool down and facilitate manipulation;
6. finally, the mass of the set was measured again (recipient with lid).

[Note: three samples for each location were used during the experiments in order to take into account possible error sources and to have a better statistical significance. The reported values were calculated using the arithmetic mean value if there were not outliers.]

19.2.3 Ash yield analysis

The process used to measure ash yield was as follows:

1. The equipment was set up to operate: a muffle oven (Nabertherm, GmbH, 30 °C to 3000 °C with controller P320MB1) was set to operate following a program given by Figure 19.1 (set up but not started!) and a analytical balance (Mettler Toledo AX 204, $d = 0.1\,\mathrm{mg}$) was tared;
2. a ceramic crucible recipient used to hold the sample during the thermal treatment was tared;
3. into the recipient, approx. 1.3 g of sample was placed and then its actual mass was measured;
4. the set recipient-sample was placed into the cold oven (room temperature), then the oven heating program was started;
5. when the retention time was finished, the set was taken out the oven and placed into a desiccator for few minutes (regularly 10 min) to cool down and facilitate manipulation;

6. finally, the mass of the set was measured again (recipient with lid).

[Note: three samples for each location were used during the experiments in order to take into account possible error sources and to have a better statistical significance. The reported values were calculated using the arithmetic mean value if there were not outliers.]

19.3 RESULTS AND DISCUSSION

For the Gaal's sample, the mean value of the moisture content as received was 7.78 %, the mean value of the volatile matter content in dried basis (value corrected using the moisture content figure) was 83.24 % and the mean value of the ash yield in dried basis (value corrected using the moisture content figure) was 3.76 %.

For the Eppenstein's sample, the mean value of the moisture content as received was 6.84 %, the mean value of the volatile matter content in dried basis (value corrected using the moisture content figure) was 92.31 % and the mean value of the ash yield in dried basis (value corrected using the moisture content figure) was 0.24 %

From these values, it can be seen that both samples (forest residues from Gaal and wood chips from Eppenstein) have similar moisture content. This is due to the fact that both samples were kept at the same conditions and had similar sizes during storage.

Volatile matter content and ash yield are, on the other hand, different. This is due to the nature of the samples. Forest residues are very heterogeneous in their composition (leaves, bark, branches, and so on), whereas wood chips are formed mainly by wood.

Fixed carbon can be calculated using the volatile matter content and the ash yield: for the forest residues: $w_{\text{fc, dry}} = 100-(83.24+3.76) = 13\,\%$, for the wood chips: $w_{\text{fc, dry}} = 100-(92.31+0.24) = 7.45\,\%$. Thus, it can be said that wood chips are a cleaner fuel (ash yield less than 1%) than forest residues, but, also, have less fixed carbon. This is specially important when considering the future application of the biomass. Wood chips will yield a better fuel if they are to be used in syngas production, where a high volatile matter content is desirable, but forest residues will yield a better starting material if they are to be used in the preparation of biocoal.

20

CARBONIZATION

The present chapter reports the carbonization protocol for the concrete case of the material sampled in Eppenstein. However, the same methodology was applied in the other described cases.

20.1 INTRODUCTION

Biomass carbonization is the process of heating biomass at high temperatures under inert conditions with the intention of producing biocoal. Thus, thermal biocoal production is a form of pyrolysis, [129].

The process begins when biomass is fed into a thermal reactor. There, it is gradually heated from 200 °C to 900 °C for a couple of hours while moving from the reactor feeder to its outlets. The reactor inlet is normally sealed to prevent the inclusion of O_2 that, otherwise, would burn biomass, thus yielding ash, [67].

During heating, biomass undergoes (thermal) decomposition that forces it to release gases (moisture and volatile matter content) leaving behind biocoal: a black, coal-like solid mostly composed of the initial biomass' fixed carbon content. This could be represented as a (unbalanced) symbolic reaction, [102, 108]

$$\mathrm{CHONS(s)} \xrightarrow{\Delta} \text{gases} + \mathrm{C(s)}, \qquad [20.1]$$

where $\mathrm{CHONS(s)}$ represents biomass composition before carbonization. The end products (gases and C(s)) are pyrolysis gases and biocoal (or biocharcoal), respectively.

Then, the two reaction products (gases and biocoal) are separately redirected: gases go to two outlets (one for combustion before atmospheric release; another one for analyzing its composition). Biocoal, on the other hand, goes to a collecting unit.

Biocoal (the remaining solid) is sent to be analyzed for composition and thermal properties (Chair of Thermal Process Technology and Chair of Mineral Processing, Montanuniversität Leoben, AT): proximate and ultimate analyses and higher and lower heating values, respectively, using the methodologies described in [1, 2, 3, 4, 5, 6].

On the other hand, pyrolysis analyses are done in-situ, by means of a gas analyzer connected to the reactor.

20.2 EQUIPMENT DESCRIPTION

Biomass carbonization was carried out at the laboratories of the Chair of Non-Ferrous Metallurgy (NFM), Montanuniversität Leoben, AT. The reactor, sensors and analyzers were bought from a German vendor, but assembled by the Chair's personnel [67], *see* Figure 20.1. [The following description is a product of an interview with Thomas Griessacher (NFM member) [67] and personal notes [66].]

The equipment consists on a 4 −kg-capacity tower (feeder) covered with a hermetically sealed top. Biomass is therein placed and then drops down by gravity into a thermal reactor (referred to as the *carbonizer*).

Transport through the carbonizer is done by means of two Archimedes screws that rotate towards each other at a rate of approx. 20 rpm. Such a speed translates into horizontal displacement of biomass leading to a retention time of 2 h.

The carbonizer itself is a metallic tube (cylinder) heated up by electricity (Joules heating). It is thermally insulated (adiabatic heating) and hermetically sealed (to prevent combustion). The reactor heating is done in three stages: 200, 550, and 900 °C through the reactor's length (2.6 m); that is, at an average rate of 336 °C/m, *see* Figure 20.2. Heating is controlled by a system of thermometers placed into it and by a computer monitor that controls the amount of electric energy sent to the reactor.

There are two outlets in the reactor: one for directing gas to a burner, another for fueling a portion of the pyrolysis gases to a cleaning system before gas analysis. In the burning chamber, propane is also injected to help complete combustion before releasing combustion gases to the atmosphere. The produced biocoal, on the other hand, is kept in the reactor and allowed to cool down to room temperature for 24 h. Biocoal is then manually removed.

Before analysis, a portion of the unburned pyrolysis gases flows through a cleaning system: two flasks connected in parallel: the first one contains water; the second one, ceramic beads. The purpose of cleaning is to cool down the gas and to buffer some gases that, otherwise, could damage the gas sensors and analyzers.

A rack of electric equipment contains the gas sensors and analyzers. CO(g), CO_2(g), H_2(g) and SO_2(g) are there measured in « real » time and finally their concentrations recorded and displayed, aided by a computer, in a form of a graph, Figure 20.3.

Finally, there are other experimental considerations that must be taken into account during biomass carbonization:

1. As the only pretreatment, (raw) biomass is cut down to 7 cm to avoid reactor blockage. This is particularly important, for, if biomass does not flow properly through the reactor, then CO(g) and H_2(g) are not directed to the burner and combusted. They thus become a possible cause of explosions. Additionally, when biomass is not in motion, it becomes a place where gases condense and form tars, thus clogging the screws with this viscous liquid difficult to clean up.

2. The criterium that indicates that all the biomass was converted into either gas or biocoal is the rising of the O_2(g) at the end of the profile shown in the gas composition profile, *see* Figure 20.3. Then the experiment finishes and the feeder can be opened to allow air to enter into the carbonizer releasing its internal pressure.

20.3 METHODOLOGY

As a test, sample from Gaal was used. The sample was cut down (7 −cm long) and kept at room conditions (average moisture content: 20 %). The carbonizer was started and allowed to heat up to its optimal profile levels (200, 550 and 900 °C).

Then, the experiment began:

1. Approximately, 5 kg of (raw) biomass were placed into the feeder and then closed.
2. The screws were put to rotate at approx. 20 rpm.
3. With that speed, biomass flowed for 2 h releasing gases and producing biocoal.
4. At the end of the experiment, the solid product (biocoal) was left to cool down for 24 h, collected and removed from the end of the reactor.
5. Before, meanwhile and after the retention time, the gaseous flow was redirected to the burning chamber and to the cleaning system.
6. The « clean » gas passed through the rack of sensors that measured in « real » time CO(g), CO_2(g), H_2(g) and SO_2(g) concentrations.

20.4 RESULTS AND DISCUSSION

The outputs of the experiment are the composition profile and biocoal itself.

20.4.1 Composition profile

In the gas composition graph, Figure 20.3, one can see three zones: in the first one, biomass begins to heat up and moisture and volatile matter begin to gasify. The profile shows that, during this phase, the O_2(g) concentration drops quite sharply and CO(g), CH_4(g) CO_2(g) begin to rise.

In the second zone, biomass is readily converted into either gas or biocoal. There is a stable production of pyrolysis gases: CO(g), CO_2(g), H_2(g) and SO_2(g) are seen in large concentrations in comparison with the baseline (air composition). It is to be noticed that, at the end of 1.5 h of pyrolysis, the presence of H_2(g) is notorious: it rises from almost 0 % to 36 %; this was due to a sensor malfunction, since H_2(g) production begins in the first zone, [67].

In the third zone, when the retention time has passed, gas and biocoal production begins to decay and, as biomass rests are converted into biocoal, all of these gases concentrations begin to fade out. The gas production ending is indicated by the abrupt rise of O_2(g) in the composition profile.

20.4.2 Biocoal

As it can be seen in Figure 20.4, biocoal carbonized from wood chips looks like coal itself, but it preserves the form of the input material.

The analysis of the experiment, however, can be better understood by looking at the results of proximate analyses before and after carbonization, *see* Table 20.1. Moisture and volatile matter decrease, specially volatile matter. Nevertheless, this is an expected outcome, since it is due to the high temperatures at which biomass is exposed during carbonization.

On the other hand, fixed carbon mass fraction increases more than ten times. This change translates also in an increment on the hhv value:

Sample	TPT-code	Moisture [%] ar	Ash yield [%] dry	Volatile matter [%] dry	Fixed carbon [%] dry	hhv [kJ/kg] dry
Wood chips	25-11	7.07	0.20	92.2	7.55	20976
Biocoal	59-11	4.60	5.41	9.42	85.2	31699
Change		0.65	27.0	0.10	11.3	1.5

Table 20.1 Proximate analyses of wood chips before and after carbonization at 900 °C for 2 h

50 % more than that of raw biomass. However, on the down side, ash yield raises as well, an increase of 27 times. The increment, nevertheless, is not due to chemical transformations but to the decrease in biomass concentration. This is because ashes are the product of mineral matter that has gasification temperatures much higher than the highest exposure temperature that biomass undergoes in this experiment: 900 °C. In other words, due to their composition, while biomass components volatilize or transform (thus decreasing the solid content), mineral matter only concentrates (due to the decrement).

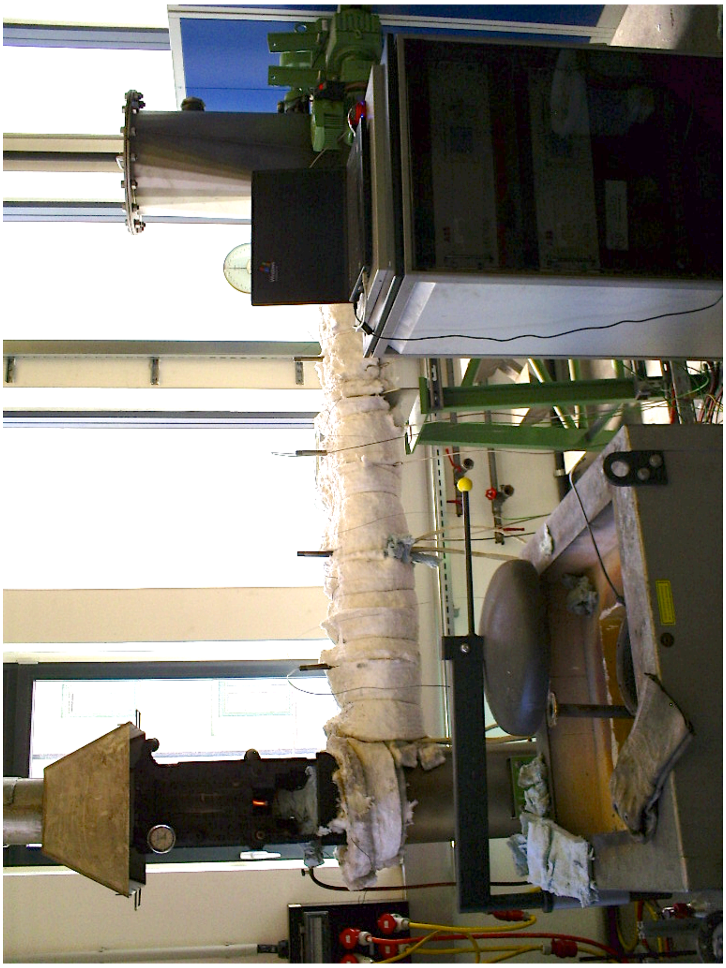

Figure 20.1 Carbonizer at Non-Ferrous Metallurgy: a) feeder, b) thermally insulated reactor, c) thermometers, d) burning chamber (combustion), e) gas sensors and analyzers and f) logging and display system

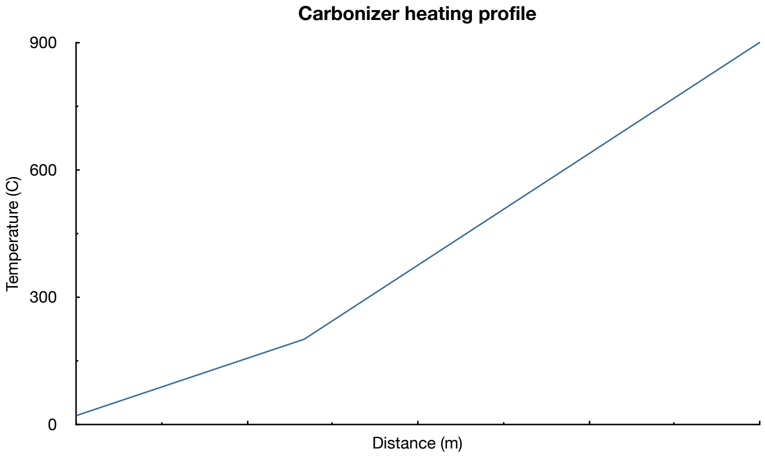

Figure 20.2 Carbonizer Heating Profile

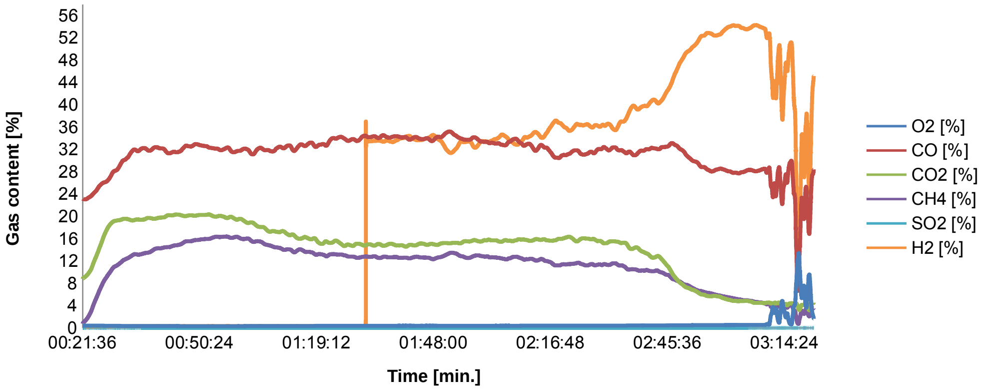

Figure 20.3 Gas composition before, during and after carbonization. The analyzed gas was first cleaned by passing it through water and ceramic beads.

Figure 20.4 Wood chips biocoal after carbonization at 900 °C for 2 h

21

BIOCOAL DEMAND

The present chapter reports the calculation of the theoretical biocoal demand necessary to reduce zinc oxide to zinc present in electric arc furnace dust.

21.1 INTRODUCTION

The biocoal demand is estimated by assuming that the carbon contained within the biocoal is consumed by two sources, zinc oxide and ferric oxide, both present in electric arc furnace dust. The consumption is assumed to be the complete combustion of carbon.

21.2 BIOCOAL DEMAND FOR ZINC OXIDE REDUCTION

The reduction of zinc oxide during complete combustion of carbon is modeled by assuming that

- the fixed carbon in biocoal is the only C source;
- electric arc furnace dust, EAFD, is the source of zinc oxides;
- all of the C goes to CO and all of the CO goes to CO_2 (complete combustion of C);
- during reduction, it is assumed good mixture, homogeneous pellets, complete combustion during reduction; *i.e.*, enough O_2 in air and inside pellets.

Under such assumptions, the chemical model is given by

$$2\mathrm{C(s)} + \mathrm{O_2(g)} + 2\mathrm{ZnO(s)} \xrightarrow{\Delta} 2\mathrm{CO_2(g)} + 2\mathrm{Zn(s)}\,, \qquad [21.1]$$

where $\xrightarrow{\Delta}$ stands for combustion.

21.2.1 *Data*

The data used for the calculations are presented in Table 21.1.

21.2.2 *Calculation*

With the data presented in Table 21.1 and with the chemical model, the biocoal demand is found to be

$$\mathrm{C_{demand}} = f\,\frac{\mathrm{C}}{\mathrm{ZnO}}\,\frac{\mathrm{ZnO}}{\mathrm{EAFD}}\,, \qquad [21.2]$$

where $\mathrm{C_{demand}}$ is the C demand to reduce the ZnO present in the electric arc furnace dust, EAFD.

For the sample under study,

$$\mathrm{C_{demand}} = f\,\frac{\mathrm{C}}{\mathrm{ZnO}} = 1.150 \times 147.6 \times 0.3547 = 60.21\,\mathrm{g\,kg^{-1}}\,. \qquad [21.3]$$

In words, 60.21 g of biocoal are needed to reduce the zinc oxide contained in 1 kg of EAFD.

Table 21.1 Data for the calculation of the biocoal, C, demand to reduce ZnO according to Equation 21.4

Parameter	Value	Unit	Reference
C atomic weight	12.011	$\mathrm{g\,mol^{-1}}$	[137]
O atomic weight	15.9994	$\mathrm{g\,mol^{-1}}$	[137]
Zn atomic weight	65.39	$\mathrm{g\,mol^{-1}}$	[137]
CO molecular mass	28.0104	$\mathrm{g\,mol^{-1}}$	calculation
ZnO molecular mass	81.40	$\mathrm{g\,mol^{-1}}$	calculation
C/ZnO molar ratio	1.	1	Equation 21.4
C/ZnO mass ratio	0.1476	$\mathrm{g\,g^{-1}}$	calculation
C/ZnO mass ratio	147.6	$\mathrm{g\,kg^{-1}}$	calculation
Stoichiometric correction factor, f	1.150	1	[68]
ZnO in EAFD, ZnO/EAFD	35.47	%	[68]
ZnO in EAFD, ZnO/EAFD	0.3547	1	[68]

21.3 BIOCOAL DEMAND FOR FE-OXIDE REDUCTION

The reduction of ferric oxide during complete combustion of carbon is modeled by assuming that

- Fixed carbon in biocoal is the C source;
- electric arc furnace dust, EAFD, is the source of iron oxides;
- all of the C goes to CO and all of the CO goes to CO_2;
- during reduction, it is assumed good mixture, homogeneous pellets, complete combustion during reduction; *i.e.*, enough O_2 in air and inside pellets.

Under such assumptions, the chemical model is given by

$$\begin{aligned} &2\mathrm{C(s)} + \mathrm{O_2(g)} \xrightarrow{\Delta} 2\mathrm{CO(g)} \\ &3\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \xrightarrow{\Delta} 2\mathrm{Fe(s)} + 3\mathrm{CO_2(g)}\,, \end{aligned} \tag{21.4}$$

where $\xrightarrow{\Delta}$ stands for combustion.

21.3.1 Data

The data used for the calculations are presented in Table 21.2.

21.3.2 Calculation

With the data presented in Table 21.2 and with the chemical model, the biocoal demand is found to be

$$C_{\mathrm{demand}} = f \frac{\mathrm{C}}{\mathrm{Fe_2O_3}} \frac{\mathrm{Fe_2O_3}}{\mathrm{EAFD}}\,, \tag{21.5}$$

where C_{demand} is the C demand to reduce the Fe_2O_3 present in the electric arc furnace dust, EAFD.

Table 21.2 Data for the calculation of the biocoal, C, demand to reduce Fe_2O_3 according to Equation 21.4

Parameter	Value	Unit	Reference
C atomic weight	12.011	$g\,mol^{-1}$	[137]
O atomic weight	15.9994	$g\,mol^{-1}$	[137]
Fe atomic weight	55.847	$g\,mol^{-1}$	[137]
CO molecular mass	28.0104	$g\,mol^{-1}$	calculation
Fe_2O_3 molecular mass	159.69	$g\,mol^{-1}$	calculation
C/Fe_2O_3 molar ratio	3.	1	Equation 21.4
C/Fe_2O_3 mass ratio	0.2256	$g\,g^{-1}$	calculation
C/Fe_2O_3 mass ratio	225.6	$g\,kg^{-1}$	calculation
Stoichiometric correction factor, f	1.150	1	[68]
Fe_2O_3 in EAFD, Fe_2O_3/EAFD	31.6	%	[68]
Fe_2O_3 in EAFD, Fe_2O_3/EAFD	0.316	1	[68]

For the sample under study,

$$C_{\text{demand}} = f\frac{C}{Fe_2O_3} = 1.150 \times 225.6 \times 0.316 = 81.98\,g\,kg^{-1}\,. \qquad [21.6]$$

In words, 81.98 g of biocoal are needed to reduce the ferric oxide contained in 1 kg of EAFD.

21.4 RESULT

With both demands calculated, the final biocoal demand is given by

$$C_{\text{total}} = C_{ZnO} + C_{Fe_2O_3} = 60.21\,g\,kg^{-1} + 81.98\,g\,kg^{-1} = 142.19\,g\,kg^{-1}\,. \qquad [21.7]$$

In other words, 142.19 g of biocoal are required to reduce 1 kg of EAFD containing zinc oxide and ferric oxide.

22

PELLETING

The present chapter reports the pelleting protocol for the concrete case of the material carbonized from the one taken in Eppenstein and electric arc furnace dust. However, the same methodology was applied in the other described cases.

22.1 INTRODUCTION

Biomass pelleting refers to the production of pellets, with a mixture of biomass, water and other additives using a pelleting machine; aka, pelletizer. Water and additives are used to hold the biomass particles together, whereas the pelletizer is used to give the mixture a fixed shape and size. The idea behind pelleting is that pellets, as being pressed by the pelletizer, have a greater density than unpressed biomass, which translates in lower transportation costs [8].

Another use of pellets include the reduction of mineral oxides by biocoal, then substituting oxide reduction with coal. This is the main aim of the pellet production described herein.

In the biomass-as-fuel literature [73] pellets refer to cylinders (normally, 6 −cm diameter and 15 −cm long) made of biomass [139]. In this report, however, pellets refer to small spheres (approx. 2 −mm radius); this usage is the common one in metallurgy.

22.2 METHODOLOGY

[The following description is a product of personal notes [66] taken during the experiment.]

The sample used in the experiment came from Eppenstein. This sample underwent carbonization (pyrolysis at 900 °C for 2 h), then it was crushed down to the size of millimeters (to become dust) and then preserved in plastic bags.

With such a sample, pellet production begun:

1. Since pellets of ≤ 2 −mm diameter were required by the reduction experiments, the biocoal sample was sieved through 0.5 mm;

2. 17.4 g of biocoal were mixed with 100 g of electric arc furnace dust, EAFD, containing ZnO and Fe-oxides, the oxides to be reduced by pellet combustion, and 1.5 g of CaO. The amounts of biocoal, EAFD and CaO were previously calculated using the reduction experiments requirements;

3. the materials were thoroughly mixed by hand, until an homogeneous mixture was seen to be formed, *see* Figure 22.1;

4. on the other hand, the pelletizer drum was set to an inclination of 45° and started to rotate at level 1, *see* Figure 22.2;

5. the mixture was placed into the rotating drum and then water was added with a spray bottle along the rotating mixture, *see* Figure 22.3;

6. at the beginning, it was seen that the water added to the mixture was slowly absorbed, thus, forming nothing but tiny spheres;
7. more water was added and the rotation speed was increased until the mixture changed from dusty to agglomerations of material; that is, pellets;
8. after a couple of hours of watering, rotating, sieving large particles and removing material stuck onto the drum surface, pellets with the required size were collected, sieved ($< 2\,\mathrm{mm}$) and then let dry for 24 h, *see* Figure 22.4;
9. finally, since approx. 300 g of pellets were required for the reduction experiments and since the pelletizer works better with a mass $\leq 150\,\mathrm{g}$ (mixture and water), the entire process had to be repeated three times.

Some important points that were kept during the pellet production:

- at the beginning, water had to be slowly added and the drum rotation speed was kept slow. If not, large pellets were produced. Even worse, they were wet on the outside, but dry in the inside, *see* Figure 22.5;
- CaO was added as the only additive. Not because it helped the mixture to form pellet (water would have been enough for this particular sample), but because, during the reduction experiments, slag formation was undesired. (Slag production is related to pellet basicity.)

Figure 22.1 Homogeneous mixture of biocoal, electric arc furnace dust and CaO before watering and rotation

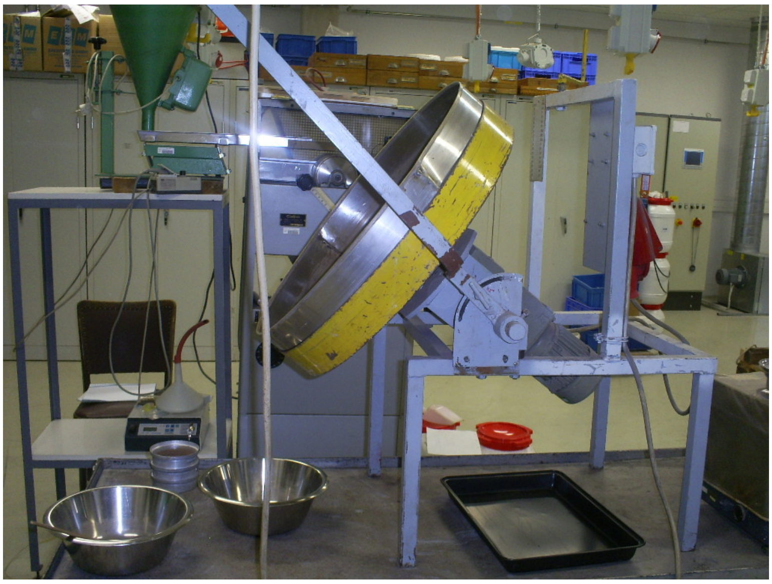

Figure 22.2 Pelletizer with an inclination of 45° of its drum

Figure 22.3 Pellet production: pellets being formed by the addition of water and by rotation of the pelletizer drum

Figure 22.4 Pellets after production, sieving and drying for 24 h

Figure 22.5 Large pellets produced by over watering the mixture or excessive drum rotation speed

Part III

CARBOTHERMIC MODEL

23

FUNDAMENTALS

We establish herein the thermodynamic bases for further analyses. We follow closely the reasoning presented in [43] and, to a lesser extend, in [23, 25, 89, 130].

23.1 ENERGY CONSERVATION AND ENTROPY PARACONSERVATION

Consider a bounded physical system. On physical grounds, the system has well defined energy and entropy. The system energy obeys a *local conservation law*:

any decrease in the amount of energy in a given region of space must be exactly balanced by a *simultaneous* increase in the amount of energy in an *adjacent* region of space.

Since the energy transport from region to region can be quantified, energy conservation may be written as

$$\begin{array}{c} \text{change in energy} \\ \text{(inside boundary)} \end{array} = \begin{array}{l} \text{net flow of energy} \\ \text{(inward minus outward across boundary)} \end{array} . \qquad [23.1]$$

So defined, the law automatically sets the *sign convention* for any energy flow:

- positive for inward flow across the boundary and
- negative for outward flow.

On the other hand, the system entropy obeys a *local paraconservation law*:

$$\begin{array}{c} \text{change in entropy} \\ \text{(inside boundary)} \end{array} \geq \begin{array}{l} \text{net flow of entropy} \\ \text{(inward minus outward across boundary)} \end{array} . \qquad [23.2]$$

That is, entropy is *nearly* conserved; for the inequality 23.2 states that the entropy in a given region can increase, but cannot decrease, but by flowing into adjacent regions.

Neither temperature nor heat were needed to state the laws. Nor they define energy or entropy. Mechanics defines and quantifies energy; while information theory (probability), entropy. However, temperature, energy, and entropy are indeed connected, as diagrammed in fig. 23.1. Finally, see that energy conservation was not defined in terms of entropy, nor the other way around: both laws are independent.

Table 23.1 Types of boundaries of a physical system. Adapted from [87]

Boundary type	Mass flow	Work flow	Heat flow
Open	Yes	Yes	Yes
Closed	No	Yes	Yes
Thermally isolated	No	Yes	No
Mechanically isolated	No	No	Yes
Isolated	No	No	No

Notice also that the « type » of system boundary was not mentioned as traditionally required (see table 23.1). Only a boundary is needed. If energy flows through it, then it is accounted for.

23.2 INTERNAL ENERGY, ENTROPY, AND VOLUME

Hereafter in the current document, given a physical system, we denote its *internal energy*, its *entropy*, and its *volume* as follows:

- internal energy by U,
- entropy by S, and
- volume by V.

23.3 MACROSTATE AND PARAMETER SPACE

Before further development, let us agree on some definitions.

State function of a system is a quantity uniquely determined by the system macrostate, *aka* thermodynamic state. A state function value does not depend on the path whereby the system arrived at a macrostate.

The introduction of state functions rests on the idea that

> a macrostate ought to be described by a few macroscopic quantities; rather than by a myriad of microscopic ones.

Chemical composition, energy (enthalpy, Helmholtz, Gibbs), entropy, mass, mass density (specific volume), particle number, pressure, temperature, and volume are examples of state functions.

State equation is a mathematical relation between state functions.

Parameter space is the set of all possible combinations of values for all the different physical quantities contained in a physical model. The size of a parameter space is the number of quantities required to span it; that is, the number of independent quantities required to describe the system macrostate. This size can be computed by using *Gibbs' phase rule*, section 23.4.

Isentropic process is a process that occurs without entropy changes.

Adiabatic process is a process that occurs without changes of internal energy. During an adiabatic change, temperature may change; *e.g.*, during adiabatic heating and adiabatic cooling.

Heating or cooling: we use the terms in the sense of temperature changes: *heating* means an increase in a species temperature, with respect to a reference temperature; while *cooling*, a decrease in temperature. So defined, these terms will not invoke then the concept of « heat ».

23.4 GIBB'S PHASE RULE

When system state functions change or are changed, the chemical species forming the system themselves change. For instance, when a solid-containing system is isobarically heated, the solid temperature raises and the solid volume increases: the solid expands. If heating is high enough, then the solid reaches a critical temperature (melting point) and begins to melt. If heating continues and if all the solid has been melted to the liquid phase, then the liquid temperature starts to change. Thermodynamics studies and quantifies all of these behaviors. We will see that, by using few basic concepts of differential forms, we can study multiple function changes. Therefore, it is useful to have a guide to establish the minimum information required to describe a system and thus focus work. This guide is *Gibbs' phase rule*. (Herein we closely follow [13].)

Before stating the rule, we need to agree on some terminology:

Phase: a state of matter uniform throughout, not only in chemical composition, but in physical state. We denote by p the number of phases in a system.

Constituent: a chemical species present in a system.

Component: chemically independent constituent of a system. The number of components, c, in a system is the minimum number of species necessary to define the system composition. When no chemical reactions occur and there are no other constraints (such as charge balance), the number of components equals the number of constituents (species).

Variance: the number of intensive quantities that can be changed independently without disturbing the number of phases in equilibrium.

Gibbs' phase rule relates the variance of a system, its components, and its phases in equilibrium as follows:

$$f = c - p + 2 \, .$$

So stated, the rule suggests a convenient way of applying it to a system under study:

1. Write down the chemical equation for the reaction.
2. Identify the constituents of the system as well as the phases.
3. Decide whether, under the conditions prevailing in the system, any of the constituents can be prepared from any of the other constituents.
4. Remove these constituents to have the number of independent constituents (components).
5. Calculate the minimum number of these independent constituents needed to specify the composition of all the phases using Gibbs' rule.

Let's give some examples to clarify these ideas.

Consider first a fixed amount of an ideal gas in a box. By being ideal, the gas consists of a non-reactive species in one phase. Then, since there are no chemical reactions, the number of constituents equals the number of components $c = 1$. Therefore, the system variance is ($f = 1-1+2 = 2$) two. Historically, for a defined amount of the gas, these quantities are two out of three: the gas pressure, temperature, and volume, because all are related by the ideal gas state equation: $pV = n\hat{r}t$.

Next, consider a metal Me being melted. The process can be represented as

$$\mathrm{Me(s)} \xrightarrow{\Delta} \mathrm{Me(l)}\,.$$

That is, there are two constituents in two phases. But, since the constituents are not independent, the number of components reduces to one. Then, by Gibbs' rule, the process variance is $f = 1 - 2 + 2 = 1$, which means that we require only one quantity to describe the system composition; *e.g.*, pressure. In this way, we could track temperature or volume in terms of pressure; *i.e.*, $t(p), V(p)$.

As a final example, consider the complete combustion of methane at room state:

$$\mathrm{CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)}\,.$$

There are four constituents and two phases. Then, Gibbs' rule tells us that the variance of the system is ($4 - 2 + 2 = 4$) four. One can choose, for instance, $t, p, p(\mathrm{CH_4})/p, p(\mathrm{O_2})/p$ to determine the system composition.

23.5 PRESSURE AND TEMPERATURE

Herein we review the theoretical definitions of the fundamental concepts of pressure and temperature for thermodynamic systems.

23.5.1 *Definitions of pressure and temperature*

Consider a bound physical system. Denote by U, S, V the system internal energy, entropy, and volume. Suppose the system be endowed with a well defined macrostate representable in a parameter space with state functions running through well defined values that vary smoothly. Finally, suppose the system contain a defined amount of a non-reactive chemical species in one phase.

Then, the system macrostate is spanned by a three-quantity parameter space. Choose the set $\{U, S, V\}$ to span the space. Hence, the system internal energy becomes a state function of the system entropy and volume: $U(S, V)$. This allows us to model system internal energy changes by its *total differential*:

$$\mathrm{d}U = \partial_S U|_V \, \mathrm{d}S + \partial_V U|_S \, \mathrm{d}V\,. \qquad [23.3]$$

(Throughout the current document, we use *Jacobi's notation* for partial derivatives:

$$\partial_S U|_V \equiv \left.\frac{\partial U}{\partial S}\right|_V ,$$

where the symbol $\equiv$ means *logical equivalence*.)

Since the total differential of state function plays the role of the gradient of a real-valued function in vector analysis, eq. (23.3) states that $\mathrm{d}U$ points in the direction wherein U increases the fastest (direction of the slope line). Hence, the partial $\partial_S U|_V$ measures the internal energy change in the $\mathrm{d}S$-direction; while the partial $\partial_V U|_S$, the change in the $\mathrm{d}V$-direction.

The partials in eq. (23.3) appear so often in thermodynamics that they obtained formal (and familiar) interpretations and symbols:

The first partial is defined as the system *thermodynamic temperature*:

$$t \mathrel{\hat{=}} \partial_S U|_V \, ;$$

and

the second, the system *pressure*:

$$-p \mathrel{\hat{=}} \partial_V U|_S \, .$$

The negative sign in p accords with the fact that internal energy changes and volume changes scale inversely to one another; then, so must pressure. Hence, it measures the decrease in internal energy change in the $\mathrm{d}S$ direction.

These defined quantities render a concise expression for the system internal energy changes:

$$\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V \, , \qquad [23.4]$$

which is our final result.

Some final ideas on this section:

- We use hereafter the shorter term *temperature* in lieu of thermodynamic temperature.
- It is customary to assign the dimensions of Θ to temperature.
- It is customary to assign the dimensions of E/L^3 to pressure.
- Equation (23.4) is made of *paired quantities* having energy dimensions. These pairs have an intensive and an extensive quantity: temperature pairs with entropy; pressure with volume. This suggests that

  > each intensive quantity is a *generalized force* acting upon its corresponding extensive quantity to change the overall system energy.

- We now know why pressure and temperature only appear in system analysis (not in particle analysis): it is due to entropy, which is a probability measure.
- Since energy, entropy, and volume are extensive properties, their ratios, temperature and pressure, are *intensive*.

23.5.2 *Partial pressure*

Consider an ideal homogeneous mixture of j ideal gases, each contributing with an amount n_j to the mix. Since the mixture is itself a gas (a physical system), it has a well defined pressure p and a well defined amount $n = \sum_j n_j$.

Now, choose a gas from the mixture, say the i-th gas. Then, define the gas *partial pressure* as

$$p_i \mathrel{\hat=} x_i p \,,$$

where x_i is the gas *molar fraction*:

$$x_i \mathrel{\hat=} \frac{n_i}{n} \,.$$

Hence, it follows that the amount and pressure of the gas are related by

$$x_i = \frac{n_i}{n} = \frac{p_i}{p} \,.$$

The last relation proves to be handy in multicomponent analysis, along with the extent of reaction, defined in section 23.7.

Finally, note that the total pressure of the mixture equals the sum of the partial pressures of each individual gas:

$$p = \sum_j p_j \,.$$

The concept of partial pressure is necessary, because ideal gases dissolve, diffuse, and react following their partial pressures, and *not* their concentrations in ideal gaseous mixtures or liquids.

23.6 ENERGY LIKE STATE FUNCTIONS

Besides internal energy, there are three other functions, having dimension of energy, that are often used in practice: Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy. Here, we define and study them.

23.6.1 *Definitions of energy like state functions*

Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy are defined, based on internal energy, as follows:

Helmholtz' free energy: $F \mathrel{\hat=} U - tS$.

Gibbs' free enthalpy: $G \mathrel{\hat=} U - tS + pV$.

Enthalpy: $H \mathrel{\hat=} U + pV$.

These functions and their interrelations are compiled in fig. 23.2.

23.6.2 *Exterior derivatives of energy like state functions*

Recall that

thermodynamics is concerned with *changes* in state functions rather than with their absolute values.

It is thus necessary to find the changes in F, G, H. Such variations are expressed as the exterior derivatives of the functions. However, such derivatives are not only mapped to energy, but also to other state functions, such as p, t, V. These maps can be found by appealing to the definitions of F, G, H and by using *a* general form of $\mathrm{d}U$, such as eq. (23.4), since the mathematical form of $\mathrm{d}U$, and thus of $\mathrm{d}F, \mathrm{d}G, \mathrm{d}H$, depends on the physical process under analysis and the particular representation of $\mathrm{d}U$ in the process parameter space.

To construct the state changes in energy like functions, apply the properties of the exterior derivative and algebra to the definitions of the functions. For instance, consider a system whose *internal energy* changes are $\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V$. Then, by definition, the system enthalpy is $H = U + pV$. Now, use the linearity and product rule of the exterior derivative to find the enthalpy changes: $\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p$. But $\mathrm{d}U + p\,\mathrm{d}V = t\,\mathrm{d}S$, thus

$$\mathrm{d}H = t\,\mathrm{d}S + V\,\mathrm{d}p\,. \qquad [23.5]$$

This gives enthalpy changes in terms of temperature and volume.

The same method was used to find $\mathrm{d}F, \mathrm{d}G$. The results are summarized in fig. 23.3.

Alternatively, changes in energy like functions can be found by Legendre transformations of one to another. For instance, to find enthalpy changes, one needs to transform $\mathrm{d}U$ as shown in fig. 23.3; *i.e.*, to interchange $\mathrm{d}U$ to $\mathrm{d}H$ and $p\,\mathrm{d}V$ to $-V\,\mathrm{d}p$:

$$\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V \xrightarrow[p\,\mathrm{d}V \to -V\,\mathrm{d}p]{\mathrm{d}U \to \mathrm{d}H} \mathrm{d}H = t\,\mathrm{d}S - (-V\,\mathrm{d}p)\ ,$$

in agreement with eq. (23.5).

23.7 EXTENT OF REACTION

This section follows [19, 115].

Definition: consider a system wherein a chemical reaction happens. Consider the chemical equation be of the form:

$$\sum_{\mathrm{X}} \mathrm{X}\nu(\mathrm{X})\,,$$

where X are the reaction chemical species and $\nu(\mathrm{X})$ its stoichiometric number.

Let R be a *reactant* in the last reaction. Suppose now an amount $\mathrm{d}\xi$ of R change. Then, the change in the amount of R is $\mathrm{d}n(\mathrm{R}) = -\nu(\mathrm{R})\mathrm{d}\xi$. Thus, the *extent of the reaction* is

$$\mathrm{d}\xi = \frac{\mathrm{d}n(\mathrm{R})}{-\nu(\mathrm{R})}\,.$$

Now, let P be a *product* in the last reaction. Then, the change in the amount of P is $\mathrm{d}n(\mathrm{P}) = +\nu(\mathrm{P})\mathrm{d}\xi$. Thus, we have that

$$\mathrm{d}\xi = \frac{\mathrm{d}n(\mathrm{P})}{+\nu(\mathrm{P})}\,.$$

We can generalize these results for a species X:

$$\mathrm{d}\xi \mathrel{\hat{=}} \frac{\mathrm{d}n(\mathrm{X})}{\nu(\mathrm{X})}\,, \qquad [23.6]$$

being careful to give the proper sign to its stoichiometric number: negative if reactant, positive if product.

We see that $\mathrm{d}\xi$ can be interpreted as the amount being changed in the *reaction* and is thus independent on the species. Note additionally that, since $\dim \xi = \mathrm{N}$, it is also an *extensive* quantity. Moreover, since defined as the change of a state function, ξ is also a *state function*.

On the other hand, for finite changes, we have that

$$\Delta\xi = \frac{\Delta n(\mathrm{S})}{\nu(\mathrm{S})} \,.$$

In particular, if the initial amount of S, $n^{\mathrm{o}}(\mathrm{S})$, is known, then the change in the reaction extent is

$$\Delta\xi = \frac{n(\mathrm{S}) - n^{\mathrm{o}}(\mathrm{S})}{\nu(\mathrm{S})} \,.$$

Finally, see that in both cases, differential and finite changes:

- the extend of the reaction, $\mathrm{d}\xi$, vanishes at the beginning of the reaction;
- $\mathrm{d}\xi$ equals a maximum set by the stoichiometry at the completion of the reaction; and
- $\mathrm{d}\xi$ varies between both limits while the reaction happens.

Relations: the extent of a reaction can be related to the reaction enthalpy and Gibbs' free enthalpy *via* the relations

$$\Delta_{\mathrm{r}}\hat{h} = \partial_\xi H\Big|_{p,t} \,, \qquad \Delta_{\mathrm{r}}\hat{g} = \partial_\xi G\Big|_{p,t} \,.$$

Note that both relations are isobaric and isothermal; *i.e.*, they work at constant pressure and temperature.

On the other hand, we can relate the reaction extent with mass changes, instead of amount changes. Recall that the amount of a substance and its mass are related by $\hat{m}n = m$, where $\hat{m}$ is the molar mass of the substance. Then, $\hat{m}\,\mathrm{d}n = \mathrm{d}m$, for $\hat{m}$ is constant. Replacing this into the definition of ξ, eq. (23.6), gives

$$\mathrm{d}\xi = \frac{\mathrm{d}m}{\hat{m}\nu} \,,$$

wherefrom one gets the changes in *specific* enthalpy and Gibbs' free enthalpy

$$\Delta_{\mathrm{r}}h = \hat{m}\nu\,\partial_m H|_{p,t} \,, \qquad \Delta_{\mathrm{r}}g = \hat{m}\nu\,\partial_m G|_{p,t} \,.$$

Reaction kinetics: in the study of reaction kinetics, the extent of reaction varies with time, τ. Then, we define the *reaction rate* as

$$\begin{aligned} r &\mathrel{\hat{=}} \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}\tau} \,, \\ &= \frac{1}{V}\frac{1}{\nu(\mathrm{S})}\frac{\mathrm{d}n(\mathrm{S})}{\mathrm{d}\tau} \,, \end{aligned}$$

which is independent of the compound chosen to measure r.

Application: consider the carbothermic reduction of zinc oxide to zinc. The process chemical equation is

$$2\,\mathrm{ZnO(s)} + \mathrm{C(s)} \xrightarrow{\Delta} 2\,\mathrm{Zn(g)} + \mathrm{CO_2(g)}\,.$$

If ZnO changes by an amount $\mathrm{d}n(\mathrm{ZnO(s)})$, then we have that the extent of reaction changes by

$$\begin{aligned}\Delta\xi &= \frac{\Delta n(\mathrm{ZnO(s)})}{-2}\,,\\ &= -\frac{1}{2}\Delta n(\mathrm{ZnO(s)})\,,\end{aligned}$$

provided the change is finite. Moreover, since $\Delta\xi$ is species independent, we have that

$$\Delta\xi = -\frac{1}{2}\Delta n(\mathrm{ZnO(s)}) = -\Delta n(\mathrm{C(s)}) = \frac{1}{2}\Delta n(\mathrm{Zn(g)}) = \Delta n(\mathrm{CO_2(g)})\,.$$

Multicomponent system: To appreciate the utility of the extent of reaction, consider a system wherein a fraction of (solid) carbon totally burns; while another, partially does:

$$2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO(g)}\,,\quad \mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)}\,. \qquad [23.7]$$

At the beginning, C(s) reacts by an amount $\mathrm{d}n(\mathrm{C(s)})$. Then, we have that

$$\mathrm{d}\xi_1 = \frac{1}{2}\mathrm{d}n(\mathrm{CO(g)})\,,\quad \mathrm{d}\xi_2 = \mathrm{d}n(\mathrm{CO_2(g)})\,.$$

Therefore, the total change of $\mathrm{d}n(\mathrm{C(s)})$ is

$$\begin{aligned}\mathrm{d}n(\mathrm{C(s)}) &= -2\mathrm{d}\xi_1 - \mathrm{d}\xi_2\,,\\ &= -\,\mathrm{d}n(\mathrm{CO(g)}) - \mathrm{d}n(\mathrm{CO_2(g)})\,.\end{aligned}$$

A similar analysis can be done for the rest of the species involved ineq. (23.7):

$$\begin{aligned}\mathrm{d}n(\mathrm{C(s)}) &= -2\mathrm{d}\xi_1 - \mathrm{d}\xi_2\,, & \mathrm{d}n(\mathrm{O_2(g)}) &= -\mathrm{d}\xi_1 - \mathrm{d}\xi_2\,,\\ \mathrm{d}n(\mathrm{CO(g)}) &= 2\mathrm{d}\xi_1\,, & \mathrm{d}n(\mathrm{CO_2(g)}) &= \mathrm{d}\xi_2\,.\end{aligned}$$

23.8 ENERGY CHANGES IN REACTIVE SYSTEMS

In the past sections, we laid the theoretical ground for fundamental concepts in non-reactive systems. In this section, on the other hand, we extend such ideas on the more general footing for systems in which chemical reactions happen.

23.8.1 General formulation

Consider a homogeneous system containing i different species. Suppose a chemical reaction occur in the system. The system internal energy can then be expanded as $U(S, V, \xi)$. Thus, the system internal energy changes become

$$\mathrm{d}U = \partial_S U|_{V,\xi}\,\mathrm{d}S + \partial_V U|_{S,\xi}\,\mathrm{d}V + \partial_\xi U\Big|_{S,V}\mathrm{d}\xi\,,$$

where $\partial_S U|_{V,\xi}$, $\partial_V U|_{S,\xi}$, $\partial_\xi U\Big|_{S,V}$ are the system temperature, pressure, and molar energy of reaction, $t, -p, \hat{\eta}$. Therefore, we can rewrite $\mathrm{d}U$ as

$$\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V + \hat{\eta}\,\mathrm{d}\xi\,. \qquad [23.8]$$

On the other hand, to have $\mathrm{d}F, \mathrm{d}G, \mathrm{d}H$, Legendre transform $\mathrm{d}U$ to the various energy like functions as explained in section 23.6.2. We summarized the calculation in fig. 23.4.

23.8.2 Utility of Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy

Suppose the internal energy of a system change, due to a process, in a manner given by eq. (23.8):

$$\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V + \hat{\eta}\,\mathrm{d}\xi\,.$$

That is, the system internal energy changes, or can be changed, by altering any of three factors: $t\,\mathrm{d}S, p\,\mathrm{d}V, \hat{\eta}\,\mathrm{d}\xi$. Hence, to study how a factor affects $\mathrm{d}U$, it would be ideal to isolate it. Here is where the different energy like functions come into handy:

- To isolate $p\,\mathrm{d}V$ changes, carry out the process isothermally and at constant composition (no mass flow, no chemical reaction). Then, $\mathrm{d}F$ simplifies to

  $$\mathrm{d}F = -p\,\mathrm{d}V\,.$$

  That is, Helmholtz' free energy is useful for studying $p\,\mathrm{d}V$ changes.

- To isolate $\hat{\eta}\,\mathrm{d}\xi$ changes, carry out the process isobarically and isothermically. Then, $\mathrm{d}G$ simplifies to

  $$\mathrm{d}G = \hat{\eta}\,\mathrm{d}\xi\,.$$

  That is, Gibbs' free enthalpy is useful for studying $\hat{\eta}\,\mathrm{d}\xi$ changes.

- To isolate $t\,\mathrm{d}S$ changes, carry out the process isobarically and at constant composition (no mass flow, no chemical reaction). Then, $\mathrm{d}H$ simplifies to

  $$\mathrm{d}H = t\,\mathrm{d}S\,.$$

  That is, enthalpy is useful for studying $t\,\mathrm{d}S$ changes.

23.9 CONNECTIONS BETWEEN STATE FUNCTIONS

In section 23.8, we found two forms of expressing internal energy changes in a system:

$$\begin{aligned}\mathrm{d}U &= \partial_S U|_{V,\xi}\,\mathrm{d}S + \partial_V U|_{S,\xi}\,\mathrm{d}V + \partial_\xi U\Big|_{S,V}\,\mathrm{d}\xi\,,\\ &= t\,\mathrm{d}S - p\,\mathrm{d}V + \hat{\eta}\,\mathrm{d}\xi\,,\end{aligned}$$

wherefrom we identify the system properties $t, p, \hat{\eta}$ as

$$t = \partial_S U|_{V,\xi}\,, \qquad -p = \partial_V U|_{S,\xi}\,, \qquad \hat{\eta} = \partial_\xi U\Big|_{S,V}\,.$$

In analogous manner, Helmholtz's free energy, Gibbs' free enthalpy, and enthalpy can be expressed in two different forms. Then, similar associations follow. Such associations are summarized in fig. 23.5, which shows that the different state functions are connected to each other by their fundamental relations to internal energy and entropy, *via* definitions and Legendre transforms. Additionally, as mentioned in section 23.8.2, some state functions are more suitable to work with in some situations, but, since connected to one another, there are no exclusivities. All the representations are context dependent.

23.10 ENERGY OF REACTION

Up to this point, we have been using the symbol $\hat{\eta}$ without a proper discussion of it. We do so here.

First, recall its definition and its relations with other state functions:

$$\hat{\eta} \circeq \partial_\xi U\Big|_{S,V} = \partial_\xi F\Big|_{p,V} = \partial_\xi G\Big|_{p,t} = \partial_\xi H\Big|_{S,p} .$$

Since $\dim \xi = \mathrm{N}$ and since all the partials are of energy with respect to the reaction extent, we have that $\dim \hat{\eta} = \mathrm{E}/\mathrm{N}$. We are dealing with the change of an energy like function per unit amount; *i.e.*, a molar energy. Hence, $\hat{\eta}$ is an *intensive* quantity.

Now, recall that the functions F, G, H all are more suitable for different purposes, depending on what is to be studied. We saw above that, whenever pressure and temperature are kept constant, changes in composition are more easily studied by using Gibbs' free enthalpy, because, under such conditions, $\mathrm{d}G$ becomes simply

$$\mathrm{d}G = \hat{\eta}\, \mathrm{d}\xi = \partial_\xi G\Big|_{p,t} . \qquad \text{[isobaric, isothermal]}$$

Therefore, $\hat{\eta}$ is better thought of (but not exclusively) as the isobaric, isothermal molar Gibbs free enthalpy change with respect to the reaction extent or more simply as the molar Gibbs' free enthalpy of reaction.

Finally, similarly to pressure (intensive) acting on volume (extensive) to change the system energy as $p\, \mathrm{d}V$, we interpret $\hat{\eta}\, \mathrm{d}\xi$:

the molar Gibbs' free enthalpy of reaction (intensive) acts on the extent of the reaction (extensive) to change the system energy.

23.11 CHEMICAL POTENTIAL

Consider a system whose number of particles varies. Particles may come in or leave the system due to transport (convection, diffusion), or they may be produced or consumed due to chemical reactions. Then, the system parameter space needs to be enlarged to take into account for these particle variations. Let us say, for the sake of argument, that there are μ_i number of particles of the i-th species in the system. Then, the system parameter space can be spanned by the set $\{U, S, V, \mu_i\}$, where the index i runs through all the species. System internal energy changes are thus given by

$$\mathrm{d}U = \partial_S U|_{V,\mu_i}\, \mathrm{d}S + \partial_V U|_{S,\mu_i}\, \mathrm{d}V + \partial_{\mu_i} U|_{S,V}\, \mathrm{d}\mu_i .$$

Associate the partial derivatives as

$$t = \partial_S U|_{V,\mu_i} , \quad -p = \partial_V U|_{S,\mu_i} , \quad \hat{\mu}_i \circeq \partial_{\mu_i} U|_{S,V} ,$$

where μ_i is the *chemical potential* of the i-th species in the system.

Lastly, express $\mathrm{d}U$ in terms of the associated partials:

$$\mathrm{d}U = t\, \mathrm{d}S - p\, \mathrm{d}V + \hat{\mu}_i\, \mathrm{d}\mu_i ,$$

which is our final result.

There are some technicalities to keep in mind when using chemical potentials:

- the « chemical potential » is not exclusively related to chemical reactions. As derived, the equation expresses energy changes even if there is no chemical reaction occurring. For example, material transport can also change energy without changing the chemistry of the system.

- Note that $\dim \partial_\mu U|_{S,V} = \mathrm{E}/\mathrm{S}$. Thus, $\hat{\mu}$ is a *molar energy* and so an *intensive* quantity. More properly, $\hat{\mu}$ is an isochoric, isentropic molar energy.

- The defining property of $\hat{\mu}$ is that it is the conjugate to $\mathrm{d}\mu$; *i.e.*, $\hat{\mu}$ acts upon $\mathrm{d}\mu$ to change the energy of the system, just as p acts on $\mathrm{d}V$, for the same reason.

Finally, recall that all of the state quantities of a system are interconnected to one another. Then, we can rewrite $\hat{\mu}$ in different forms, as we did for the extent of reaction. We did so and collected the results in fig. 23.6.

Note that, as we did in section 23.8.2, if we keep the system at constant pressure and temperature, then Gibbs' free enthalpy reduces to

$$\mathrm{d}G = \hat{\mu}_i \, \mathrm{d}\mu_i \, .$$

This relation provides us with a mean to compute $\hat{\mu}_i$, when $\mathrm{d}G$ is known. This equation also implies that

$$\hat{\mu}_i = \partial_{\mu_i} G|_{p,t} \, ,$$

which is sometimes taken as the definition of chemical potential.

23.12 PHASE TRANSITION THERMODYNAMICS

Consider a system composed of a non-reactive species S(s) in its solid state. Suppose the system be isobarically heated so the species melts. Then, the phase change can be represented as

$$\mathrm{S(s)} \xrightarrow{\Delta} \mathrm{S(l)} \, .$$

To span the system parameter space, choose the set $\{H, p, t, \xi\}$, wherefrom enthalpy expands as $H(p, t, \xi)$. Hence, enthalpy changes are given by the total differential

$$\mathrm{d}H = \partial_t H|_{p,\xi} \, \mathrm{d}t + \partial_\xi H\Big|_{p,t} \mathrm{d}\xi \, . \qquad \text{[isobaric]}$$

Let us interpret physically both partials in the last equation:

- The first partial represents the thermal change in enthalpy at constant composition and pressure. It is then the *isobaric enthalpy capacity*, C_p; while

- the second partial, the compositional change in enthalpy at constant pressure and temperature. This partial has $\dim \partial_\xi H\Big|_{p,t} = \mathrm{E}/\mathrm{N}$, because $\dim \xi = \mathrm{N}$. Then, it is a *molar* quantity and thus *intensive*. Notice that the partial says that, even if enthalpy is required to change the species phase, this enthalpy change is isothermal. So, it will *not* be recorded by a thermometer in thermal contact with the system. For this reason, it was historically known as « latent heat », from the Latin *latere*, to lie hidden. Finally, due to the fact that this enthalpy expresses the changes from the species solid state to the liquid one, it is called *fusion*. Thus, we can define a new material property:

$$\hat{h}_{\mathsf{fus}} = \partial_\xi H\Big|_{p,t}\,, \qquad [23.9]$$

called the *molar enthalpy of fusion*.

With both quantities properly defined and interpreted, we can write enthalpy changes during heating as

$$\mathrm{d}H = C_p\,\mathrm{d}t + \hat{h}_{\mathsf{fus}}\,\mathrm{d}\xi\,.$$

Now, if the total enthalpy change is required, then we can integrate $\mathrm{d}H$ between two macrostates:

$$\begin{aligned}\Delta H = \int \mathrm{d}H &= \int_{t_1,t_2} C_p\,\mathrm{d}t + \int_{\xi_1,\xi_2} \hat{h}_{\mathsf{fus}}\,\mathrm{d}\xi\,,\\ &= C_p\,\Delta t + \Delta_{\mathrm{fus}}\hat{h}^{\circ}\,\Delta\xi\,,\end{aligned}$$

where the last equality was obtained by assuming constant capacity and constant molar enthalpy of fusion. Moreover, the molar enthalpy of fusion is in itself a change and normally quoted from tables at its standard state; *i.e.*, for the *change in standard molar enthalpy of fusion*, $\Delta_{\mathrm{fus}}\hat{h}^{\circ}$.

Finally, the same method can be used to obtain enthalpy changes if the phase transition is not from solid to liquid, but from any phase to another; *e.g.*, from liquid to solid, solid to gas, gas to liquid, and so on. For instance, the enthalpy required by a species to turn from its solid into its gaseous state is

$$\mathrm{d}H = C_p{}^{\mathrm{sol}}\,\mathrm{d}t + \Delta_{\mathrm{fus}}\hat{h}^{\circ}\,\mathrm{d}\xi^{\mathrm{fus}} + C_p{}^{\mathrm{liq}}\,\mathrm{d}t + \Delta_{\mathrm{vap}}\hat{h}^{\circ}\,\mathrm{d}\xi^{\mathrm{vap}} + C_p{}^{\mathrm{gas}}\,\mathrm{d}t\,.$$

The entire process is summarized in an *enthalpy curve*, such as fig. 23.7.

23.13 THERMODYNAMICS OF CHEMICAL REACTIONS

In this section, we review some basis of chemical reactions from the viewpoint of chemistry and link them to thermodynamics, the main subject of this chapter.

23.13.1 Classification of chemical reactions

In general, it is useful to classify the chemical reactions involved in an engineering process to get a deeper understanding into the process: are there phase, electric, temperature, or the like, changes in the process? We hence give some criteria to classify chemical equations, based on [116, 29]:

Acid-base reaction: an acid reacts with a base to yield a salt.

Exchange reaction: a reaction of the form $\mathrm{AB} + \mathrm{C} \longrightarrow \mathrm{AC} + \mathrm{B}$ or $\mathrm{AB} + \mathrm{CD} \longrightarrow \mathrm{AD} + \mathrm{CB}$.

Synthesis reaction: two or more species combine to form one compound, *aka* combination or synthesis reactions, with the form $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB}$.

Decomposition reaction: a chemical reaction of the form $\mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B}$.

Redox reaction: a chemical reaction that exhibits a change in the oxidation states of one or more elements in the reactants with the form $\mathrm{oxidant} + \mathrm{reductant} \longrightarrow \mathrm{reducedoxidant} + \mathrm{oxidizedreductant}$.

Table 23.2 The different types of transition enthalpies encountered in thermochemistry. Adapted from [13]

Transition	Process [1]	Symbol
Atomization	species(s_{lg}) $\longrightarrow$ atoms(g)	$\Delta_{\mathrm{at}} H$
Combustion	compounds(s_{lg}) + O_2(g) $\longrightarrow$ CO_2(g)H_2O(l_g)	$\Delta_{\mathrm{c}} H$
Electron gain	X(g) + e^-(g) $\longrightarrow$ X^-(g)	$\Delta_{\mathrm{eg}} H$
Formation	elements $\longrightarrow$ compound	$\Delta_{\mathrm{f}} H$
Fusion	s $\longrightarrow$ l	$\Delta_{\mathrm{fus}} H$
Hydration	$X^{\pm}$(g) $\longrightarrow$ $X^{\pm}$(aq)	$\Delta_{\mathrm{hyd}} H$
Ionization	X(g) $\longrightarrow$ X^+(g) + e^-(g)	$\Delta_{\mathrm{ion}} H$
Mixing	pure $\longrightarrow$ mixture	$\Delta_{\mathrm{mix}} H$
Phase transition	phaseα $\longrightarrow$ β	$\Delta_{\mathrm{trs}} H$
Reaction	reactants $\longrightarrow$ products	$\Delta_{\mathrm{r}} H$
Solution	solute $\longrightarrow$ solution	$\Delta_{\mathrm{sol}} H$
Sublimation	s $\longrightarrow$ g	$\Delta_{\mathrm{sub}} H$
Synthesis	X + Y $\longrightarrow$ XY	$\Delta_{\mathrm{syn}} H$
Vaporization	l $\longrightarrow$ g	$\Delta_{\mathrm{vap}} H$

Decomposition reaction: one species is converted into two or more simpler species. They not need be redox.

Combustion reaction: a redox reaction wherein oxidation is very rapid and accompanied by thermal energy release and usually electromagnetic radiation, *e.g.*, light. Generally, oxygen is one of the reactants.

Single displacement reactions: atoms of one element in a species are displaced (or replaced) by atoms from a pure element. They can be redox reactions as well.

These definitions are summarized in table 23.2.

In the current document, on the other hand, we will deal exclusively with the carbothermic reduction of ZnO to Zn. So our main concern will be redox reactions. For them, there is a useful mnemonic for recalling which species oxides and which reduces:

oil rig: oxidation is lost, reduction is gain.

That is, oxidation means loosing electrons; while, reduction gaining. The reductant species becomes oxidized and the oxidant becomes reduced. For these reasons, the reductant is also known as *reducing agent* and the oxidant as the *oxidation agent*.

23.13.2 Energy transfer during chemical reactions

Consider a process wherein a chemical reaction occurs. Then, it is common to ask whether the reaction takes place as written or the reverse process indeed happens. This question is related to the thermodynamics of the chemical reaction, because every change in the chemical structure of a system influences its energy.

When a chemical reaction takes place, the chemical bonds of the atoms or molecules in a system species are affected and thus change. Depending on the stability of the reacting species (reactants) bonds, energy is released or absorbed during the reaction. Moreover, if temperature differences accompany energy changes, then energy is released or absorbed during the reaction.

The last considerations can be formalized in the following definitions: [43]

Endenthalpic process: a process or reaction wherein enthalpy is added to a system.

Exenthalpic process: a process or reaction wherein enthalpy is released by a system.

Even though the terms endenthalpic and exenthalpic precisely denote that enthalpy changes are involved, they are not common. Thus, to prevent confusion, we fall back into the more common terms:

Endothermic process: a process or reaction wherein enthalpy is absorbed from the surroundings of a system.

Exothermic process: a process or reaction wherein enthalpy is released to the surroundings of a system.

Energy transfers during a chemical reaction can be quantified, and thus predicted, by analyzing two (out of three) changes in a reactive system:

- changes in the system enthalpy;
- changes in the system entropy;
- changes in the system Gibbs' free enthalpy.

We need only analyze two, since the three are related *via* Gibbs free enthalpy changes; *i.e.*,

$$\Delta G = \Delta H - t\Delta S\,.$$

23.13.3 Standard state for thermodynamic properties

Values for enthalpies, entropies, and Gibbs' free enthalpies are tabulated with respect to a chosen standard state. Thus, before calculating them for a given reaction or system of reactions, it is necessary to agree on such convention.

In our case, hereafter we adopt the *standard state* for standard enthalpy and standard entropy for chemicals as defined in [88]:

- the standard state thermodynamic temperature is 298.15 K (25 °C);
- the standard state pressure is 10^5 Pa (1 bar);
- the standard state of a *pure gaseous element* is that of the element as a (hypothetical) ideal gas at the standard state pressure and temperature;

- the standard state of a *pure liquid element* is that of the liquid under the standard state pressure and temperature; and
- the standard state of a *pure crystalline element* (solid) is that of the crystalline element under the standard state pressure and temperature.

23.13.4 Change in standard enthalpy of reaction

Once agreed on the standard state wherein to gather data for the different state functions, we suggest a procedure to calculate changes in enthalpies of reaction.

Consider a system wherein a chemical reaction of the following form happens:

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \longrightarrow \nu_{\mathrm{P}}\mathrm{P} + \nu_{\mathrm{Q}}\mathrm{Q}\,,$$

which can be rewritten more compactly as

$$\sum_{\mathrm{S}} \nu(\mathrm{S})\mathrm{S}\,,$$

where S are the reaction chemical species, whose sign convention was adopted to be:

- the sign of a stoichiometric number is negative for a reactant;
- the sign of a stoichiometric number is positive for a product.

As the reaction takes place, the enthalpy of the system is affected: the *enthalpy of the reaction*. Reaction enthalpies can be quantified by means of the standard enthalpies of *formation* of the chemical species involved in a reaction. Standard enthalpies are tabulated with respect to a standard state (see section 23.13.3).

Now, we can describe the process of calculating changes in standard enthalpies of reaction:

1. Establish the process chemical reaction.
2. Verify that the reaction is balanced and that the involved species have their state of aggregation (solid, liquids, gases) explicitly stated.
3. Establish the *standard state* for changes in enthalpy.
4. Gather values for the standard *molar* enthalpy of *formation*, $\Delta_{\mathrm{f}}\hat{h}^{\circ}(\mathrm{B})$, for a chemical species B present in the chemical reaction, from tables of thermodynamic properties, such as the ones in [88].
5. Calculate the standard enthalpy, $\Delta_{\mathrm{f}}\hat{h}^{\circ}(\mathrm{B})$, by multiplying the molar enthalpy of formation of the species by its stoichiometric number: $\Delta_{\mathrm{f}}\hat{h}^{\circ}(\mathrm{B}) = \nu(\mathrm{B})\Delta_{\mathrm{f}}\hat{h}^{\circ}(\mathrm{B})$.

   Recall that the stoichiometric number of a *reactant is negative*; while that of a *product is positive*. Additionally, see that $\dim \nu(\mathrm{B}) = 1$; *i.e.*, stoichiometric numbers are dimensionless.
6. Repeat the last step for every species involved in the reaction.
7. Calculate the standard enthalpy of reaction, $\Delta_{\mathrm{r}}\hat{h}^{\circ}$:

$$\Delta_{\mathrm{r}}\hat{h}^{\circ} = \sum_{i} \nu_i \Delta_{\mathrm{f}}\hat{h}^{\circ}(i)\,, \qquad [23.10]$$

where the index i runs over all the involved species.

8. Interpret the sign of $\Delta_\mathrm{r}\hat{h}^\circ$: note that eq. (23.10) can be rephrased as

$$\Delta_\mathrm{r}\hat{h}^\circ = \Delta_\mathrm{f}\hat{h}^\circ(\text{products}) - \Delta_\mathrm{f}\hat{h}^\circ(\text{reactants})\,,$$

where it can be seen that

- if $\Delta_\mathrm{r}\hat{h}^\circ < 0$, then the reactants have more enthalpy than the products and thus the reaction releases enthalpy. Therefore, the reaction is said to be *exenthalpic* (or, more traditionally, exothermic).
- if $\Delta_\mathrm{r}\hat{h}^\circ > 0$, then the products have more enthalpy than the reactants and thus the reaction requires enthalpy to proceed as written. Therefore, the reaction is said to be *endenthalpic* (endothermic).

23.13.5 Enthalpy and the extent of reaction

In section 23.12, we stated that the partial $\partial_\xi H\big|_{p,t}$ in eq. (23.9) can be viewed as the enthalpy of fusion of a solid; whereby we just found a relation between enthalpy and its extent. Herein, we generalize the relation between enthalpy and the extent of reaction to cover reactive systems.

Consider a system wherein a chemical equation of the following form occurs:

$$\sum_\mathrm{S} \nu(\mathrm{S})\mathrm{S}\,,$$

where S is a general reaction species. Then, the enthalpy of the reaction is

$$H = \sum_\mathrm{S} n(\mathrm{S})\Delta_\mathrm{f}\hat{h}^\circ(\mathrm{S})\,.$$

On the other hand, we know that the amount $n(\mathrm{S})$ is related to its initial value $n^0(\mathrm{S})$ and the reaction extent by

$$n(\mathrm{S}) = n^0(\mathrm{S}) + \nu(\mathrm{S})\xi\,.$$

Now, replace this value into the enthalpy of reaction, distribute the summation symbol over its terms, and collect them to have

$$H = \sum_\mathrm{S}\left(n^0(\mathrm{S})\Delta_\mathrm{f}\hat{h}^\circ(\mathrm{S})\right) + \xi\sum_\mathrm{S}\left(\nu(\mathrm{S})\Delta_\mathrm{f}\hat{h}^\circ(\mathrm{S})\right)\,,$$

which upon differentiation with respect to ξ becomes

$$\begin{aligned}\frac{\mathrm{d}H}{\mathrm{d}\xi} &= \sum_\mathrm{S}\left(\nu(\mathrm{S})\Delta_\mathrm{f}\hat{h}^\circ(\mathrm{S})\right)\,,\\ &= \Delta_\mathrm{r}\hat{h}^\circ\,.\end{aligned}$$

That is,

the change in the enthalpy of a system with respect to its reaction extent equals the enthalpy of reaction.

Note that the reaction enthalpy of the system simply depends on the amounts of the species (reagents).

Finally, in analogous way as we did in section 23.12, where we studied enthalpy changes in an isobaric system, we represent the current system state as $\{H, p, t, \xi\}$. Then, we expand enthalpy as $H(p, t, \xi)$, which leads to formulate enthalpy changes as

$$\mathrm{d}H = \partial_t H|_{p,\xi}\,\mathrm{d}t + \partial_\xi H\Big|_{p,t}\mathrm{d}\xi\,, \qquad \text{[isobaric]}$$

where the first partial represents the thermal change in enthalpy at constant composition and pressure; *i.e.*, the *isobaric enthalpy capacity*, C_p; while the second partial, the isobaric, isothermal compositional change in enthalpy. Now, from the previous results of the current section, we know that $\partial_\xi H\Big|_{p,t}$ is the standard change in the enthalpy of formation; *i.e.*,

$$\partial_\xi H\Big|_{p,t} = \Delta_\mathrm{r}\hat{h}^\circ\,.$$

Therefore, we can rewrite enthalpy changes in the considered system as

$$\mathrm{d}H = C_p\,\mathrm{d}t + \Delta_\mathrm{r}\hat{h}^\circ\,\mathrm{d}\xi\,,$$

which is our final result.

23.13.6
Change in entropy of a system

For the system undergoing the reaction described in section 23.13.4, we can also calculate its standard entropy, $\Delta_\mathrm{r}\hat{s}^\circ$.

The procedure to calculate $\Delta_\mathrm{r}\hat{s}^\circ$ is very similar to the one to calculate $\Delta_\mathrm{r}\hat{h}^\circ$, as described in section 23.13.4. The difference is in the values to be gathered.

Once the values for the standard molar entropies, $\hat{s}^\circ$, are gathered for every species participating in a reaction, the standard entropy for the reaction is calculated as

$$\Delta_\mathrm{r}\hat{s}^\circ = \sum_\mathrm{S} \nu(\mathrm{S})\hat{s}^\circ(\mathrm{S})\,,$$

for the species S. The last equation can be rewritten in terms of the reaction reactants and products as

$$\Delta_\mathrm{r}\hat{s}^\circ = \sum \hat{s}^\circ(\text{products}) - \sum \hat{s}^\circ(\text{reactants})\,.$$

23.13.7
Change in Gibbs' free enthalpy

Once the enthalpy and entropy of a reaction are calculated, it is possible to calculate its Gibbs' free enthalpy.

Gibbs' free enthalpy for a reaction measures the maximum enthalpy performed by a isothermal, isobaric thermodynamic system. Recall that Gibbs' free enthalpy of a system at a given macrostate is defined as $G = U + pV - tS$. But $H = U + pV$, also by definition. So, Gibbs' free enthalpy can be written as

$$G = H - tS\,,$$

whose exterior derivative is

$$\mathrm{d}G = \mathrm{d}H - t\,\mathrm{d}S\,,$$

since G measures, by definition, isothermal changes.

Now, calculate $\mathrm{d}G$ between two states and express the result per unit amount to have

$$\Delta_\mathrm{r}\hat{g} = \Delta_\mathrm{r}\hat{h}^\circ - t\Delta_\mathrm{r}\hat{s}^\circ\,.$$

Reinterpret the last equation in terms of reactants and products:

$$\Delta_\mathrm{r}\hat{g} = \sum \Delta_\mathrm{r}\hat{g}(\text{products}) - \sum \Delta_\mathrm{r}\hat{g}(\text{reactants})\,.$$

23.13.8 Spontaneity of a chemical reaction

It is time to put everything together. So far, for a given reaction, we know how to calculate standard enthalpy, standard entropy, and Gibbs' free enthalpy. Then, to determine the spontaneity of a reaction, we look at the signs of $\Delta_\mathrm{r}\hat{h}^\circ$ and $\Delta_\mathrm{r}\hat{s}^\circ$ and compare them with a reference: table 23.3:

- if a reaction is non-spontaneous or spontaneous at all temperatures, then there is all to it; however,
- if the spontaneity of a reaction depends on temperature, then choose a temperature, calculate $\Delta_\mathrm{r}\hat{g}$, and finally look at its sign:
  - if $\Delta_\mathrm{r}\hat{g} < 0$, then the reaction is favored, *spontaneous*, at the chosen temperature. The reaction proceeds from reactants to products;
  - if $\Delta_\mathrm{r}\hat{g} = 0$, then the reaction is at equilibrium, at the chosen temperature; and
  - if $\Delta_\mathrm{r}\hat{g} > 0$, then the reaction is disfavored, *non-spontaneous*, at the chosen temperature. The reaction proceeds in reverse direction: from products to reactants.

23.14 EQUILIBRIUM CONSTANT

The *chemical activity*, a, of a species measures the species « effective concentration » in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution.

By convention, activity is treated as a dimensionless quantity, although its value depends on temperature and pressure. The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity. Activity depends on temperature, pressure and composition of the mixture, among other things. For gases, the activity is the effective partial pressure, and is usually referred to as *fugacity*.

The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other. The activity of an ion is particularly influenced by its surroundings.

Consider a chemical reaction of the form:

$$\sum_\mathrm{S} \nu(\mathrm{S})\mathrm{S}\,,$$

where S is a general chemical species.

Then, define the *reaction quotient* as the division of the activities of the products over the activities of the reactants:

$$q \circeq \frac{\prod_\mathrm{P} a(\mathrm{P})^{\nu(\mathrm{P})}}{\prod_\mathrm{R} a(\mathrm{R})^{\nu(\mathrm{R})}}\,,$$

where P_R are the reaction reactants and products.

Table 23.3 Factors affecting the spontaneity of a chemical reaction. Source: [111]

	$\Delta_\mathrm{r}\hat{h} > 0$	$\Delta_\mathrm{r}\hat{h} < 0$
$\Delta_\mathrm{r}\hat{s} > 0$	Spontaneity depends on temperature (spontaneous at high temperatures)	Spontaneous at all temperatures
$\Delta_\mathrm{r}\hat{s} < 0$	Non-spontaneous at all temperatures (proceeds in reverse direction)	Spontaneity depends on temperature (spontaneous at low temperatures)

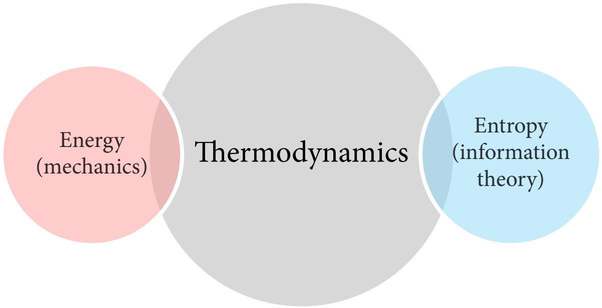

Figure 23.1 Modern view of thermodynamics: the theory of energy and entropy. The concept of energy comes from (the physical theory of) mechanics; while that of entropy from (the mathematical theory of) information, wherein entropy is defined as the opposite of information; *i.e.*, the uncertainty of information. [25] Diagram adapted from [43]

$$\begin{tikzcd}
U \arrow[d, "-tS"'] & & H \overset{\circ}{=} U + pV \arrow[ll, "-pV"'] \\
F \overset{\circ}{=} U - tS \arrow[rr, "+pV"'] & & G \overset{\circ}{=} U - tS + pV \arrow[u, "+tS"']
\end{tikzcd}$$

Figure 23.2 Definitions of Helmholtz' free energy, F, Gibbs' free enthalpy, G, and enthalpy, H, state functions, departing from the macrostate internal energy, entropy, pressure, temperature, and volume state functions. Source: [43]

$$\begin{tikzcd}
\mathrm{d}U = -p\,\mathrm{d}V + t\,\mathrm{d}S \arrow[r, leftrightarrow, "\text{Interchange } p, V"] \arrow[d, leftrightarrow, "\text{Interchange } t, S"'] & \mathrm{d}H = V\,\mathrm{d}p + t\,\mathrm{d}S \arrow[d, leftrightarrow, "\text{Interchange } t, S"] \\
\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}t \arrow[r, leftrightarrow, "\text{Interchange } p, V"'] & \mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}t
\end{tikzcd}$$

Figure 23.3 Exterior derivatives of (the four macrostate function) energy, Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy and their Legendre transforms. Adapted from [43]

$$\begin{tikzcd}
\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V + \hat{\eta}\,\mathrm{d}\xi \arrow[r, leftrightarrow, "\text{Interchange } p, V"] \arrow[d, leftrightarrow, "\text{Interchange } t, S"'] & \mathrm{d}H = t\,\mathrm{d}S + V\,\mathrm{d}p + \hat{\eta}\,\mathrm{d}\xi \arrow[d, leftrightarrow, "\text{Interchange } t, S"] \\
\mathrm{d}F = -S\,\mathrm{d}t - p\,\mathrm{d}V + \hat{\eta}\,\mathrm{d}\xi \arrow[r, leftrightarrow, "\text{Interchange } p, V"'] & \mathrm{d}G = -S\,\mathrm{d}t + V\,\mathrm{d}p + \hat{\eta}\,\mathrm{d}\xi
\end{tikzcd}$$

Figure 23.4 For a reactive system, internal energy, Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy exterior derivatives and their Legendre transforms

$$-S = \partial_t F|_{V,\xi} = \partial_t G|_{p,\xi} \qquad V = \partial_p G|_{t,\xi} = \partial_p H|_{S,\xi}$$

$$-p = \partial_V U|_{S,\xi} = \partial_V F|_{p,\xi} \qquad t = \partial_S U|_{V,\xi} = \partial_S H|_{p,\xi}$$

$$\hat{\eta} = \partial_\xi U\Big|_{S,V} = \partial_\xi F\Big|_{p,V} = \partial_\xi G\Big|_{p,t} = \partial_\xi H\Big|_{p,S}$$

Figure 23.5 Partials appearing in the exterior derivatives of the internal energy, Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy of a reactive system and their relations with the system entropy, pressure, temperature, volume, and the energy of reaction

$$\begin{tikzcd}
\mathrm{d}U = t\,\mathrm{d}S - p\,\mathrm{d}V + \hat{\mu}_i\,\mathrm{d}\mu_i \arrow[r, leftrightarrow, "\text{Interchange } p, V"] \arrow[d, leftrightarrow, "\text{Interchange } t, S"'] & \mathrm{d}H = t\,\mathrm{d}S + V\,\mathrm{d}p + \hat{\mu}_i\,\mathrm{d}\mu_i \arrow[d, leftrightarrow, "\text{Interchange } t, S"] \\
\mathrm{d}F = -S\,\mathrm{d}t - p\,\mathrm{d}V + \hat{\mu}_i\,\mathrm{d}\mu_i \arrow[r, leftrightarrow, "\text{Interchange } p, V"'] & \mathrm{d}G = -S\,\mathrm{d}t + V\,\mathrm{d}p + \hat{\mu}_i\,\mathrm{d}\mu_i
\end{tikzcd}$$

Figure 23.6 For a reactive system, internal energy, Helmholtz' free energy, Gibbs' free enthalpy, and enthalpy exterior derivatives and their Legendre transforms in terms of the system chemical potential

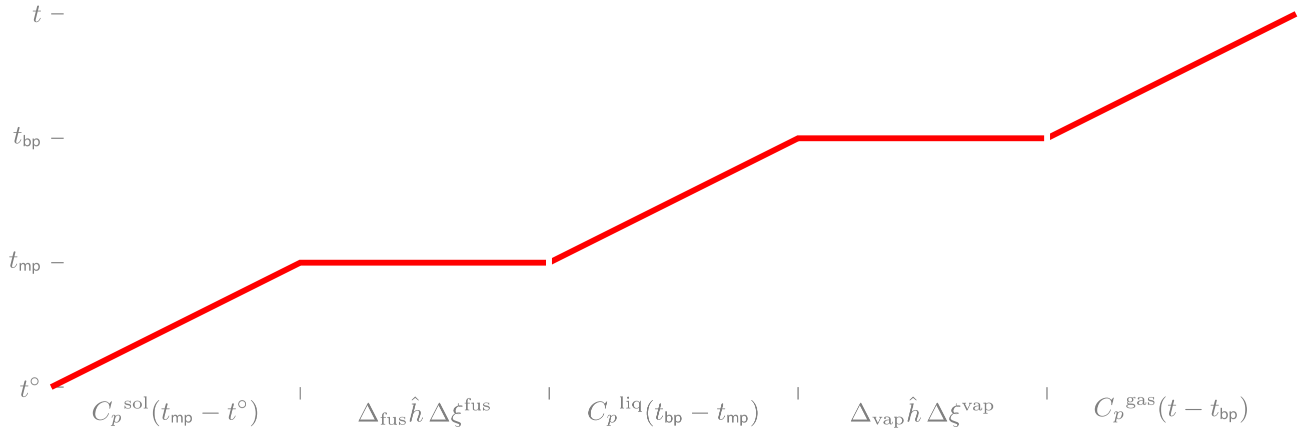

Figure 23.7 The enthalpy curve of a hypothetical solid chemical species during phase transitions. (The species is assumed to be initially in its solid state at standard temperature, t°, wherefrom it is brought to its gaseous state. In the beginning, an initial enthalpy of $C_p{}^{\text{sol}}(t_{\mathsf{mp}} - t^{\circ})$ is required to increase the species temperature up to its melting point, t_{mp}. Up to this point, the species temperature changes accordingly. However, once t_{mp} is reached and despite more enthalpy, $\Delta_{\text{fus}}\hat{h}\,\Delta\xi^{\text{fus}}$, being required to complete the melting, the temperature does *not* change anymore. Analogously, for vaporization, $C_p{}^{\text{liq}}(t_{\mathsf{bp}} - t_{\mathsf{mp}})$ is required to reach the substance boiling point, t_{bp}. From here, $\Delta_{\text{vap}}\hat{h}\,\Delta\xi^{\text{vap}}$ is required to complete the vaporization. Finally, if the species temperature in its gaseous phase is to be increased up to t, then an additional enthalpy of $C_p{}^{\text{gas}}(t - t_{\mathsf{bp}})$ is necessary.)

24

MATERIAL PROPERTIES

Energy, entropy, enthalpy, pressure, volume and the like are system properties. They provide the general framework upon which to study *material properties*. We briefly define and describe some of them here.

(This section is based on [32, 30, 77].)

24.1 ENTHALPY AND ENTROPY CAPACITIES (HEAT CAPACITIES)

When internal energy changes inside a system, its volume and temperature are affected. In this section, we study the responses of temperature and pressure to energy changes.

Consider the system described in section 23.5. Now, recall that

> the system internal energy can be expanded as a function of *any* parameter spanning the parameter space.

Since temperature and volume are of concern here, choose the set $\{U, t, V\}$ to span the space. Such a set leads to expand energy as $U(t, V)$, whose total differential is

$$\mathrm{d}U = \partial_t U|_V \,\mathrm{d}t + \partial_V U|_t \,\mathrm{d}V \,.$$

Let the first partial be the *isochoric energy capacity*, C_V:

$$C_V \mathrel{\hat{=}} \partial_t U|_V \,, \qquad [24.1]$$

whose dimensions are those of entropy: $\dim C_V = \mathrm{E}/\Theta$. See that C_V is an *extensive* quantity.

Let the second partial be the *isothermal volumetric energy*

$$\pi_t \mathrel{\hat{=}} \partial_V U|_t \,,$$

whose dimensions are those of pressure: $\dim \pi_t = \mathrm{E}/\mathrm{L}^3$. See that π_t is an *intensive* quantity. The isothermal volumetric energy is also called « internal pressure ». [13]

Lastly, using C_V, π_t, rewrite $\mathrm{d}U$ as

$$\mathrm{d}U = C_V \,\mathrm{d}t + \pi_t \,\mathrm{d}V \,.$$

On the other hand, however, it is easier in practice to maintain the system at constant pressure, rather than at constant volume. Then, measuring devices record enthalpy instead of internal energy. Thus, if we expand enthalpy as $H(p, t)$, then its exterior derivative is

$$\mathrm{d}H = \partial_t H|_p \,\mathrm{d}t \,. \qquad \text{[isobaric]} \qquad [24.2]$$

Let the partial be the *isobaric enthalpy capacity*:

$$C_p \mathrel{\overset{\circ}{=}} \partial_t H|_p \,,$$

whose dimensions are those of entropy: $\dim C_p = \mathrm{E}/\Theta$. See that C_p is an *extensive* quantity.

The traditional names for C_V, C_p are « heat (thermal) capacity at constant volume » and « heat (thermal) capacity at constant pressure ». It is important to keep this in mind, since, even though here they have been put in a logical ground and thus relabeled, their values are used as « heat » capacities in thermodynamic references and quoted and tabulated as such in thermodynamic databases, like in [88].

24.2 MOLAR AND SPECIFIC CAPACITIES

Due to their utility, energy and enthalpy capacities often appear when applying thermodynamics to systems of substances. Thus, for many materials, their values are readily available in thermodynamic tables and in actual process reports or experiments. However, the capacities are therein quoted as intensive, molar or specific, or extensive. The conversions between such bases, on the practical side, is not difficult. We show how in this section.

In general, the adjective *molar* means per unit amount of substance. Thus, a *molar capacity* is defined as the ratio between a capacity and the amount:

$$\hat{c} \mathrel{\overset{\circ}{=}} \frac{C}{n} \,. \qquad [24.3]$$

On the other hand, the adjective *specific* is meant to be understood as per unit mass. So, a *specific capacity* is defined accordingly:

$$c \mathrel{\overset{\circ}{=}} \frac{C}{m} \,.$$

By dividing $\hat{c}$ by c, one has a relationship between specific and molar capacities:

$$\frac{\hat{c}}{c} = \hat{m} \,, \qquad [24.4]$$

where $\hat{m}$ is the *molar mass* of the substance.

Finally, for the current work, we use the various bases depending on the context. As a guideline,

- for theoretical work or when the composition of a material (or mixture) under analysis is known, we prefer the *molar* basis; while,
- when the material composition is unknown or difficult to determine, we prefer the *specific* basis.

24.3 ENTROPY CAPACITY

Now we are in position of merging energy and enthalpy capacities, defined in previous sections, into the more general, and useful in practice, *generalized entropy capacity*.

24.3.1 Definition of generalized entropy capacity

Consider the system described in section 23.5. Since the system has internal energy with well defined partials, reinterpret then the system isochoric energy capacity by applying the chain rule to it:

$$\begin{aligned} C_V &= \partial_t U|_V = \partial_S U|_V \, \partial_t S|_V \,, \\ &= t\,\partial_t S|_V \,, \end{aligned}$$

thanks to the definition of temperature.

By the same token, reinterpret the system isobaric enthalpy capacity (isobaric heat capacity):

$$\begin{aligned} C_p &= \partial_t H|_p = \partial_S H|_p \, \partial_t S|_p \,, \\ &= t\,\partial_t S|_p \,, \end{aligned}$$

since $t = \partial_S H|_p$, according to fig. 23.5.

See now that the last equalities of both reinterpreted capacities suggest the definition of a *generalized entropy capacity*:

$$C_x \mathrel{\hat{=}} t\,\partial_t S|_x \,, \qquad [24.5]$$

$$= \left.\frac{\partial S}{\partial \ln(t)}\right|_x , \qquad [24.6]$$

where x can be any state function, including p or V, and $\ln(t)$ is the (natural) logarithmic function.

By construction, eq. (24.5) relates the system properties with entropy, under isobaric, isochoric, and isothermal conditions. Hence, it becomes extremely handy when calculating entropy changes under such conditions.

Finally, note that the dimensions of the generalized capacity are those of entropy, $\dim C_x = \dim S = \mathrm{E}/\Theta$, and that C_x is an *extensive* quantity.

24.3.2 Ratio between entropy capacities

Consider the system described in section 23.5. Then, from the definition of the generalize entropy (heat) capacity, the system change in enthalpy is $\mathrm{d}H = V\,\mathrm{d}p + t\,\mathrm{d}S$. If the change is isobaric, then we have that $\mathrm{d}H = t\,\mathrm{d}S$, which can be rewritten as

$$\mathrm{d}H = C_p\, t \,.$$

On the other hand, the system change in internal energy is $\mathrm{d}U = t\,\mathrm{d}S$ if the change is isochoric. Then, we have that

$$\mathrm{d}U = C_V\, t \,.$$

Finally, dividing both equations, we get

$$\gamma = \frac{\mathrm{d}H}{\mathrm{d}U} = \frac{C_p}{C_V} \,. \qquad [24.7]$$

The last equation suggests naming γ the system *entropic capacity ratio* (heat capacity ratio). This would add another name to γ, which traditionally goes by many others: « heat capacity ratio », « isentropic expansive factor », or « adiabatic index », among others.

24.3.3 *Entropy changes during heating or cooling*

As our second use of entropy capacities, let us find out the isobaric and isochoric entropy changes between two temperatures t°, t.

Consider a fixed amount n of material be isobarically heated (or cooled). Then, specialize the generalized entropy capacity, eq. (24.6), to the isobaric case to have $\mathrm{d}S = C_P \,\mathrm{d}\ln(t)$, which becomes $\mathrm{d}\hat{s} = \hat{c}_P \,\mathrm{d}\ln(t)$, since n is fixed. Integrate now $\mathrm{d}\hat{s}$ between the given temperatures to get

$$\Delta\hat{s} = \hat{c}_P \ln\left(\frac{t}{t^\circ}\right), \qquad \text{[isobaric]}$$

where we assumed $\hat{c}_P$ is constant during the thermal change. This equation gives the *molar isobaric entropy changes between two temperatures*.

On the other hand, suppose the material be isochorically heated. Then, an analogous calculation establishes the *molar isochoric entropy changes between two temperatures*:

$$\Delta\hat{s} = \hat{c}_V \ln\left(\frac{t}{t^\circ}\right). \qquad \text{[isochoric]}$$

24.4 MASS AND NUMBER DENSITIES

During theoretical development, thermodynamic quantities appear as *extensive*. In practice, on the other hand, it is common report them as *intensive*. Hence, one is often required to convert from one to the other. There are two conversion factors regularly helpful:

Mass density: defined as the mass of a system per unit volume:

$$\varrho = \frac{m}{V}.$$

Number density: defined as the number of particle a system has per unit volume. By definition, it is related to mass density *via* the equation:

$$\varrho_\mu = \frac{k_{\mathsf{av}}\varrho}{\hat{m}},$$

where $k_{\mathsf{av}}, \hat{m}$ are *Avogadro's constant* and *molar mass*. Note that $\dim \varrho_\mu = \mathrm{L}^{-3}$.

With them, it is possible to define the *molar volume* of a substance:

$$\hat{v} = \frac{\hat{m}}{\varrho},$$

whose $\dim \hat{v} = \mathrm{L}^3/\mathrm{N}$.

24.5 VOLUMETRIC CHANGES DUE TO PRESSURE AND TEMPERATURE

When the pressure or the temperature of a system change, the system volume responds accordingly to such variations. It is experimentally found that, in general,

> when pressure increases, volume decreases and, when temperature increases, volume increases.

Let us quantify such relations using the framework provided by thermodynamics, keeping volumetric changes in mind.

To begin with, consider the system described in section 23.5. Then, since the system holds fixed an amount of a non-reactive chemical species, the system mass is constant. Choose the set $\{V, p, t\}$ to span the system parameter space, wherefrom $V(p, t)$ and thus, to find volume changes,

$$\mathrm{d}V = \partial_p V|_t \,\mathrm{d}p + \partial_t V|_p \,\mathrm{d}t\,. \tag{24.8}$$

However, it is more convenient to work with *fractional* volumetric changes instead of total. Then, $\mathrm{d}V$ becomes

$$\frac{1}{V}\,\mathrm{d}V = \frac{1}{V}\,\partial_p V|_t \,\mathrm{d}p + \frac{1}{V}\,\partial_t V|_p \,\mathrm{d}t\,. \tag{24.9}$$

The partials in eq. (24.9) lead to define two macroscopic properties relating volume changes to pressure and temperature changes: compressibility and thermal expansion.

24.5.1 Compressibility and bulk modulus

Compressibility measures the fractional volumetric change of a substance as a response to a pressure change. Since compressibility depends on whether the change is isothermal or isentropic, we define two coefficients, based on eq. (24.9):

1. *Isothermal compressibility*, when the volumetric change is carried out at constant temperature:
$$\kappa_t \stackrel{\circ}{=} -\frac{1}{V}\,\frac{\partial V}{\partial p}\bigg|_t\,. \tag{24.10}$$
2. *Isentropic compressibility*, when the volumetric change is carried out at constant entropy (adiabatically):
$$\kappa_S \stackrel{\circ}{=} -\frac{1}{V}\,\frac{\partial V}{\partial p}\bigg|_S\,.$$

Note that the dimensions of both quantities are $\dim \kappa_t = \dim \kappa_S = \dim p^{-1} = \mathrm{L}^3/\mathrm{E}$; the negative signs in both definitions correspond to the experimental fact that volume scales with the *inverse* of pressure; and both quantities are *intensive*, since they are defined per unit volume.

Finally, following the same line of reasoning, define the *bulk modulus* of a material as the inverse of compressibility to measure the system resistance to uniform compression:

$$\beta_t \stackrel{\circ}{=} {\kappa_t}^{-1} = -V\,\frac{\partial p}{\partial V}\bigg|_t\,, \qquad \text{[isothermal bulk modulus]}$$

$$\beta_S \stackrel{\circ}{=} {\kappa_S}^{-1} = -V\,\frac{\partial p}{\partial V}\bigg|_S\,, \qquad \text{[isentropic bulk modulus]}$$

with $\dim \beta = \dim p = \mathrm{E}/\mathrm{L}^3$. As defined from an intensive quantity, the bulk modulus is also *intensive*.

24.5.2 Thermal expansion

Thermal expansion measures the relative volumetric change of a substance as a response to a temperature change. Based on eq. (24.9), the coefficient of *cubic isobaric thermal expansion* is defined as

$$\eta_p \stackrel{\circ}{=} \frac{1}{V}\,\frac{\partial V}{\partial t}\bigg|_p\,, \tag{24.11}$$

whose $\dim \eta_p = \dim t^{-1} = \Theta^{-1}$.

24.5.3 Volumetric changes

We are now in position to answer the question that opened this section: how to describe and quantify volumetric changes using thermodynamics.

Replace the definitions of isothermal compressibility and cubic isobaric thermal expansion in eq. (24.8) to get

$$\mathrm{d}V = \eta_p V \,\mathrm{d}t - \kappa_t V \,\mathrm{d}p \,.$$

Then, as fractional volumes are usually reported, divide the last equation by V to have

$$\frac{1}{V}\,\mathrm{d}V = \eta_p \,\mathrm{d}t - \kappa_t \,\mathrm{d}p \,. \qquad [24.12]$$

Finally, as mentioned in section 23.5, see that, to change the volume of the system, (the intensive) $\mathrm{d}t$ acts upon (the extensive) $\eta_p V$ and (the intensive) $\mathrm{d}p$, upon (the extensive) $-\kappa_t V$.

24.6 MASS DENSITY CHANGES

We are at one step to quantify mas density changes, $\mathrm{d}\varrho$, based on previous results. Since, under hypothesis, the system under study has a fixed number of particles, μ, the mass contained in the system is (the constant) ϱV. Then, by the product rule of the total differential, by the *local mass conservation* (the analog of eq. (23.1) for mass), and by the fractional volume changes, eq. (24.12), one gets that $\varrho\,\mathrm{d}V + V\,\mathrm{d}\varrho = 0$, which, after some algebra, yields

$$\frac{1}{\varrho}\,\mathrm{d}\varrho = -\frac{1}{V}\,\mathrm{d}V = \kappa_t \,\mathrm{d}p - \eta_p \,\mathrm{d}t \,,$$

thanks to eq. (24.12).

24.7 RELATION BETWEEN ENERGY AND ENTHALPY CAPACITIES

Consider the system in section 23.5. By definition, the system isochoric energy capacity is $C_V = \partial_t U|_V$. Reinterpret then the partial using Bridgman's method, appendix F.2:

$$\begin{aligned} C_V = \left.\frac{\partial U}{\partial t}\right|_V \equiv \frac{\partial U|_V}{\partial t|_V} &= \frac{C_p\,\partial_p V|_t + t\,\partial_t V|_p^2}{\partial_p V|_t}\,, \\ &= C_p + t\,\partial_t V|_p^2\,\partial_V p|_t\,, \end{aligned}$$

where we used the inverse rule for partials, appendix F.4, to get $\partial_V p|_t$.

Now, let us work out the values of the partials. From the definition of the isothermal compressibility, eq. (24.10), one gets $\partial_V p|_t = -1/\kappa_t V$; whereas, from the definition of the isobaric thermal expansion, eq. (24.11), one has $\partial_t V|_p = \eta_p$. Replace both definitions in C_V,

$$C_V = C_p + t\,(\eta_p V)^2 \left(-\frac{1}{\kappa_t V}\right)\,,$$

and perform algebra to get

$$C_p - C_V = \frac{t V \eta_p^2}{\kappa_t}\,. \qquad [24.13]$$

This equation relates the system isochoric energy capacity with the isobaric enthalpy capacity. The relation is important, because the isochoric capacity appears often in theoretical work, but the isobaric capacity is easier to measure in the laboratory.

24.8 MICROSCOPIC LAWS AND EQUATIONS

As mentioned above, thermodynamics does not provide by itself with an explanation of the atomic inner workings of a system. Atomic theories are required to supply this input. However, once the gap is filled, we can apply thermodynamics to find the different macrostates of a system. We will do so when dealing with ideal gases, chapter 25. Therein, the task will be eased, since an ideal gas has a defined energy function equation and a state equation.

On the other hand, as required for the current work, we also need input for solids. But, albeit there are solid state theories that provide input for thermodynamics, discussing such theories will drive us away from the topic. Hence, we present in the following approximations, experimental results, and the like on the physics of the solid state.

24.8.1 Enthalpy and energy capacities (heat capacities)

Dulong-Petit's law is an experimental finding that generalizes the isobaric enthalpy capacity (heat capacity) for solid elements. [82] In modern terms, the rule states that

for solid elements, the molar isobaric enthalpy capacity is constant with a value of $\hat{c}_p \sim 3\hat{r}$.

Now, Dulong-Petit's law is accurate for elements. However, it can be used to estimate within an *order-of-magnitude* for all solids and all liquids. This is possible since solids and liquids at low pressures (nearly standard state pressure: $p/p^\circ \sim 1$) can be considered as incompressible. [30] Additionally, this also implies that the molar isobaric enthalpy and molar isochoric energy capacities can be approximated to be equal and did not depend on temperature. Hence, we have the *generalized Dulong-Petit's law*:

all solids (elements or otherwise) and all liquids have constant molar isochoric energy capacity and molar isobaric enthalpy capacity equal to $3\hat{r}$,

which translates into numbers as

$$\begin{aligned} \hat{c}_p \sim \hat{c}_V &\sim 3\hat{r}\,, \\ &\sim 25\ \mathrm{J/mol\,K}\,. \end{aligned}$$

24.8.2 Thermal expansion of solids

According to [82], based on solid state physics, it is possible to show that

the cubic isobaric thermal expansion of a substance scales inversely with its melting point.

In particular, for metallic elements and oxides:

$$\eta_p \sim \begin{cases} \dfrac{a}{t_{\mathsf{mp}}}\,, & \text{for metallic elements;} \\[2ex] \dfrac{b}{t_{\mathsf{mp}}} - c\,, & \text{for metallic oxides;} \end{cases} \qquad [24.14]$$

where $a = 0.060$, $b = 0.114$, $c = 2.1 \times 10^{-5}\ \mathrm{K}^{-1}$.

These expressions should be used to estimate η_p, since they generalize data and ignore η_p temperature dependence. However, if more refined values are required, then one can consult curated databases such as [88].

24.8.3 Lattice energy

The *lattice energy* of a crystalline solid is the crystal formation energy from infinitely-separated ions. This energy gives an indicative on the bond strength of a solid. We will use it when drawing Born-Haber cycles.

Following [80, 131], let us estimate the lattice energy of a crystal using Coulombs' force. Consider two static ions forming a crystal. Let cation have a charge z^+e and the anion a charge z^-e, where e, z are the elementary charge and the ions valencies. Then, the electrostatic force between the two charged particles is

$$\vec{F} = k\frac{\left|z^+z^-\right|e^2}{r^2}\,,$$

where k, r are *Coulomb's constant* and the separation between the ionic centers of mass. See that $\dim k = \mathrm{F\,L^2/Q^2}$.

Since Coulomb's force does not depend on velocity, it is conservative. Then, $\vec{F}$ can be written as the gradient of a potential: $\vec{F} = \operatorname{grad}\varphi$, where φ is the potential, called the *electrostatic potential energy* and is given by

$$\varphi = k\frac{\left|z^+z^-\right|e^2}{r}\,,$$

whose $\dim \varphi = \mathrm{E}$.

Note that φ is the energy between two ions. It is thus a microscopic quantity. However, lattice energies are quoted per chemical amount; *i.e.*, as macroscopic properties. Thus, φ needs to be rescaled to a unit amount:

$$\hat{u} = k_{\mathsf{av}}k\frac{\left|z^+z^-\right|e^2}{r}\,, \qquad [24.15]$$

where $\hat{u}$ is the estimated crystal molar lattice energy with $\dim \hat{u} = \mathrm{E/N}$.

Finally, by supposing r equal Bohr's radius and by seeing that k_{av}, k, e are universal constants, eq. (24.15) can be used to estimate the *order-of-magnitude* of lattice energies:

$$\begin{aligned}\hat{u} &\sim 10^{23}\,\mathrm{mol^{-1}} \times 10^{10}\,\mathrm{J\,m\,C^{-2}}\frac{\left(10^{-19}\,\mathrm{C}\right)^2}{10^{-11}\,\mathrm{m}}\,,\\ &\sim 1\times 10^{6}\,\mathrm{J/mol}\,,\end{aligned}$$

where the values were approximated from the ones found in [88]. That is, lattice energies should be in the order of $\sim 1\,\mathrm{MJ/mol}$.

24.8.4 Kapustinskii equation

Equation (24.15) provides with an order-of-magnitude of molar lattice energies. We would like, however, to improve the estimate. This can be done by modifying $\hat{u}$. Max Born, Alfred Landé, and Anatoli Kapustinskii did modify eq. (24.15) by hypothesizing the repulsive term additionally to the attractive term we deduced to account for affects of neighbor cations and anion, not accounted for in our model.

Kapustinskii's equation to estimate the molar lattice energy of a crystal is as follows: [141]

$$\hat{u} = k\nu\frac{\left|z^+z^-\right|}{r^+ + r^-}\left(1 - \frac{d}{r^+ + r^-}\right)\,, \qquad [24.16]$$

where $k = 1.2025 \times 10^{-4}\,\mathrm{J/m\,mol}$, $d = 3.45 \times 10^{-11}\,\mathrm{m}$ and ν is the number of ions in the crystal empirical formula; d, a mean distance between adjacent cation and anion within a crystal; z^{+}, z^{-}, the ion valencies; r^{+}, r^{-}, the radii of the cation and anion.

Equation (24.16) agrees within 5 % of actual data on lattice energies.

24.8.5 Mass density

Herein, we give an equation to give the order-of-magnitude of the mass density of a solid or liquid (material) known its atomic number.

We assume the macroscopic mass density of the material equals the mass density of its nucleus. Since the mass of a proton is approximately 2000 times that of an electron, we assume the mass of an atom is solely given by the atomic nucleus. Moreover, recalling that the atomic number is the number of protons in the atom and that the mass of the proton is approximately equal to that of a neutron, we assume the nucleus is made up only of protons and thus has the double of its atomic number. Finally, we assume the atomic mass is concentrated in a region given by a multiple of Bohr's radius.

Choose an atom of a material. Denote its atomic number by a. Then, the atomic mass is $2am_\mathrm{p}$, provided the atom is made up of protons of mass m_p. On the other hand, suppose the atom is a cube, whose edge's length is two times *Bohr's radius*, $2r_0$. Then, the atomic volume is $8r_0^3$. Therefore, the mass density of the element is

$$\varrho = \frac{1}{4}\frac{am_\mathrm{p}}{r_0^3}\,.$$

The last equation should overestimate the density of the material by a large factor, because, during its derivation, we implicitly assumed that atoms are tightly packed together within the material. This is not the case in macroscopic substances. Atoms are spaced from one another, for instance, forming lattices in solids. Thus, we need to correct the atomic separation by a factor. As a rule of thumb, this factor happens to be five. [63] Therefore, our corrected estimate is

$$\varrho = \frac{2}{125}\frac{am_\mathrm{p}}{r_0^3}\,.$$

Now, we generalize this equation to cover not only elements, but any solid or liquid substance known its atomic number.

Finally, to have an easy to use equation, plug in the values for m_p and r_0, [88] to have:

$$\varrho \sim ak\,, \qquad \text{where } k = 0.18\,\mathrm{g/cm^3}\,, \tag*{[24.17]}$$

our final result.

To assess eq. (24.17), table 24.1 presents some mass density estimations and actual data.

24.8.6 Mass density - crystallography

Under very general assumptions, eq. (24.17) only gives the order of magnitude on the density of a given material. However, mass density estimations for solids can be greatly improved by considering their crystallographic properties.

Consider a crystal (pure solid). Recall that since mass density is a *intensive* property, the unit cell density of the crystal must equal the bulk mass density.

Now, suppose the crystal unit cell. Then, the mass of a cell atom is $\hat{m}/k_{\mathsf{av}}$ and thus the total cell mass is $z\hat{m}/k_{\mathsf{av}}$, where z is the *number of atoms within the unit cell.* On the other hand, using crystallographic information on the crystal system, it is possible to calculate the unit cell volume, v. Hence, the crystal mass density is

$$\varrho = \frac{z\hat{m}}{k_{\mathsf{av}} v}\,. \qquad [24.18]$$

The *volume of the unit cell* depends on the *crystal system*; *i.e.*, the cell shape and the atomic distribution therein. This information is summarized in table 24.2.

24.9 PHYSICAL CONSTANTS

Table 24.3 collects the values of physical properties of selected inorganic compounds.

24.10 STANDARD THERMO PROPERTIES

In future sections, we will need the standard molar enthalpy of formation and the standard molar entropy of several species. They are presented in table 24.4. The standard state is defined in section 23.13.3. Additionally, the same information will be required, but at a temperature of 1800 K and so it was collected in table 24.5.

24.11 APPLICATIONS

24.11.1 *Heating up substances*

Consider a homogeneous, isotropic solid material being isobarically heated from the standard state temperature to a (higher) process temperature. Denote the material mass by m; while the standard state temperature, process temperature, and the efficiency of the heating process by t°, t, η.

Then, since there is only one species, three state functions define the material macrostate through its parameter space. Span the space by the set $\{U, S, V\}$, so to expand the system internal energy as $U(S, V)$ and thus it changes as $\mathrm{d}U = -p\,\mathrm{d}V + t\,\mathrm{d}S$. Legendre transform $\mathrm{d}U$ to $\mathrm{d}H$; *i.e.*, $\mathrm{d}H = V\,\mathrm{d}p + t\,\mathrm{d}S$, which at constant pressure becomes

$$\mathrm{d}H = t\,\mathrm{d}S\,. \qquad \text{[isobaric]}$$

On the other hand, from the generalized entropy (heat) capacity, which was defined in eq. (24.5), the isobaric entropy (heat) capacity is $C_p = t\,\partial_t S|_p$, wherefrom $t\,\mathrm{d}S = C_p\,\mathrm{d}t$ (isobaric), which, after replacing in $\mathrm{d}H$, gives

$$\mathrm{d}H = C_p\,\mathrm{d}t\,. \qquad \text{[isobaric]}$$

Recall that tabulated values for isobaric enthalpy (heat) capacities are not given for the extensive C_p, but rather for the intensive c_p. Then,

$$\mathrm{d}H = c_p m\,\mathrm{d}t\,.$$

Now, to find the enthalpy change between two states (the two given temperatures), integrate $\mathrm{d}H$:

$$\begin{aligned}\Delta H &= \int \mathrm{d}H = c_p m \int_{t^\circ, t} \mathrm{d}t \\ &= c_p m \left(t - t^\circ\right) ,\end{aligned}$$

where we assumed that c_p, m are constant during heating.

Finally, note that, since ΔH is a theoretical value, it has to be modified to take into account heating efficiency η:

$$Q \sim \frac{1}{\eta} c_p m \left(t - t^\circ\right) , \qquad \text{[isobaric]} \qquad [24.19]$$

where we used Q to stress the fact that H is a state function and thus should not be mixed with efficiency.

Equation (24.19) can be used to estimate the energy requirement to heat a material up to any temperature.

24.11.2 Energy requirements to heat up slag

As an application of eq. (24.19), let us estimate the energy required to heat up slag.

To estimate the energy consumption to smelt slag, we assume that

- the smelting overall efficiency is 30 %;
- the slag is heated up from state temperature to process temperature: 25 °C to 1500 °C, which gives a temperature change of $\Delta t = 1475$ K;
- the slag specific enthalpy capacity is constant during Δt and has a value of $c_p = 0.75$ kJ/kg K, as shown in table 24.6.

In the literature, energy requirements are often quoted for a ton of processed material; *i.e.*, 10^3 kg of slag. Then, the energy required to heat up slag can be estimated by using the specific enthalpy capacity of slag in eq. (24.19):

$$\begin{aligned} Q &\sim \frac{1}{0.30} \times 0.75\,\mathrm{kJ/kg\,K} \times 10^3\,\mathrm{kg} \times 1475\,\mathrm{K} , \\ &\sim 3.7 \times 10^9\,\mathrm{J} .\end{aligned}$$

That is, nearly 4 GJ are required to smelt 1 t of slag. This value agrees with the reported values of 2.6 GJ to 3.0 GJ found in actual industrial slag treatment. [126]

Table 24.1 Estimated and actual mass densities of selected solids and liquids. The actual data was gathered from [88]; while the estimated values, calculated with eq. (24.17).

Material	State	Atomic number	$\varrho / \mathrm{g\,cm^{-1}}$		Notes
		a	Estimated	Actual	
Carbon	solid	6	1.1	2.25	graphite
Iron	solid	26	4.7	7.35	
Lithium	solid	3	0.54	0.54	
Mercury	liquid	80	14	13.56	
Zinc	solid	30	5.4	7.14	
Iron(II) oxide	solid	34	6.1	5.74	a of iron and oxygen
Iron(III) oxide	solid	34	6.1	5.24	a of iron and oxygen
Water	liquid	9	1.6	1.0	a of hydrogen and oxygen
Zinc oxide	solid	38	6.8	5.61	a of zinc and oxygen

Table 24.2 Unit cell volume as function of the crystal system. The quantities a, b, c are the lengths of the cell edges. Source: [12]

Crystal system	Unit cell volume	Crystal system	Unit cell volume
Cubic	a^3	Rhombohedral	$a^3 f(\alpha)$
Tetragonal	$a^2 c$	Hexagonal	$a^2 c \sin(\pi/3)$
Orthorhombic	abc		

Table 24.3 Physical constants of selected inorganic compounds. For solubilities, dil, i, s, sl mean diluted, insoluble, soluble and slightly soluble. Source: [88]

Name	Formula	Molar mass	Melting point	Boiling point	Mass density	Solubility
		$\hat{m}/10^{-3}\,\mathrm{kg\,mol^{-1}}$	$t_{\mathsf{mp}}/\mathrm{K}$	$t_{\mathsf{bp}}/\mathrm{K}$	$\varrho/10^{-3}\,\mathrm{kg\,m^{-3}}$	
Carbon (black)	C	12.011	3823	5100	2.2	i H_2O
Iron (II) oxide	FeO	71.844	1650	3687	6.0	i H_2O; s acid
Iron(III) oxide	Fe_2O_3	159.6888	1838	2260	5.25	i H_2O; s acid
Zinc	Zn	65.38	693	1180	7.134	s acid
Zinc oxide	ZnO	81.408	2248	2633	5.6	i H_2O; s dil acid
					$\varrho/\mathrm{kg\,m^{-3}}$	
Carbon dioxide	CO_2	44.010	-56.558	-78.464	1.145	s H_2O
Carbon monoxide	CO	28.010	-205.02	-191.5	1.799	sl H_2O

Table 24.4 Standard molar enthalpy of formation, $\Delta_f \hat{h}^\circ$, and standard molar entropy, $\hat{s}^\circ$, of selected species. Standard state: 298.15 K and 10^5 Pa. Source: [88, 36, 81, 100]

Species	State	Molecular formula	$\Delta_f \hat{h}^\circ / \mathrm{kJ\,mol^{-1}}$	$\hat{s}^\circ / \mathrm{J\,mol^{-1}\,K^{-1}}$
Carbon	gas	$C(g)$	716.7	158.1
Carbon (graphite)	solid	$C(s)$	0.0	5.7
Carbon dioxide	gas	$CO_2(g)$	-393.5	213.8
Carbon monoxide	gas	$CO(g)$	-110.5	197.7
Methane	gas	$CH_4(g)$	-74.6	186.3
Hydrogen	gas	$H_2(g)$	0.0	130.7
Oxygen (atomic)	gas	$O(g)$	249.2	161.1
Oxygen	gas	$O_2(g)$	0.0	205.2
Iron(II) oxide	solid	$FeO(s)$	-272.0	60.75
Iron(III) oxide	solid	$Fe_2O_3(s)$	-824.2	87.4
Zinc	gas	$Zn(g)$	130.415	160.984
Zinc	solid	$Zn(s)$	0.0	41.6
Zinc oxide	solid	$ZnO(s)$	-350.5	43.7

Table 24.5 Molar enthalpy of formation, $\Delta_\mathrm{f}\hat{h}$, and molar entropy, $\hat{s}$, of selected species. State: 1800 K and 10^5 Pa. Source: [22]

Species	State	Molecular formula	$\Delta_\mathrm{f}\hat{h}/\mathrm{kJ\,mol^{-1}}$	$\hat{s}/\mathrm{J\,mol^{-1}\,K^{-1}}$
Carbon (graphite)	solid	C(s)	30.441	38.125
Carbon dioxide	gas	$CO_2(g)$	-314.070	302.950
Carbon monoxide	gas	CO(g)	-61.015	254.921
Iron(II) oxide	liquid	FeO(l)	-158.675	177.918
Iron(III) oxide (hematite)	solid	$Fe_2O_3(s)$	-623.732	328.599
Oxygen	gas	$O_2(g)$	51.673	264.796
Zinc	gas	Zn(g)	161.633	198.356
Zinc oxide	solid	ZnO(s)	-272.484	132.976

Table 24.6 Selected properties of cast slag products. Source: [69, 126]

Property [a]	Value	Geometric mean	Unit
Mass density	$(2.9 \text{ to } 3.0) \times 10^3$	2.95×10^3	$\mathrm{kg/m^3}$
Thermal conductivity at 293.2 K	1.07 to 1.52	1.27	W/m K
Specific enthalpy capacity at 293.2 K	0.67 to 0.85	0.75	kJ/kg K
Linear thermal expansion within 293.2 K to 873.2 K	$(0.60 \text{ to } 0.83) \times 10^{-5}$	0.71×10^{-5}	$\mathrm{K^{-1}}$
Slag particles enthalpy of fusion from 1073 K to 1223 K	294		kJ/kg

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[a] Temperatures: 293.2 K, 873.2 K, 1073 K, 1223 K = 20 °C, 600 °C, 800 °C, 950 °C.

25

IDEAL GASES

Recall that thermodynamics relies only on having a well defined parameter space whose quantities vary smoothly (differentiable state functions) and that thermodynamics analysis is based on macrostates – not microstates. This makes theory *atomic model agnostic*. Thermodynamics does not know, nor care, about the atomic nature of matter. The description of, and interrelations between, macroscopic properties of substances (their macrostates) is important, not its atomic origin.

Practically, this means that thermodynamics needs input from atomic theories, such as kinetic theory of gases, classical or quantum statistical mechanics, solid state theories, and so on, to carry out any analysis. For our purposes, due to its simplicity, we choose to model ideal gases using basic kinetic theory.

Now, we need to decide the kinetic theory input to our thermodynamic analysis of the gas. Recall that, by definition, the gas is non-reactive; *i.e.*, one species, one phase, no chemical reactions. Thus, the parameter space describing the gas macrostate is spanned by ($f = 1 - 1 + 2 = 2$) two quantities. Traditionally, these quantities are chosen to be two of the following: pressure, volume, and temperature, because they were experimentally related by a state equation: the ideal gas law.

However, in our treatment, we know that energy and entropy define pressure and temperature, as seen in section 23.5. Thus, what we require from kinetic theory is the energy that a system containing an ideal gas has. This knowledge plus the ideal gas state equation will enable us to calculate the different thermodynamic quantities defining an ideal gas macrostate.

25.1 STATE EQUATION OF AN IDEAL GAS

As mentioned in section 23.3, a state equation is a mathematical relation between state functions. In the general case of physical systems, it is not possible to find general state equations. However, in the particular case of an ideal gas, there exists one: the celebrated *ideal gas law*.

The ideal gas state equation relates the gas pressure and volume with the gas amount and its temperature. It was first found *a posteriori* experimental evidence, but can be deduced departing from atomic theories. [30, 130, 112] Hereafter, however, we are satisfied with merely quoting the law:

for an amount n of an ideal gas in a box, the gas state equation is

$$pV = n\hat{r}t\,. \qquad [25.1]$$

25.2 ENERGY OF AN IDEAL GAS IN A BOX

Throughout this section, we specialized the fundamental of thermodynamics to the particular case of an ideal gas in a box. This is useful not only to see the applications of the general machinery of thermodynamics in action, but also in modeling the physical behavior of real gases as ideals.

25.2.1 *Energy of an ideal gas based on dimensional analysis*

Consider a fixed amount of an ideal gas inside a thermally insulated, rigid box. From experimental evidence, we know the gas pressure, temperature, and volume are related by $pV = n\hat{r}t$. On the other hand, recall that the *molar gas constant* is the product of Avogadro's and Boltzmann's constants: $\hat{r} \circeq k_{\mathsf{av}} k_{\mathsf{b}}$. This means that we can rewrite the gas equation as

$$\frac{pV}{nk_{\mathsf{av}}} = k_{\mathsf{b}} t\,.$$

Both sides of the formula have dimensions of energy and are both microscopic measurements: in the denominator, Avogadro's constant scales pV/n down to the molecular level; while, in the numerator, Boltzmann's does the same for t. Based on these observations, we hypothesize a microscopic (molecular) energy of the form:

$$\begin{aligned} \widetilde{e} &\sim \frac{pV}{nk_{\mathsf{av}}}\,, \\ &\sim k_{\mathsf{b}} t\,, \end{aligned}$$

where the $\sim$ symbol states that the two sides of $\widetilde{e}$ have the same dimensions, but might differ from a (currently unknown) dimensionless quantity, Π. In other words, we expect the molecular energy of the gas to be

$$\begin{aligned} \widetilde{e} &= \Pi \frac{pV}{nk_{\mathsf{av}}}\,, \\ &= \Pi k_{\mathsf{b}} t\,. \end{aligned} \qquad [25.2]$$

25.2.2 *Energy of an ideal gas based on kinetic theory*

Consider an ideal gas within a closed, thermally insulated, rigid box. Suppose the gas be composed of μ identical molecules. Pick up a molecule. Say it masses m. Then, from kinetic theory, [30] we know the molecule mean kinetic energy is

$$\widetilde{k} = \frac{1}{2} m \widetilde{v}^2 = \frac{3}{2} k_{\mathsf{b}} t\,,$$

where $\widetilde{v}$ is the molecule mean velocity.

Then, since ideal, the molecule energy is only kinetic (and not kinetic and potential):

$$\widetilde{e} = \frac{3}{2} k_{\mathsf{b}} t\,.$$

Real gas molecules, on the other hand, do not have only translational energy. Nevertheless, $\widetilde{e}$ is useful because it suggests *energy equipartition*:

the molecule total energy comes not only from its translational (kinetic) energy, but also from its rotational and vibrational energies, represented in the molecule *degrees of freedom*, f:

$$\widetilde{e} = \frac{1}{2} f k_{\mathsf{b}} t\,.$$

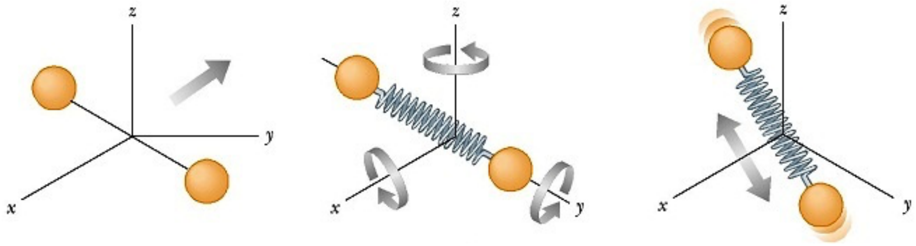

Figure 25.1 Degrees of freedom of a diatomic molecule. From left to right, translational motion, rotational motion about various axes, and vibrational motion along the molecule center of mass. Source: [30]

Not only does this equation coincide with the one guessed by dimensional analysis, eq. (25.2), satisfying our intuition, but also provides us with the value of the (formerly unknown) dimensionless constant: $\Pi = 1/2f$.

Now, scale up $\widetilde{e}$ to the macroscopic world by multiplying both of its sides by nk_{av} and thus have the *total internal energy of the ideal gas* in the box:

$$\begin{aligned} U &= \frac{1}{2} f n k_{\mathsf{av}} k_{\mathsf{b}} t \,, \\ &= \frac{1}{2} f n \hat{r} t \,. \end{aligned} \qquad [25.3]$$

In the last result, notice that

- Boltzmann's constant (through $\hat{r}$) relates the microscopic energy of the molecule with the temperature measurable in the bulk; and
- the total energy of a fixed amount of ideal gas depends only on the gas temperature and the degrees of freedom of its molecules.

Next, to find out the exact value of U, we need to determine f. We do so aided by fig. 25.1:

- a *monoatomic* molecule only translates in space, so it has 3 degrees of freedom; while
- a *diatomic* molecule translates in space (3 degrees), rotates (2 degrees), and vibrates (2 degrees), hence it has 7 degrees of freedom. However, on *quantum mechanical* grounds, two of these degrees are *frozen* at nearly standard state temperature, then f reduces to 5 when $t/t^\circ \sim 1$.

Mathematically, the above considerations turn into

$$f = \begin{cases} 3\,, & \text{for monoatomic gases}\,; \\ 5\,, & \text{for diatomic gases at } t/t^\circ \sim 1\,; \\ 7\,, & \text{for diatomic gases at } t/t^\circ \gg 1\,. \end{cases}$$

Finally, as seen, the energy of an ideal gas depends only on its temperature. This means that the partials of energy-like state functions (Helmholtz free energy, Gibbs' free enthalpy, and enthalpy) do *not* vanish when differentiated with respect to temperature; but *do* vanish when differentiated with respect to any other state function; that is,

$$\partial_V U|_x = \partial_p U|_x = 0\,, \quad \partial_V H|_x = \partial_p H|_x = 0\,,$$

where the x in the partials, say $\partial_p U|_x$, represents any quantity kept fixed. This is sometimes taken as the defining property of an ideal gas.

25.2.3 Scaled formulation of the ideal gas equations

When working out the physics of ideal gases, one soon notices (and gets tired of writing) certain common factors appearing in equations. Then, it is not only useful, but also advisable to *rescale* those equations, so to remove such commonness. It is advisable, because, when equations are presented in scaled form, one clearly sees the important relations between quantities.

Now, as mentioned in chapter 23, thermodynamics is based on two pillars: energy and enthalpy. Therefore, the chosen scaling factors should also be based on them. The question is then how to choose the *scaling* factors. One way is to analyze the ideal gas state equation:

$$pV = n\hat{r}t\,.$$

Notice that *both* sides of the last equation have dimensions of energy. So we could choose *any* side as scaling factor for energy (and energy-like state functions). However, based on experience, the scaling factor that works best is given by its right-hand side: $n\hat{r}t$. On the other hand, when working with entropy (or quantities having dimensions of entropy, such as energy and enthalpy capacities), the repeating factor is $n\hat{r}$, with entropy dimensions. Hence, we *could* use two different scaling factors: when working and presenting results involving energy or quantities having energy dimensions, the scaling factor could be $n\hat{r}t$; while, when working and presenting results involving entropy or quantities having entropy dimensions, $n\hat{r}$. However, using two very similar factors could lead to confusion and produce the counter effect of using them. Hence, we will use only one:

when working and presenting results involving energy (or quantities having energy dimensions) or involving entropy (or quantities having entropy dimensions), their scaling factor is hereafter $n\hat{r}$.

As an aside, since, on physical grounds, $n\hat{r}$ is a strictly positive real, we will never run into the risk of division by zero.

For instance, when rescaled, the energy of a fixed amount of ideal gas in a box, eq. (25.3), takes the simple form

$$\begin{aligned} \overline{u} \overset{\circ}{=} \frac{U}{n\hat{r}} &= \frac{1}{2}\frac{fn\hat{r}t}{n\hat{r}}\,, \\ &= \frac{1}{2}ft\,, \end{aligned} \qquad [25.4]$$

where we decorated the *scaled* internal energy, as we will do onward for *any* scaled quantity. Here, one sees the advantage of scaled equations: first, $2\overline{u} = ft$ reads more pleasantly than $2U = fn\hat{r}t$ and, second, $2\overline{u} = ft$ makes *explicit* the factors affecting the gas energy: f, t.

On the other hand, in the following sections, we will derive the isochoric energy (heat) capacity of an ideal gas. Since it has dimension of entropy, we will present it as

$$\bar{c}_V = \frac{1}{2} f \,.$$

See that $\bar{c}_V$ is dimensionless: $\dim \bar{c}_V = \dim f = 1$. Then, to recover its dimensional form, C_V, one has to multiply it by $n\hat{r}$; *viz.*,

$$C_V = \bar{c}_V n\hat{r} = \frac{1}{2} f n\hat{r} \,,$$

which has dimensions of entropy, as it should.

From both of the preceding examples, we immediately get our first scaling result: a simpler form of the (scaled) energy of an ideal gas:

$$\bar{u} = \bar{c}_V t \,.$$

25.3 ENTHALPY OF AN IDEAL GAS

Consider a fixed amount of ideal gas in a box. As for any other physical system, the gas enthalpy is $H = U + pV$, which, upon scaling, becomes $\bar{h} = \bar{u} + pV/n\hat{r}$. See that the second term equals the system temperature, due to the gas state equation. This leaves us with

$$\bar{h} = \bar{u} + t \,,$$

the *scaled enthalpy of the gas*.

Finally, note that, as the scaled energy, $\dim \bar{h} = \Theta$, and that

the scaled enthalpy of a fixed amount of an ideal gas depends only on its molecularity and temperature.

25.4 ENTROPY CHANGES IN EXPANSION OF IDEAL GASES

Herein, we continue to consider a fixed (chemical) amount of ideal gas in a box and calculate for it its entropy changes during isothermal expansion.

25.4.1 *Isothermal entropy changes under pressure change*

Consider a fixed amount of an ideal gas in a closed, rigid box. Suppose the gas expand isothermally between pressures p_1, p_2. Then, since ideal, the gas parameter space can be spanned by $\{\bar{s}, p, t\}$, which means that $\bar{s}(p,t)$ and hence $\mathrm{d}\bar{s} = \partial_p \bar{s}|_t \,\mathrm{d}p$. Using a Maxwell's relation, appendix F.1, find the value of the partial, $-\partial_t V|_p$, and use it to differentiate the gas equation to have $\mathrm{d}\bar{s} = \mathrm{d}(\ln p)$. Finally, integrate the result between the two given states:

$$\begin{aligned} \Delta\bar{s} &= \int \mathrm{d}\bar{s} = -\int_{p_1, p_2} \mathrm{d}(\ln p) \;, \\ &= \ln\left(\frac{p_1}{p_2}\right) . \qquad \text{[isothermal]} \end{aligned}$$

The last equality gives the (scaled) entropy change of an ideal gas expanding isothermally between two pressures.

25.4.2 *Isothermal entropy changes under volume change*

Consider a fixed amount of an ideal gas in a closed, rigid box. Suppose the gas expand isothermally between volumes V_1, V_2. Then, since ideal, the gas parameter space can be spanned by $\{\bar{s}, V, t\}$, which means that $\bar{s}(V, t)$ and hence $\mathrm{d}\bar{s} = \partial_V \bar{s}|_t \, \mathrm{d}V$. Using a Maxwell's relation, find the value of the partial, $\partial_t p|_V$, and use it to differentiate the gas equation to have $\mathrm{d}\bar{s} = \mathrm{d}\,(\ln V)$. Finally, integrate the result between the two given states:

$$\begin{aligned} \Delta\bar{s} &= \int \mathrm{d}\bar{s} = \int_{V_1,V_2} \mathrm{d}\,(\ln V) \;, \\ &= \ln\left(\frac{V_2}{V_1}\right) . \qquad\qquad \text{[isothermal]} \end{aligned}$$

The last equality gives the (scaled) entropy change of an ideal gas expanding isothermally between two volumes.

25.5 THERMO PROPERTIES OF AN IDEAL GAS

Throughout this section, consider a fixed amount of an ideal gas in a box and find its thermodynamic properties, based on the theory developed in the previous sections.

25.5.1 *Isothermal compressibility*

The gas *isothermal compressibility* follows from its definition, eq. (24.10), and the gas state equation:

$$\begin{aligned} \kappa_t &= -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_t = \frac{n\hat{r}t}{Vp^2} \;, \\ &= \frac{1}{p} \;. \qquad\qquad [25.5] \end{aligned}$$

See that dimensions match and that κ_t scales with the inverse of pressure. It has then dimensions of inverse pressure, $\dim \kappa_t = \mathrm{L}^3/\mathrm{E}$.

25.5.2 *Isobaric thermal expansion*

By the same token, using eq. (24.11) and the gas state equation, the *cubic isobaric thermal expansion* of the gas is

$$\begin{aligned} \eta_p &= \frac{1}{V}\left.\frac{\partial V}{\partial t}\right|_p = \frac{n\hat{r}}{Vp} \;, \\ &= \frac{1}{t} \;. \qquad\qquad [25.6] \end{aligned}$$

Dimensions match and η_p scales with the inverse of temperature. It has then dimensions of inverse temperature, $\dim \eta_p = \Theta^{-1}$.

25.5.3 *Pressure and temperature driven volumetric changes*

Now, we are in position of calculating pressure and temperature driven volumetric changes in the gas. Recall that, in general, fractional volumetric changes for any material, eq. (24.12), are given by $\mathrm{d}\,(\ln V) = \eta_p \, \mathrm{d}t - \kappa_t \, \mathrm{d}p$. Specialize this result by plugging in the values of κ_t, η_p we just found for the gas

$$\frac{1}{V}\,\mathrm{d}V = \frac{1}{t}\,\mathrm{d}t - \frac{1}{p}\,\mathrm{d}p \;,$$

which gives us the fractional volumetric changes for the ideal gas.

25.5.4 *Energy and enthalpy capacities (heat capacities)*

On the one hand, knowing the energy contained in the box, eq. (25.3), the *isochoric energy capacity* (heat capacity) of the gas is, by definition, eq. (24.1), $2C_V = 2\,\partial_t U|_V = f n\hat{r}$, which, upon scaling, gives the *scaled isochoric energy capacity*:

$$\bar{c}_V = \frac{1}{2} f \,. \tag*{[25.7]}$$

Next, replace the values of κ_t, η_p into the relation of capacities, eq. (24.13), use the ideal gas equation, and scale the result to have the *scaled relation between capacities*:

$$\bar{c}_p - \bar{c}_V = 1 \,,$$

which immediately leads to the (intensive) *scaled isobaric enthalpy capacity*:

$$\begin{aligned} \bar{c}_p &= \bar{c}_V + 1 = \frac{1}{2} f + 1 \,, \\ &= \frac{1}{2} (f + 2) \,. \end{aligned} \tag*{[25.8]}$$

On the other hand, by eq. (24.7), establish the *isentropic capacity ratio* for the gas as

$$\gamma = \frac{C_p}{C_V} = \frac{\bar{c}_p}{\bar{c}_V} = \frac{\bar{c}_V + 1}{\bar{c}_V} = 1 + \frac{1}{\bar{c}_V} \,,$$

but, given that $2\bar{c}_V = f$, this yields

$$\gamma = 1 + \frac{2}{f} \,. \tag*{[25.9]}$$

Now, since the gas is ideal, hence non-reactive, replace C_p, C_V for the gas in eq. (24.7) and integrate that to find

$$pV^{\gamma} = \text{constant} \,, \qquad \text{or} \qquad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^{\gamma} \,.$$

Finally, note that the scaled isochoric energy capacity, the scaled isobaric enthalpy capacity, and their ratio depend only on the ideal gas molecularity, therefore macrostate independent, and that all are dimensionless.

25.6 ENERGY AND ENTHALPY OF AN IDEAL GAS

In the previous sections, we studied the energy and enthalpy of an ideal gas in terms of its degrees of freedom. It is possible to be more general and reformulate the these equations in terms of the isochoric energy (heat) capacity and isobaric enthalpy (heat) capacity of the gas. We do so here.

Consider a fixed amount of an ideal gas in a box. The gas energy is $\bar{u}/t = f/2$. But the right-hand side is the gas isochoric energy capacity. This means that

$$\bar{u} = \bar{c}_V t \,.$$

On the other hand, the gas enthalpy is $\bar{h}/t = (f + 2)/2$. But the right-hand side is the gas isobaric enthalpy capacity. This means that

$$\bar{h} = \bar{c}_p t \,.$$

Finally, the gas enthalpy and energy are related to the gas temperature by $\bar{h} = \bar{u} + t$. Thus, $\bar{c}_p t = \bar{c}_V t + t$, which immediately yields

$$\bar{c}_p = \bar{c}_V + 1 \,,$$

since the temperature is absolute (non-zero).

25.7 SCALED GENERALIZED ENTROPY CAPACITY FOR AN IDEAL GAS

Recall that the generalized entropy capacity is given by eq. (24.5): $C_x = t\,\partial_t S|_x$, where x is a state function. Divide both sides of C_x and push the (constant) scaling factor, $n\hat{r}$, into S to scale it:

$$\begin{aligned} \bar{c}_x &= t\,\frac{\partial \bar{s}}{\partial t}\bigg|_x\,, \\ &= \frac{\partial \bar{s}}{\partial \ln t}\bigg|_x\,. \end{aligned} \qquad [25.10]$$

25.8 SCALED GIBBS' FREE ENTHALPY FOR AN IDEAL GAS

Consider a fixed amount of an ideal gas in a box. Then, as for any other system, we have that $G = H - tS$, which upon scaling becomes

$$\bar{g} = \bar{h} - t\bar{s}\,,$$

the *gas scaled Gibbs' free energy*.

Now, between two states, we have the *scaled Gibbs free enthalpy changes for an ideal gas*:

$$\Delta\bar{g} = \Delta\bar{h} - t\Delta\bar{s}\,.$$

25.9 MASS DENSITY OF AN IDEAL GAS

By applying the definition of chemical amount, $n = m/\hat{m}$, to the ideal gas state equation, the *mass density* of an ideal gas can be readily derived:

$$\varrho = \frac{\hat{m}p}{\hat{r}t}\,. \qquad [25.11]$$

Note that dimensions match in both sides, and that ϱ scales with pressure and molar mass; while, inversely with temperature.

25.10 NUMERIC VALUES OF VARIOUS PROPERTIES OF AN IDEAL GAS AT STANDARD STATE

Consider the standard state described in section 23.13.3. Then, using the equations developed in previous sections, it is possible to calculate the numeric values of various properties of an ideal gas at that state: isothermal compressibility, cubic isobaric thermal expansion, molar isochoric energy capacity, molar isobaric enthalpy capacity, ratio between entropy capacites, and density. The results of such calculations are presented in tables 25.1 and 25.2.

25.11 ADIABATIC CHANGES OF AN IDEAL GAS

25.11.1 *Adiabatic pressure and temperature changes*

Consider a fixed amount of an ideal gas in a box. To study how pressure and temperature change adiabatically, expand the gas entropy as $\bar{s}(p, t)$, find $\mathrm{d}\bar{s}$, and apply the adiabatic condition to have

$$\partial_p\bar{s}|_t\,\mathrm{d}p + \partial_t\bar{s}|_p\,\mathrm{d}t = 0\,.$$

The first partial comes readily from Maxwell's relations, appendix F.1, and the (scaled) gas equation: $\partial_p\bar{s}|_t = -1/p$; the second partial, from the generalized entropy capacity, eq. (24.5), in the isobaric case: $\partial_t\bar{s}|_p = \bar{c}_p/t$. Replace the results of both partials into the entropy expansion and use the logarithmic derivative to have

$$\bar{c}_p\,\mathrm{d}\,(\ln t) - \mathrm{d}\,(\ln p) = 0\,.$$

Since $\bar{c}_p$ is fixed, pull it in the temperature exterior derivative and use the properties of logarithmic function to get

$$\mathrm{d}\left(\ln\frac{t^{\bar{c}_p}}{p}\right) = 0\,.$$

Finally, integrate the last equation:

$$\frac{t^{\bar{c}_p}}{p} = \text{constant}\,.$$

25.11.2 *Adiabatic temperature and volume changes*

Consider a fixed amount of an ideal gas in a box. To study how temperature and volume change adiabatically, expand the gas entropy as $\bar{s}(t, V)$, find $\mathrm{d}\bar{s}$, and apply the adiabatic condition to have

$$\left.\frac{\partial\bar{s}}{\partial t}\right|_V \mathrm{d}t + \left.\frac{\partial\bar{s}}{\partial V}\right|_t \mathrm{d}V = 0\,.$$

The first partial comes from the generalized entropy capacity in the isochoric case: $\partial_t\bar{s}|_V = \bar{c}_V/t$; the second partial, from Maxwell's relations and the (scaled) gas equation: $\partial_p\bar{s}|_t = 1/V$. Replace the results of both partials into the entropy expansion, recalling that $\bar{c}_V$ is fixed, use the logarithmic derivative to have

$$\mathrm{d}\left(\ln\left(t^{\bar{c}_V}V\right)\right) = 0\,.$$

Finally, integrate the last equation:

$$\ln\left(t^{\bar{c}_V}V\right) = \text{constant}\,,$$

which upon rearranging becomes

$$t^{\bar{c}_p}V = \text{constant}\,.$$

25.12 ISOBARIC AND ISOCHORIC ENTROPY CHANGES OF AN IDEAL GAS

Consider a fixed amount of an ideal gas being *isobarically* heated (or cooled) from a temperature t_1 to t_2. Then, since isobarically heated, we particularize the scaled generalized entropy capacity, eq. (25.10), to $\bar{c}_p = \partial_{\ln t}\bar{s}|_p$, which means that $\mathrm{d}\bar{s} = \bar{c}_p\,\mathrm{d}(\ln t)$, whereupon integration between the two temperatures yields

$$\Delta\bar{s} = \bar{c}_p \ln\left(\frac{t_2}{t_1}\right)\,.$$

The last equation gives the *scaled isobaric entropy changes* for the gas.

On the other hand, consider now the gas being *isochorically* heated (or cooled) from t_1 to t_2. Then, since isochorically heated, we particularize the scaled generalized entropy capacity to $\bar{c}_V = \partial_{\ln t}\bar{s}|_V$, which means that $\mathrm{d}\bar{s} = \bar{c}_V\,\mathrm{d}(\ln t)$, whereupon integration between the two temperatures yields

$$\Delta\bar{s} = \bar{c}_V \ln\left(\frac{t_2}{t_1}\right)\,.$$

The last equation gives the *scaled isochoric entropy changes* for the gas.

25.13 ISOBARIC ENTHALPY AND ENTROPY CHANGES OF AN IDEAL GAS

In future sections, we will meet the overall chemical equation of the carbothermic reduction of zinc oxide:

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \xrightarrow{1800\,\mathrm{K}} \mathrm{Zn(g)} + \mathrm{CO(g)}\,.$$

Note that the reaction products are both gases. As mentioned above, we will treat them as ideal. Additionally, since the reduction is regularly carried out isobarically, we need therefore to determine the isobaric changes in enthalpy and entropy of an ideal gas. More specifically, we need to determine how temperature and volume influence enthalpy and entropy.

25.13.1 Isobaric enthalpy changes of an ideal gas

Consider a fixed amount of an ideal gas in a box. Since ideal, there are no chemical reactions in the box, and, since the enthalpy of the gas depends only on temperature, one has

$$\mathrm{d}\overline{h} = \overline{c}_p\,\mathrm{d}t\,,$$

which gives the *scaled isobaric enthalpy changes* for the gas.

25.13.2 Isobaric entropy changes of an ideal gas

Consider a fixed amount of an ideal gas in a box. Since ideal, there are no chemical reactions in the box. Then, the parameter space is spanned by three quantities. Choose $\{\overline{s}, t, V\}$. We can then expand the gas entropy as $\overline{s}(t, V)$. Thus, $\overline{s}$ changes are given by

$$\mathrm{d}\overline{s} = \partial_t \overline{s}|_V\,\mathrm{d}t + \partial_V \overline{s}|_t\,\mathrm{d}V\,.$$

The first partial can be computed from the generalized entropy capacity, eq. (24.5), in the isochoric case: $\partial_t \overline{s}|_V = \overline{c}_V/t$. The second partial comes readily from Maxwell's relations, appendix F.1, and the (scaled) gas equation:

$$\begin{aligned}\partial_V \overline{s}|_t &= \partial_t p|_V\,,\\ &= \frac{1}{V}\,.\end{aligned}$$

Finally, replace the results of both partials into $\mathrm{d}\overline{s}$ and use the logarithmic derivative to have

$$\mathrm{d}\overline{s} = \overline{c}_V\,\mathrm{d}\left(\ln t\right) + \mathrm{d}\left(\ln V\right)\,.$$

The last equation gives the *scaled isobaric entropy changes* for the gas.

Table 25.1 Various thermodynamic properties of ideal gases at standard state: 298.15 K, 10^5 Pa

Property	Symbol	Value	Equation	Notes
Isothermal compressibility	${\kappa_t}^\circ/10^{-5}\,\mathrm{Pa}^{-1}$	1.00	25.5	
Cubic isobaric thermal expansion	${\eta_p}^\circ/10^{-3}\,\mathrm{K}^{-1}$	3.35	25.6	
Scaled (dimensionless) isochoric energy (heat) capacity	$\bar{c}_V$	1.5	25.7	Monoatomic gas
		2.5		Diatomic gas at standard state temperature
		3.5		Diatomic gas at high temperature
Scaled (dimensionless) isobaric enthalpy (heat) capacity	$\bar{c}_p$	2.5	25.8	Monoatomic gas
		3.5		Diatomic gas at standard state temperature
		4.5		Diatomic gas at high temperature
Isentropic capacity ratio	γ	1.667	25.9	Monoatomic gas
		1.4		Diatomic gas at standard state temperature
		1.286		Diatomic gas at high temperature

Table 25.2 Mass densities of gases participating in the carbothermic reduction of ZnO, chapter 26. All gases are taken to be ideal at standard state and at the non-standard temperature of 1800 K corresponding to the ZnO reduction process temperature. The data on molar masses were collected from [88]; while densities, calculated using eq. (25.11).

Species	Formula	$\hat{m}/10^{-3}\,\mathrm{kg\,mol^{-1}}$	Calculated	
			$\varrho^{\circ}/\mathrm{kg\,m^{-3}}$	$\varrho/\mathrm{kg\,m^{-3}}$
Carbon monoxide	CO(g)	28.0	1.13	0.187
Carbon dioxide	CO_2(g)	44.0	1.78	0.294
Oxygen	O_2(g)	32.0	1.29	0.214
Zinc	Zn(g)	65.4	2.64	0.437
Zinc oxide	ZnO(g)	81.4	3.28	0.544

26

ZINC OXIDE

Once the foundations for thermodynamic analysis have been established and applied to ideal gases, we focus hereafter on their applications to engineering. In particular, since we are dealing with the carbothermic reduction of zinc oxide, we would like to answer some questions:

- Are the reactions involving the carbothermic reduction of zinc oxide endenthalpic (endothermic), exenthalpic (exothermic)? Spontaneous?
- If not spontaneous, then what changes in the process conditions are required for the reduction to happen?
- What are the minimum, maximum, « ideal » process parameters: pressures and temperatures?
- Is there the possibility for Zn to oxidize to ZnO? If yes, then under which conditions?

We deepen into the reduction process by studying the main properties of Zn and its oxide, then on how ZnO is formed, and finally on the thermodynamics of the process.

26.1 ZINC

In this section, we use thermodynamics and microscopic laws and equations to estimate some (thermodynamic) material properties of Zn. As developed in section 26.5, we require the properties of Zn in its gaseous and solid state. We take the properties of Zn gas to be those of an ideal gas, as treated in chapter 25. Therefore, herein, we estimate those properties of solid Zn.

Consider zinc to be a crystal. The average experimental value of Zn bulk modulus is 6.44×10^{10} Pa. [85] On the other hand, the standard pressure is 10^5 Pa. Thus, their ratio is

$$\frac{\beta}{p^\circ} = \frac{6.44 \times 10^{10}\,\mathrm{Pa}}{10^5\,\mathrm{Pa}} = 6.44 \times 10^5 \, .$$

It can be seen that the bulk modulus of Zn is five orders of magnitude larger than the standard pressure. This means, that under such conditions, Zn(s) can be considered as incompressible.

On the other hand, the experimentally determined melting point of zinc is *ca.* 700 K. [88] Then, according to eq. (24.14), the isobaric thermal expansion of zinc is

$$\eta_p(\mathrm{Zn}) \sim \frac{0.060}{700\,\mathrm{K}} \sim 8.6 \times 10^{-5}\,\mathrm{K}^{-1} \, .$$

The experimental value for $\eta_P(\mathrm{Zn})$ is $8.93 \times 10^{-5}\,\mathrm{K}^{-1}$. [90]

Next, recall that, according to Petit-Dulong law, section 24.8.1, the molar isobaric enthalpy (heat) capacity of solids, and thus of zinc, is

$$\hat{c}_P \sim \hat{c}_V \sim 3\hat{r} \sim 25\,\mathrm{J/mol\,K}\,.$$

The experimentally determined value of $\hat{c}_P(\mathrm{Zn}) = 25.2\,\mathrm{J/mol\,K}$ at standard state. [119]

See that in all cases there are notable agreements between experimentally found laws and equations and experimentally measured values.

26.2 CRYSTAL DATA

Table 26.1 presents crystallographic data for various chemical species involved in the thermochemical reduction of zinc. With such data, along with table 24.2, and eq. (24.18), it is possible to calculate material mass densities, assuming they are crystals. Table 26.2 summarizes such calculations for Zn and for other species treated in the current work.

26.3 MATERIAL PROPERTIES OF ZINC OXIDE

As done for zinc, in this section, we use thermodynamics and microscopic laws and equations to estimate some thermodynamic properties of ZnO. We require the properties of ZnO in its gaseous and solid state. We take the properties of ZnO(g) to be those of an ideal gas, as treated in chapter 25. Therefore, herein, we estimate those properties of ZnO(s).

Consider zinc oxide to be a crystal. The average experimental value of ZnO bulk modulus is 1.57×10^{11} Pa. [83] Thus, its isothermal compressibility of zinc is $6.37 \times 10^{-12}\,\mathrm{Pa}^{-1}$. As in the case of zinc, zinc oxide can be considered incompressible.

On the other hand, zinc oxide melting point is *ca.* 2250 K. [88] Then, according to eq. (24.14), the isobaric thermal expansion of zinc is

$$\begin{aligned}\eta_P(\mathrm{ZnO}) &\sim \frac{0.114}{2250\,\mathrm{K}} - 2.1 \times 10^{-5}\,\mathrm{K}^{-1}\,,\\ &\sim 3 \times 10^{-5}\,\mathrm{K}^{-1}\,.\end{aligned}$$

The experimental value for $\eta_P(\mathrm{ZnO})$ is $2.5 \times 10^{-5}\,\mathrm{K}^{-1}$. [90]

Next, recall that, according to Petit-Dulong law, section 24.8.1, the molar isobaric enthalpy capacity of solids, and thus of zinc oxide, is

$$\begin{aligned}\hat{c}_P \sim \hat{c}_V &\sim 3\hat{r}\,,\\ &\sim 25\,\mathrm{J/mol\,K}\,.\end{aligned}$$

The experimentally determined value of $\hat{c}_P(\mathrm{ZnO}) = 41.1\,\mathrm{J/mol\,K}$. [84, 92]

Next, let's estimate the ZnO lattice energy. Recall that zinc oxide is an oxide bonded from Zn^{+2} and O^{-2}. Thus, using Kapustinskii's equation, eq. (24.16):

$$\begin{aligned}\hat{u} &= 1.2025 \times 10^{-4} \times 2\,\frac{|+2 \times -2|}{(135+60)\,10^{-12}}\left[1 - \frac{3.45 \times 10^{-11}}{(135+60)\,10^{-12}}\right]\\ &\sim 4.1 \times 10^{6}\,\mathrm{J/mol}\,,\end{aligned}$$

where the empirical values for the radii of Zn^{+2}, O^{-2} ions were taken to be 60 pm, 135 pm. [88]

In a previous section, we derived an expression, eq. (24.19), to estimate the energy required to isobarically heat up chemical species up to a given temperature:

$$Q \sim \frac{1}{\eta} c_p m \left(t - t^\circ\right) . \qquad \text{[isobaric]} .$$

It is regularly assumed that the isobaric enthalpy (heat) capacity is constant provided the temperature change is not large. However, if the temperature change is large, then the capacity during heating varies with temperature. Therefore, a *constitutive equation* for c_p is required. Regularly, such equations are available either for specific or molar capacities based on experimental data. For instance, according to [101], the dependence of the molar isobaric enthalpy capacity (*solid phase heat capacity* in the original) for zinc can be calculated by

$$\hat{c}_p = A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2} , \qquad [26.1]$$

where the nomenclature and values are given in table 26.3.

26.4 ZINC OXIDE FORMATION

The aim of the current work is to reduce ZnO to Zn by means of biocoal. Thus, in order to estimate the energetic requirements of such a reduction, it is useful to understand how ZnO is produced in the first place.

26.4.1 *Mechanism of zinc oxide formation*

By studying ZnO formation, we may gain insight on ZnO reduction.

Zinc is a metal whose electron configuration is $[\mathrm{Ar}]4\,\mathrm{s}^2 3\,\mathrm{d}^{10}$, its oxidation state is $+2$ (two valence electrons to donate), and has a Pauling electronegativity of 1.65. [37, 88]

On the other hand, oxygen is a non-metal whose electron configuration is $[\mathrm{He}]2\,\mathrm{s}^2 2\,\mathrm{p}^4$, its oxidation state is -2 (two valence electrons to get), and has a Pauling electronegativity of 3.44. [37, 88]

Now, since oxygen electronegativity is significantly larger than that of zinc, oxygen attracts to itself the two valence electrons of zinc and thus becomes O^{-2}; while zinc, Zn^{+2}, forming then an *ionic* bond; *i.e.*, both electrons donated by zinc are completely taken by oxygen, as depicted in fig. 26.1.

The last discussion can be put in the form of two half reactions:

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{+2} + 2\,\mathrm{e}^- , \qquad \text{[oxidation]}$$

$$\mathrm{O} + 2\,\mathrm{e}^- \longrightarrow \mathrm{O}^{-2} . \qquad \text{[reduction]}$$

The overall reaction can thus be written as

$$2\,\mathrm{Zn(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{ZnO(s)} .$$

Note that, since zinc looses electrons, it oxidizes; while oxygen gain electrons, thus reduces.

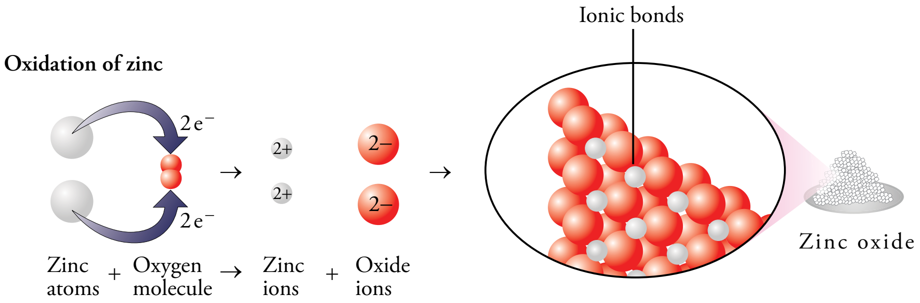

Figure 26.1 Zinc oxide is formed when solid zinc is oxidized by oxygen (gas). During oxidation, zinc completely transfers its two valence electrons to oxygen. Thus, Zn is left as a cation, Zn^{+2}, and O as an anion, O^{-2}. The ZnO molecule is therefore held by an ionic bond. The reverse process, reduction of zinc oxide to zinc, is of concern in the present work. Source: [29]

26.4.2

Born-Haber cycle for zinc oxide formation

The energetics of ZnO formation can be represented in a diagrammatic form called the Born-Haber's cycle. Hereafter, we construct Born-Haber's cycle (BHC) for the formation of zinc oxide, whose chemical model is represented by the chemical equation

$$2\,\mathrm{Zn(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{ZnO(s)}\,.$$

We base the BHC construction on molar enthalpies for the species, $\hat{h}$. By definition, $\Delta_f\hat{h}$ values are presented for unit amounts of products at their standard states, as defined in section 23.13.3. Thus, to have a unit amount of ZnO(s) as product, we half both sides of the chemical equation:

$$\mathrm{Zn(s)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{ZnO(s)}\,, \qquad \Delta_f\hat{h} = -352\,\mathrm{kJ/mol}\,.$$

That is, in terms of the standard quantities, a unit amount of pure crystalline zinc reacts with half unit amount of ideal gas molecular oxygen to produce a unit amount of pure crystalline zinc oxide. This is the reaction on which we construct the cycle.

The hypothetical path for the ZnO(s) BHC is that crystalline zinc sublimes and ionizes, loosing two electrons; gaseous (atomic) oxygen dissociates and gains the free electrons; finally, the cationic zinc and the anionic oxygen combine to form zinc oxide.

Then, the energetic information needed to construct the cycle is:

- change in standard molar enthalpy of formation for the total reaction;
- enthalpy of sublimation of Zn: energy needed to transform a unit amount of a substance from the solid to the gaseous phase;
- first ionization energy of Zn: energy required to remove the outermost electron of each atom in a unit amount of its *gaseous* phase;
- second ionization energy of Zn;
- bound energy of O_2: energy required to break a unit amount of bonds between two atoms;

- electron affinity of O: energy released or absorbed when an electron is added to each atom or ion in a unit amount of a substance in its gaseous phase;
- lattice energy of ZnO: energy released when a unit amount of an ionic compound is formed from its ion in their *gaseous* phase.

The values are gathered from dedicated databases, as in [88]. Be aware that the values are often quoted as *molar*; that is, for a unit amount of substance.

In particular, for the formation of ZnO, we have departed from its balanced formation reaction:

$$2\mathrm{Zn(s)} + \mathrm{O_2(g)} \longrightarrow 2\mathrm{ZnO(s)}\,.$$

However, since by definition, cycles are constructed for a unit amount of *product*, we half the last reaction to have

$$\mathrm{Zn(s)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{ZnO(s)}\,,$$

whose change in standard molar enthalpy of reaction is $-352\,\mathrm{kJ/mol}$.

Similar work is done for the rest of the reactions involved in the hypothetical path for the formation of ZnO, resulting in $-352\,\mathrm{kJ/mol}$ for the overall reaction. The results are presented in fig. 26.2.

26.5 ZINC OXIDE REDUCTION

Before going into the precise details on zinc oxide reduction, we can use what we have learned in previous sections on ZnO formation to estimate process parameters, such as the reaction path and process temperature. This is possible because formation and reduction are inverse processes. Then, we review actual process parameters to carbothermic reduce zinc oxide and compare the estimations and real world data. However, it is to be remembered that BHC is only a hypothetical path (of the many paths) of reaction sequences, since enthalpy is a state function.

26.5.1 Overview of different technologies to obtain zinc from zinc oxide

Herein following [142], we briefly discuss electrowinning and thermal reduction of zinc oxide.

Electrowinning and thermal reduction are two categories of methods to obtain zinc from zinc oxide. Electrowinning rests upon the electrolysis of zinc oxide with sulfuric acid, the electrolysis at nickel electrodes, or the recovery using a hydrogen depolarized anode.

Thermal reduction, on the other hand, relies upon the thermal dissociation of zinc oxide, or the reduction of the oxide with reductants (reducing agents). Some variations of these technologies are patented, such as the SOLZINC process, the SYNMET process, and the ENVIROPLAS process, among others. The first three are treated in this section; while the last, in a section of its own, section 26.5.2.

Carbothermic reduction.

The carbothermic reduction of zinc oxide is a technology that at high temperatures uses carbon and carbon monoxide as reductants. The reactions that occur during the process are

$$\begin{aligned} ZnO(s) + C(s) &\longrightarrow Zn(g) + CO(g)\,, \\ ZnO(s) + CO(s) &\longrightarrow Zn(g) + CO_2(g)\,. \end{aligned}$$

Notice that zinc leaves the reduction reactor as gas and thus must be collected in a condenser. This is the route under analysis in the current work. So we will dig more into it in future sections.

Thermal dissociation of zinc oxide.

In this method, no reductant is used. Only high temperature is required to drive the process:

$$2\,ZnO(s) \longrightarrow 2\,Zn(g) + O_2(g)\,.$$

The process temperatures in this case are higher than those required during carbothermic reduction, because no reductant is used. This is important if the process is fuel-driven.

The common process temperature is 2000 K. Above this value, the process becomes inefficient, since re-radiation (heat) scales with the fourth power of temperature; *i.e.*, black body radiation.

Additionally, such high temperatures require special temperature resistant material, such as state-of-the-art refractories.

SOLZINC process.

The SOLZINC process uses carbon as reductant and produces zinc gas and carbon monoxide:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)\,.$$

The temperatures required to drive this reaction are between 1370 K to 1470 K (1100 °C to 1200 °C).

SynMET process.

Methane is used as reductant in the SYNMET process, unlike other methods that use carbon. The products are zinc gas and *syngas*: a mixture of hydrogen gas and carbon monoxide:

$$ZnO(s) + CH_4(g) \longrightarrow Zn(g) + 2\,H_2(g) + CO(g)\,.$$

The process temperature is lower than in other processes: 1350 K (1075 °C). The conversion of ZnO reaches 100 %; while that of CH_4, 90 %.

Comparison between zinc oxide reduction methods.

Table 26.4 summarizes the different methods to reduce zinc oxide discussed in this section.

In the table, the following is noted:

- All the processes have positive standard enthalpy of reaction; *i.e.*, all require energy input to keep the process temperature.
- From all the processes, thermal dissociation has the largest enthalpy of reaction. However, the SYNMET process needs lower temperatures to proceed than the SOLZINC process. This means that methane is a more effective reductant than solid carbon, but the latter is better than carbon monoxide.

26.5.2 Review on an actual zinc oxide reduction process

In the previous section, we compared some technologies for the reduction of zinc oxide: thermal dissociation of ZnO, the SOLZINC process, and the SYNMET process. All of them are currently being implemented at laboratory or pilot plant scales. In this section, on the other hand, we briefly review the ENVIROPLAS process: an actual industrial process for zinc oxide reduction. [7]

During the ENVIROPLAS process, electric arc furnace dust, EAFD, is pretreated to remove unwanted species from the dust and to transform it into a more suitable form for smelting in a fuming furnace. Then, the dust, dried coke (reductant), and fluxing agent are added to the furnace. The zinc oxide contained in the dust is reduced in the furnace bath to zinc at a temperature of 1773 K (1500 °C). The result is zinc gas that is then condensed into a splash condenser operated at 770 K to 820 K (500 °C to 550 °C). Lastly, the condenser dross, fumes, and residual slag exit the furnace and are post-treated before final disposition.

Conceptually and operationally, the Enviroplas ZnO reduction process is *similar* to iron smelting in a blast furnace, depicted in fig. 26.3.

26.5.3 Chemical path for the carbothermic reduction of zinc oxide

We have seen that the bond between Zn^{+2} and O^{-2} in ZnO is ionic. This is the strongest type of bond.

Since we will use carbon to reduce ZnO, we hypothesize the overall reaction path of be of the form:

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Zn(.)} + \mathrm{CO(g)}\,, \qquad [26.2]$$

where the dot in Zn(.) indicates the state of matter in which Zn is collected in *the process reactor* – not in post-treatment. There are then three possible states for zinc recovery: solid, liquid, or gas, represented as

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Zn(s)} + \mathrm{CO(g)}\,, \qquad [26.3]$$

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Zn(l)} + \mathrm{CO(g)}\,, \qquad [26.4]$$

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Zn(g)} + \mathrm{CO(g)}\,. \qquad [26.5]$$

The standard enthalpy, entropy, and Gibbs' free enthalpies of the three reactions can be calculated, as described in section 23.13.4, to establish the spontaneity of the chemical model. The results of such computations are presented in table 26.5.

It can be seen that, as expected, all of the reactions are endenthalpic, since all the values of $\Delta_\mathrm{r}\hat{h}^\circ$ are positive. Energy input is required into them to keep the temperature if the reaction is to proceed from left to right. Such an input may be chemical, electromagnetic (microwaves), thermal, or the like. [7, 10, 114]

Additionally, since all the values of $\Delta_\mathrm{r}\hat{g}^\circ$ are positive, all of the reactions are not favored at standard temperature. Therefore, energy is required to raise the reactants temperature for the reaction to proceed as written; *i.e.*,

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \xrightarrow{\Delta} \mathrm{Zn(.)} + \mathrm{CO(g)}\,.$$

Lastly, as we hypothesized an oxide reduction, we should check that ZnO is indeed reduced in our equation. Without lost of generality, instead of checking eqs. (26.3) to (26.5) one by one, we only do so for eq. (26.2):

$$\mathrm{Zn^{+2}O^{-2}(s)} + \mathrm{C^{0}(s)} \longrightarrow \mathrm{Zn^{0}(.)} + \mathrm{CO(g)}\,.$$

Recalling the *oil rig* mnemonic, we see that Zn is indeed reduced and is thus the reaction oxidant; while C, oxidized and is thus the reductant.

26.5.4 Process temperature for zinc oxide reduction

In table 26.4, it can be seen that the process temperatures for zinc oxide reduction range between 1000 K to 2000 K, whereas the actual process temperature used by the ENVIROPLAS process is *ca.* 1800 K.

In our case,

we choose a process temperature of 1800 K,

based, not only on the actual ENVIROPLAS process temperature, but also on experience on *chemical kinetics*. Low process temperatures, say in the order of 1400 K, are not enough for metal oxide reduction: the reaction may happen, but too slowly to be technically feasible. [9] Additionally, if the temperature is not high enough, then the recovered Zn likely to be in the liquid phase. This is not desirable, because then the recovered metal will mix with the molten slag of other components and will require a further separation treatment. Therefore, to increase kinetics and to easily recover Zn, a high process temperature is required.

26.5.5 Spontaneity of the carbothermic reduction of zinc oxide

In the previous sections, we have established the chemical path and the process temperature for the carbothermic reduction of zinc oxide, summed up as

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \xrightarrow{1800\,\mathrm{K}} \mathrm{Zn(g)} + \mathrm{CO(g)}\,.$$

In this section, we study the spontaneity of such a reaction.

By following the method presented in section 23.13, using the data from section 24.10, and our process temperature, it is possible to find not only the standard enthalpy and entropy of the reaction (342.661 kJ, 282.176 J/K), but also Gibbs' free enthalpy of the reaction:

$$\begin{aligned}\Delta_\mathrm{r}\hat{g} &= \Delta_\mathrm{r}\hat{h}^\circ - t\Delta_\mathrm{r}\hat{s}^\circ\,,\\ &= 342.661\,\mathrm{kJ/mol} - 1800\,\mathrm{K} \times 282.176 \times 10^{-3}\,\mathrm{kJ/mol\,K}\,,\\ &= -165.26\,\mathrm{kJ/mol}\,.\end{aligned}$$

Then, based on table 23.3, we determine the spontaneity of the reaction:

- Since $\Delta_{\mathrm{r}}\hat{h}^{\circ}$, $\Delta_{\mathrm{r}}\hat{s}^{\circ}$ are both positive, the reaction spontaneity depends on temperature. It is spontaneous at 1800 K.
- Since $\Delta_{\mathrm{r}}\hat{g}$ is negative, the reaction is favored at 1800 K.

These results are not surprising because of the reasoning that led to establish the process equation and the process temperature. However, it is nice to see the numbers match our model.

26.5.6 Fate of carbon on the carbothermic reduction of zinc oxide

There are two main chemical routes whereby solid carbon in the reactor can be consumed during ZnO reduction: CO synthesis or C combustion. The actual path depends on the absence of oxygen or the presence thereof.

Synthesis:

If oxygen is absent, then solid carbon reacts with carbon dioxide to yield carbon monoxide:

$$\mathrm{C^{o}(s) + CO_2(g) \xrightarrow{1800\,K} 2\,CO(g)}\,. \qquad [26.6]$$

Here, C is oxidized to CO; while CO_2, reduced to CO. Thus, it is a redox reaction. Additionally, since C and CO_2 yield CO, the reaction is also a synthesis.

On the other hand, as detailed in section 23.13, the molar enthalpy and the molar entropy of the reaction are 161.6 kJ/mol, 168.767 J/mol K. The change in Gibbs' free enthalpy of the reaction at process temperature is

$$\begin{aligned}\Delta_{\mathrm{syn}}\hat{g} &= 161.6\,\mathrm{kJ/mol} - 1800\,\mathrm{K} \times 168.767 \times 10^{-3}\,\mathrm{kJ/mol\,K}\,,\\ &= -142.18\,\mathrm{kJ/mol}\,.\end{aligned}$$

Consequently, the reaction is spontaneous and favored at 1800 K as written.

Combustion:

If oxygen is present, then solid carbon reacts with oxygen to yield carbon dioxide:

$$\mathrm{C(s) + O_2(g) \xrightarrow{1800\,K} CO_2(g)}\,. \qquad [26.7]$$

Here, C is oxidized to CO_2; while O_2, reduced to CO_2. Thus, it is a redox reaction. Moreover, since O_2 is the oxidant and CO_2 is produced, this is a combustion.

On the other hand, the molar enthalpy is -396.184 kJ/mol; the molar entropy, -2.8×10^{-3} kJ/mol K, at process temperature. Then, one gets

$$\Delta_{\mathrm{c}}\hat{g} = -396.2\,\mathrm{kJ/mol}\,.$$

Hence, the reaction is spontaneous and favored at 1800 K.

Notice, finally, that the entropy change during combustion is small due to the lack of change in the amount of gas.

Conclusion:

Note that $\Delta_{\mathrm{C}}\hat{g} < \Delta_{\mathrm{syn}}\hat{g}$ at 1800 K. This means that C combustion, eq. (26.7), is favored over CO synthesis, eq. (26.6), even if both are spontaneous. There are two ways to mitigate combustion:

- to limit the entrance of oxygen to the reactor or
- to add more solid carbon, more than the stoichiometric carbon needed for ZnO reduction, so the extra amount is burned with any oxygen present in the reactor.

26.5.7 *Chemistry of zinc oxide reduction*

A *carbothermic reaction* is a chemical reaction that uses carbon to reduce other chemical species, often metal oxides, at high temperatures. In the field of zinc oxide reduction, carbothermic reactions can be used to reduce the oxide to zinc by oxidizing carbon to carbon monoxide or carbon dioxide. Traditionally, the source of carbon is metallurgical carbon or coke. However, in the current work, the carbon source is biocoal.

When EAFD is object to a carbothermic process, the resulting reactions are numerous and complex, due to the number of chemicals involved. However, the following chemical reactions model zinc oxide extraction from the EAFD, its reduction, and volatilization: [7, 79, 99]

$$\mathrm{ZnO(s)} + \mathrm{CO(g)} \rightleftarrows \mathrm{Zn(g)} + \mathrm{CO_2(g)}\,, \qquad [26.8]$$

$$\mathrm{ZnO(s)} + 2\,\mathrm{FeO(s)} \rightleftarrows \mathrm{Zn(g)} + \mathrm{Fe_2O_3(s)}\,, \qquad [26.9]$$

$$\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \rightleftarrows \mathrm{CO_2(g)} + 2\,\mathrm{FeO(s)}\,, \qquad [26.10]$$

$$\mathrm{C(s)} + \mathrm{CO_2(g)} \rightleftarrows 2\,\mathrm{CO(g)}\,. \qquad [26.11]$$

In the carbothermic model, notice that

- eqs. (26.8) to (26.10) are *not* independent: eq. (26.8) follows from the addition of eq. (26.9) and eq. (26.10). We keep them as they stand, however, to emphasize their analysis;
- in all cases, we depart from ZnO(s) as it is the phase of the oxide in EAFD;
- iron(II) oxide and iron(III) oxide, $\mathrm{FeO}_{\mathrm{F}}\mathrm{e}_2\mathrm{O}_3$, are also present in the EAFD and both influence the reduction: FeO reduces Zn directly, as seen in eq. (26.9), whereas $\mathrm{Fe_2O_3}$ reacts with carbon monoxide, CO, and then produces FeO, which then reduces ZnO (eq. (26.10));
- solid carbon does not only directly reduce ZnO, but rather through the synthesis of CO. Thus, it is important to allow solid carbon to gasify;
- since CO reduces ZnO, we expect that the reduction happens at the solid-gas inter-phase.

Additionally, note that if the process parameters (pressure and temperature) are kept in the correct ranges, the reactions happen as written. Otherwise, the reverse reactions will happen. This is important in eq. (26.8), since re-oxidation of Zn may happen instead; *i.e.*,

$$\mathrm{Zn(g)} + \mathrm{CO_2(g)} \rightleftarrows \mathrm{ZnO(s)} + \mathrm{CO(g)}\,.$$

26.5.8 Classification of the zinc oxide reactions

Using the criteria presented in section 23.13.1, eqs. (26.8) to (26.11) can be classified. The results are presented in table 26.6. There, it can be seen that the reactions happening when ZnO is reduced to Zn, three are redox. Note that the reducing agents of ZnO are carbon, and iron, not only carbon. This is useful to know, since EAFD, the research object of the present work, contains large amounts of Fe.

26.5.9 Melting point analysis of the zinc oxide reduction model

Recall that the process temperature is 1800 K and that the information on boiling and melting points is presented in table 24.3.

Now, consider eq. (26.8):

$$\mathrm{ZnO(s)} + \mathrm{CO(g)} \rightleftharpoons \mathrm{Zn(g)} + \mathrm{CO_2(g)}\,.$$

Zinc melting and boiling points are 693 K and 1180 K. Thus, at process temperature, zinc should be a gas in the reactor. This observation matches eq. (26.8).

Consider eq. (26.9):

$$\mathrm{ZnO(s)} + 2\,\mathrm{FeO(l)} \rightleftharpoons \mathrm{Zn(g)} + \mathrm{Fe_2O_3(s)}\,.$$

Iron(III) oxide melting and boiling points are 1838 K and 2260 K. Thus, at process temperature, iron(III) oxide should be a solid in the reactor. This observation matches eq. (26.9).

Consider eq. (26.10):

$$\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \rightleftharpoons \mathrm{CO_2(g)} + 2\,\mathrm{FeO(s)}\,.$$

Iron(II) oxide melting and boiling points are 1650 K and 3687 K. Thus, at process temperature, iron(II) oxide should be a liquid in the reactor. This observation does *not* match eq. (26.10). Therefore, it needs to be rewritten as

$$\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \rightleftharpoons \mathrm{CO_2(g)} + 2\,\mathrm{FeO(l)}\,.$$

Finally, for the sake of clarity and ease of reference, we gather and renumber the equations:

$$\mathrm{ZnO(s)} + \mathrm{CO(g)} \rightleftharpoons \mathrm{Zn(g)} + \mathrm{CO_2(g)}\,, \tag{26.12}$$

$$\mathrm{ZnO(s)} + 2\,\mathrm{FeO(l)} \rightleftharpoons \mathrm{Zn(g)} + \mathrm{Fe_2O_3(s)}\,, \tag{26.13}$$

$$\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \rightleftharpoons \mathrm{CO_2(g)} + 2\,\mathrm{FeO(l)}\,, \tag{26.14}$$

$$\mathrm{C(s)} + \mathrm{CO_2(g)} \rightleftharpoons 2\,\mathrm{CO(g)}\,. \tag{26.15}$$

26.5.10 Born-Haber Cycle for the carbothermic reduction of zinc oxide

We are already familiar with the overall chemical equation for the carbothermic reduction of ZnO:

$$\mathrm{ZnO(g)} + \mathrm{C(s)} \xrightarrow{\Delta} \mathrm{Zn(g)} + \mathrm{CO(g)}\,.$$

Based on the previous sections findings, we can then draw the BHC (Born-Haber cycle) for the overall reaction by hypothesizing that zinc oxide sublimes, then atomizes; while carbon also sublimes; finally, the oxygen atomized from zinc oxide and the sublimed carbon synthesize into carbon monoxide. The whole processes is summarized in fig. 26.4.

From all the chain, as expected, we see that all of the reactions are endenthalpic, but one: carbon monoxide synthesis, which is exenthalpic. This agrees with experiment.

26.6 THERMODYNAMICS OF ZINC OXIDE REDUCTION

In the previous chapters, we reviewed the modern machinery of thermodynamics. Then, we applied it to the case of ideal gases. Herein, on the other hand, we specialize the same ideas to the main object of the current work: the carbothermic reduction of zinc oxide.

26.6.1 Spontaneity of zinc oxide reduction equations

In this section, we establish whether the reactions eqs. (26.12) to (26.15) are endenthalpic, exenthalpic, spontaneous, or non-spontaneous. We do this by computing the equations' Gibbs' free enthalpy, as discussed in section 23.13. The detailed calculations are omitted; but the results, presented in table 26.7. As shown therein, all the reactions are endenthalpic (they require enthalpy to proceed as written), since all the $\Delta_\mathrm{r} H$ are positive. Additionally, the spontaneity of all the reactions depends on temperature, but, given the process temperature of 1800 K, all except one are spontaneous, due to their $\Delta_\mathrm{r} G$ being negative.

Finally, we gather the information obtained in this section as the final set of carbothermic reactions for zinc oxide reduction:

$$\mathrm{ZnO(s)} + \mathrm{CO(g)} \xrightarrow{1800\,\mathrm{K}} \mathrm{Zn(g)} + \mathrm{CO_2(g)}\,, \tag{26.16}$$

$$\mathrm{ZnO(s)} + 2\,\mathrm{FeO(l)} \xrightarrow{1800\,\mathrm{K}} \mathrm{Zn(g)} + \mathrm{Fe_2O_3(s)}\,, \tag{26.17}$$

$$\mathrm{CO(g)} + \mathrm{Fe_2O_3(s)} \xrightarrow{1800\,\mathrm{K}} \mathrm{CO_2(g)} + 2\,\mathrm{FeO(l)}\,, \tag{26.18}$$

$$\mathrm{C(s)} + \mathrm{CO_2(g)} \xrightarrow{1800\,\mathrm{K}} 2\,\mathrm{CO(g)}\,. \tag{26.19}$$

26.6.2 Notes on the spontaneity of the zinc oxide reduction

Additionally, the process temperature was chosen to be 1673 K (1400 °C) instead of the process temperature considered herein: 1800 K ($\sim$ 1500 °C). The results of the model agree with table 26.7 and the conclusions established in section 26.6.1: all of the reactions except one are spontaneous at that lower temperature. The question then becomes « why not choosing the process temperature to be 1673 K »? The reason is kinetics.

Herein we have been discussing zinc oxide reduction from a *thermochemical* viewpoint. Accordingly, one could choose the process temperature to be 1673 K. However, due to the experience gathered in the subject and following actual (industrial) process parameters, such a lower temperature will turn into a slow reduction of zinc oxide, because of the *kinetics* of the process.

Now, a discussion on the kinetics of ZnO reduction is out of the scope of the present document. For this reason, it is recommended to study the reduction under the light of process dynamics. Nevertheless, the information gathered from thermodynamics (that which this study presents) gives a useful and enlightening starting point on the subject.

Table 26.1 Crystallographic data on selected minerals (crystals). The symbols z, a, b, c stand for the number of atoms in the unit cell and the cell edge lengths; while, the abbreviations cub, drs, hex, hex cp, rhomb, for cubic, defect rock salt, hexagonal, hexagonal close pack, rhombohedral. Source: [88]

Name	Formula	Crystal system	Structure type	z	$a/10^{-10}$ m	$b/10^{-10}$ m	$c/10^{-10}$ m
Graphite	C	hex	graphite	4	2.4612		6.7079
Hematite	Fe_2O_3	rhomb	corundum	6	5.025		13.735
Wustite	$Fe_{0.953}O$	cub	drs	4	4.3088		
Zinc	Zn	hex	hex cp	2	2.665		4.947
Zincite	ZnO	hex	zincite	2	3.2495		5.2069

Table 26.2 Calculated and reported mass densities for selected minerals (crystals). The calculated values were estimated using eq. (24.18). The unit cell volumes and the crystallographic data were collected from tables 24.2 and 26.1. The reported values were gathered from [88].

Formula	$\varrho/\mathrm{g\,cm^3}$		Notes
	Estimated	Reported	
Zn	7.137	7.14	as hexagonal with $a = b$
ZnO	5.676	5.61	as hexagonal with $a = b$
C	2.267	2.25	as hexagonal with $a = b$
Fe_2O_3	5.297	5.24	as hexagonal with $a = b$
FeO	5.965	5.74	as wustite, cubic with $a = b = c$

Table 26.3 Nomenclature and values for eq. (26.1), the molar isobaric enthalpy (heat) capacity for zinc, $\hat{c}(\mathrm{Zn})$. Source: [101]

Quantity	Symbol/unit	Value	Notes
Molar isobaric enthalpy (heat) capacity	$\hat{c}/\mathrm{J\,mol^{-1}\,K^{-1}}$		eq. (26.1)
Parameter A	$A/\mathrm{J\,mol^{-1}\,K^{-1}}$	25.60123	
Parameter B	$B/\mathrm{J\,mol^{-1}\,K^{-2}}$	-4.405292	
Parameter C	$C/\mathrm{J\,mol^{-1}\,K^{-3}}$	20.42206	
Parameter D	$D/\mathrm{J\,mol^{-1}\,K^{-4}}$	-7.399697	
Parameter E	$E/\mathrm{J\,K\,mol^{-1}}$	-0.045801	

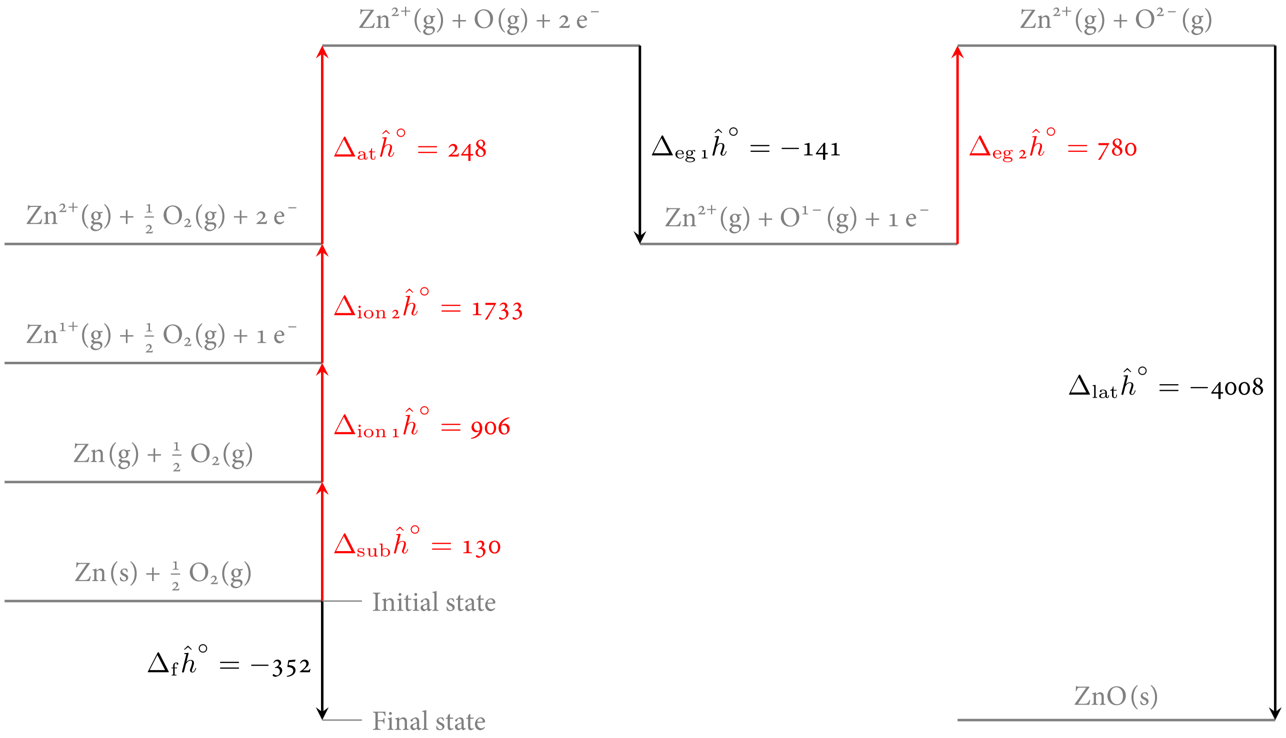

Figure 26.2 Born-Haber cycle for the formation of zinc oxide: $2\,Zn(s) + O_2(g) \longrightarrow ZnO(s)$. In kJ, the values represent changes in standard enthalpies for the chemical species at their standard states. Upward pointing arrows and positive values represent endenthalpic (endothermic) processes; while downward pointing arrows and negative values, exenthalpic (exothermic) processes. Diagram not drawn to scale. Data: [88, 100]

Table 26.4 Comparison between thermal dissociation of ZnO, the SOLZINC process, and the SYNMET process. Adapted from [142] with values recalculated with data from [88]

	Thermal dissociation	SOLZINC	SYNMET
Chemical reaction	[a]	[b]	[c]
Standard molar enthalpy of reaction	480.9 kJ/mol	370.4 kJ/mol	445.0 kJ/mol
Standard molar entropy of reaction	219.9 J/mol K	325.4 J/mol K	406.2 J/mol K
Theoretical process temperature	2190 K	1130 K	1095 K
Development status	Laboratory	Pilot plant	Laboratory
Challenge level	large, fundamental issues	medium, engineering issues	medium, engineering issues

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[a] $ZnO(s) \longrightarrow Zn(g) + (1/2)\,O_2(g)$
[b] $ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$
[c] $ZnO(s) + CH_4(g) \longrightarrow Zn(g) + 2\,H_2(g) + CO(g)$

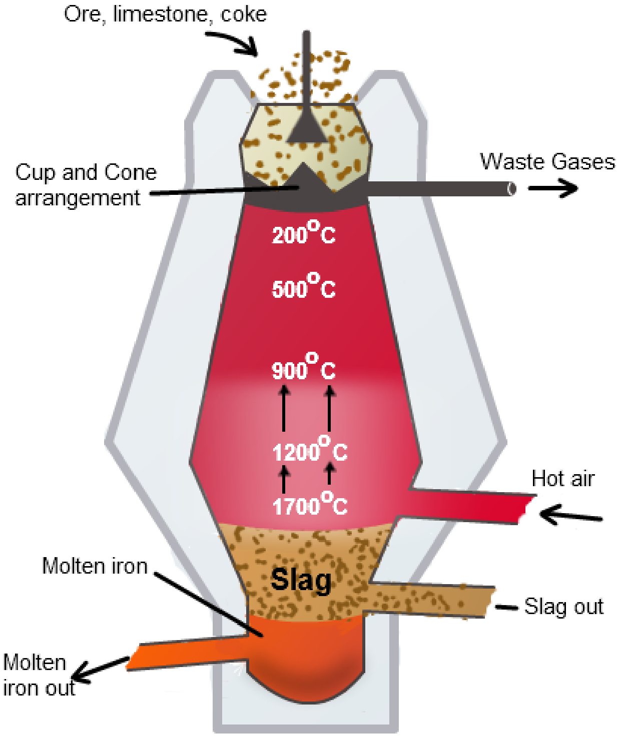

Figure 26.3 Industrial reduction of zinc oxide. The oxide is reduced *similarly* as iron is smelted in a blast furnace. EAFD containing ZnO, a reducing agent (coke), and fluxing agents (limestone) are injected to the furnace. Then, carbothermic reactions reduce the oxide to metallic Zn, which is finally collected at the output of the furnace. Source: [105]

Table 26.5 Standard enthalpy, standard entropy, and standard Gibbs' free enthalpy of reaction for three hypothetical paths during the carbothermic reduction of zinc oxide. Standard state temperature: $t^\circ = 298.15\,\mathrm{K}$. Data gathered from table 24.4.

Reaction	$\Delta_\mathrm{r}\hat{h}^\circ/\mathrm{kJ\,mol^{-1}}$	$\Delta_\mathrm{r}\hat{s}^\circ/10^{-3}\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$	Enthalpics	Spontaneity	$\Delta_\mathrm{r}\hat{g}^\circ/\mathrm{kJ\,mol^{-1}}$	Favored at t°?
eq. (26.3)	240.0	189.9	endenthalpic	dep. on temp.	183.4	no
eq. (26.4)	246.5	199.1	endenthalpic	dep. on temp.	187.1	no
eq. (26.5)	370.4	309.3	endenthalpic	dep. on temp.	278.2	no

Table 26.6 Classification of the reactions occurring in the carbothermic reduction of zinc oxide

Reaction	Type	Reason
eq. (26.8)	Redox	Zinc oxide is reduced by carbon monoxide
eq. (26.9)	Redox	Zinc oxide is reduced by iron (II) oxide
eq. (26.10)	Redox	Iron (III) oxide is reduced by carbon monoxide
eq. (26.11)	Synthesis	Carbon dioxide combines with carbon

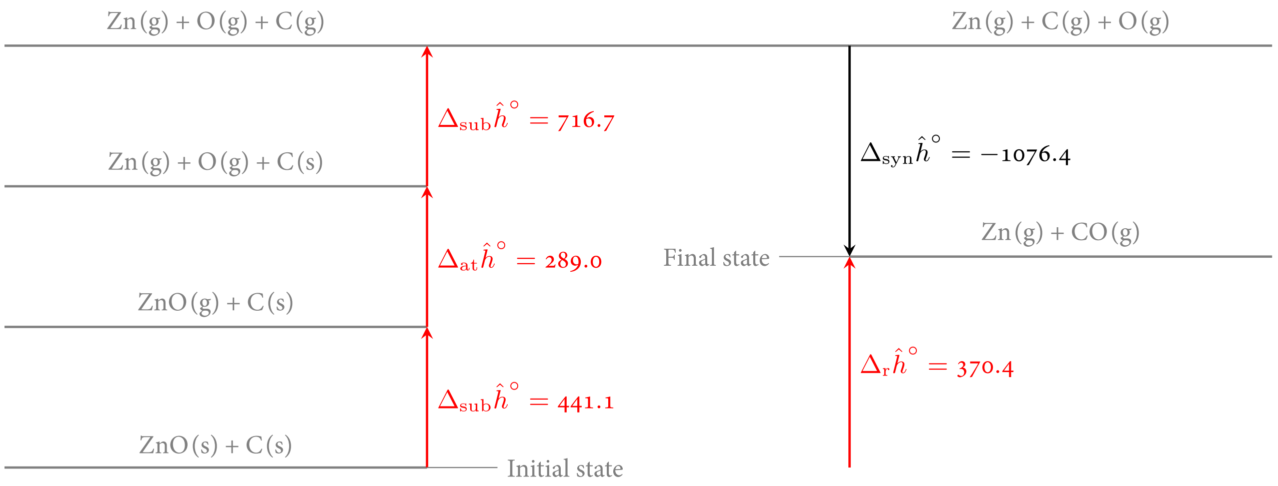

Figure 26.4 Born-Haber cycle for the carbothermic reduction of zinc oxide at 1800 K: ZnO(s) + C(s) $\xrightarrow{\Delta}$ Zn(g) + CO(g). In kJ, the values represent enthalpy changes for the chemical species at process temperatures. Upward pointing arrows and positive values represent endenthalpic processes; while downward pointing arrows and negative values, exenthalpic processes. Diagram not drawn to scale. Data: [88, 100]

Table 26.7 Changes in standard enthalpy of reaction, standard entropy, and Gibbs' free enthalpy at 1800 K for the reactions occurring during the carbothermic reduction of zinc oxide. Data gathered from table 24.5. Note: we use the terms endenthalpic and exenthalpic instead of the more traditional endothermic and exothermic.

Reaction	$\Delta_r H/\text{kJ}$	$\Delta_r S/10^{-3}\,\text{kJ}\,\text{K}^{-1}$	Enthalpics	Spontaneity	$\Delta_r G/\text{kJ}$	Favored at 1800 K?
eq. (26.12)	181.062	113.409	endenthalpic	dep. on temp.	-23.07	yes
eq. (26.13)	124.799	47.894	endenthalpic	dep. on temp.	38.589	no
eq. (26.14)	54.087	66.024	endenthalpic	dep. on temp.	-64.756	yes
eq. (26.15)	161.599	168.739	endenthalpic	dep. on temp.	-142.18	yes

Part IV

CONCLUSIONS

27

CONCLUSIONS

The most relevant conclusions of the topic treated throughout the present document can be summarized as follows:

- The Austrian legal framework that regulates forest activities imposes severe limitations to the industry, like harvesting times and amounts, regulations on felling, road construction, protection of the cutting surfaces and so forth. However, this apparent drawback guarantees sustainability of the resource, not only for recreational and conservationism purposes, but also as a renewable technical resource. Besides, there exists the possibility to enhance forest functions by means of governmental (Austrian) grants.

- There is an increasing number of industries interested in forest products and byproducts: the so-called traditional ones, as sawmill, pulp and paper, board, construction and different manufacturers of wood-based products, and, on the other hand, non-traditional or alternative industries, chiefly the energy sector. This increase in the competition for material has led to conflict of interests which are currently being solved in Austria through the Forest Dialogue. It might be interesting, as it was mentioned, to monitor the Dialogue outcomes, since they may affect the way in which forests are managed, as well as other matters.

- Additionally, this increase of competition for material has also led to a complex interaction among trade, market availability and prices. If there is a factor affecting one of them or one of the major players (forestry and traditional industries), it affects the rest. For instance, if wood demand decreases, prices become lower and there is less available material in the market because forests are not harvested. In any case, it was seen that the most affected industry is the alternative one, because it pays the lowest prices for material. The solutions to this hindrance are to deal directly with material producers (raw wood, residues or pellets), so to avoid traders, and to pay high enough prices for the products, so that, with time, the alternative sector becomes a regular costumer, instead of a passive actor.

- It was shown that logistics is a challenging but crucial step in the usage of biomass as a feedstock material. It involves a series of steps, each one dedicated to deal with the particularities of forest products: harvesting and collection of raw material from scattered sources, storage and conditioning – or densification, and transport. From all of them, the most important one is acquisition of the material. It was shown that a constant flow of material decreases storage capacities up to 100 times if compared with an unsteady flow. So to guarantee this constant supply is of primary importance, much more at large scales. The main solution is to trade biomass at relatively high prices with binding long-term contracts with producers.

- Then, it was presented that, due to the very nature of the raw feedstock, it decays rapidly and is prone to microbial attacks. Thus proper conditioning while storing the material suffices to avoid such losses of dry mass and also reduces, to some extend, transportation costs. In parallel, it was mentioned that pellets are not subject to this decay, because of their preprocessed nature.
- On the other hand, the final step in the logistic chain is transportation. This one is the most flexible of them all, since various alternatives can provide the same functions. However, transportation costs are decisive when considering alternatives, because they may account for more than the prices of the material itself. As an aid to this decision making process, analysis and optimization of the transport modes and routes are the most valuable tools.
- Finally, in the last chapter, it was seen that the usage of pellets gives good promises, because trading can be done directly with producers via producers associations, transportation may be done at large scales from established locations, storing and conditioning of the material are kept to a minimum, since pellets do not decay. Besides, due to their relatively high energy density, pellet transportation reduces to a route analysis, rather than a complex system of conditioning, storing and transport. Moreover, pellets do not pose risks of self-ignition, but have shown to be an excellent fuel with high values of the enthalpy of combustion, low emissions of CO_2, SOx, NOx and low ash yields. On top of that, there are standard methods to ensure the material quality and performance and policy support. On the down side, despite the fact that they are currently used as a fuel, their consumption in other usages is not reported, for instance, as chemical reagents. This is a true hindrance on the adoption of this type of biomass, since this interesting technology shows great potential for the benefit of industries. This topic, however, could be studied in-depth at laboratory or pilot-plant scales.

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Part V

BACK MATTER

A

LISTS OF FIGURES AND TABLES

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AUSTRIAN STANDARDS

B

Lists of Austrian Standards, ÖNORMs, gathered on 12.03.2013 from [72]

Content	Standard
Energy forecasting	ÖNORM M
Energy-economical utilization of wood and bork [sic] as fuel - Definitions and properties	ÖNORM M
Gaseous fuels and their utilization - Terms and definitions	ÖNORM M
Hydro-energy economy	
Tar and particles in product gases – Sampling and analysis	ÖNORM CEN/TS
Requirements and test specifications	ÖNORM M
Pellets and briquettes - Requirements and test specifications	ÖNORM M
Woodpellets - Quality assurance in the field of logistics of transport and storage	ÖNORM M
Woodpellets - Requirements for storage of pellets at the ultimate consumer	ÖNORM M

Table B.1 ÖNORMs [accessed on 12.03.2013]

Content	Standard
Energy accounting and energy balance	ÖNORM M
Energy of biomass, organic waste, wind and geothermal energy	ÖNORM M
Energy utilization	ÖNORM M
Environment	ÖNORM M
General terms with definitions	ÖNORM M
List of key-words	ÖNORM M
Thermic energy economy	ÖNORM M
Content	Standard
Requirements and test specifications (National supplement referring to VORNORM ÖNORM CEN/TS 14961)	ÖNORM M
Definitions, requirements, testing, marking	ÖNORM EN

Table B.2 ÖNORMs [accessed on 12.03.2013]

Content	Standard
A guide for a quality assurance system	CEN/TR
Calculation of analyses to different bases	ÖNORM CEN/TS
Determination of ash content	ÖNORM EN
Determination of bulk density	ÖNORM EN
Determination of calorific value	ÖNORM EN
Determination of major elements	ÖNORM CEN/TS
Determination of mechanical durability of pellets and briquettes - Part 1: Pellets	ÖNORM EN
Determination of minor elements	ÖNORM CEN/TS
Determination of moisture content - Oven dry method - Part 1: Total moisture - Reference method	ÖNORM EN
Determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method	ÖNORM EN
Determination of moisture content - Oven dry method - Part 3: Moisture in general analysis sample	ÖNORM EN
Determination of the content of volatile matter	ÖNORM EN
Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods	ÖNORM CEN/TS
Determination of total content of sulphur and chlorine	ÖNORM CEN/TS
Fuel quality assurance	ÖNORM CEN/TS
Fuel specifications and classes	ÖNORM CEN/TS
Fuel specifications and classes - Part 1: General requirements	ÖNORM EN
Method for the determination of ash melting behaviour - Part 1: Characteristic temperatures method	ÖNORM CEN/TS

Table B.3 ÖNORMs [accessed on 12.03.2013]

Content	Standard
Methods for determination of the water soluble content of chloride, sodium and potassium	ÖNORM CEN/TS
Methods for sample preparation	ÖNORM CEN/TS
Methods for the determination of mechanical durability of pellets and briquettes - Part 2: Briquettes	ÖNORM CEN/TS
Methods for the determination of particle density	ÖNORM CEN/TS
Methods for the determination of particle size distribution - Part 1: Oscillation screen method using sieve apertures of 3,15 mm and above	ÖNORM CEN/TS
Methods for the determination of particle size distribution - Part 2: Vibrating screen method using sieve apertures of 3,15 mm and below	ÖNORM CEN/TS
Methods for the determination of particle size distribution - Part 3: Rotary screen method	ÖNORM CEN/TS
Sampling - Methods for preparing sampling plan and sampling certificates	ÖNORM CEN/TS
Sampling - Part 1: Methods for sampling	ÖNORM CEN/TS
Sampling - Part 2: Methods for sampling particulate material transported in lorries	ÖNORM CEN/TS
Solid biofuels	ON-HB
Terminology, definitions and descriptions	ÖNORM CEN/TS

Table B.4 ÖNORMs [accessed on 12.03.2013]

Content	Standard
Determination of ash content	ÖNORM EN
Determination of calorific value	ÖNORM EN
Determination of moisture content using the oven dry method - Part 1: Determination of total moisture by a reference method (CEN/TS 15414-1:2009)	ONR CEN/TS
Determination of moisture content using the oven dry method - Part 2: Determination of total moisture by a simplified method (CEN/TS 15414-2:2009)	ONR CEN/TS
Key properties on solid recovered fuels to be used for establishing a classification system (CEN/TR 15508:2006)	ONR
Method for the determination of biomass content	ONR CEN/TS
Method for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)	ÖNORM EN
Methods for sampling	ÖNORM EN
Methods for the determination of bulk density (CEN/TS 15401:2009)	ONR CEN/TS
Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)	ÖNORM CEN/TS
Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)	ÖNORM EN
Methods for the preparation of the laboratory sample	ÖNORM EN
Terminology, definitions and descriptions	ÖNORM EN

Table B.5 ÖNORMs [accessed on 12.03.2013]

Content	Standard
Basic standard for the in-situ measurement of electromagnetic field strength related to human exposure in the vicinity of base stations (English version)	ÖVE-ÖNORM EN
Basic standard on measurement and calculation procedures for human exposure to electric, magnetic and electromagnetic fields (0 Hz - 300 GHz) (English version)	ÖVE-ÖNORM EN
Classification and designation of documents for plants, systems and equipment - Part 1: Rules and classification tables (IEC 61355-1:2008) (English version)	ÖVE-ÖNORM EN
Corrugated safety metal hose assemblies for the connection of domestic appliances using gaseous fuels	ÖNORM EN
Derivatives from coal pyrolysis - Terminology	ÖNORM EN
Determination of volatile compounds in cellulose-based materials by Solid Phase Micro Extraction (SPME)	ÖNORM A
Heat meters - Part 4: Pattern approval tests (consolidated version)	ÖNORM EN
High-voltage switchgear and control gear - Part 1: Common specifications (IEC 62271-1:2007)(English version)	ÖVE-ÖNORM EN
Safety requirements for electrical equipment for measurement, control and laboratory use - Part 1: General requirements (IEC 66/342A/CDV)	ÖVE-ÖNORM EN
Standard data element types with associated classification scheme for electric components - Part 4: IEC reference collection of standard data element types and component classes (IEC 61360-4:2005)	ÖVE-ÖNORM EN

Table B.6 ÖNORMs [accessed on 12.03.2013]

Content	Standard
Hydrogen generators using fuel processing technologies – Part 1: Safety	ISO
Standard Specification for Pyrolysis Liquid Biofuel	ASTM D
Standard Test Method for Acid-Insoluble Lignin in Wood (Reapproved 2001)	ASTM D
Standard Test Method for Ash in Biomass ASTM E 1775:2001 standard	
Standard Test Method for Bulk Density of Densified Particulate Biomass Fuels (Reapproved 1998)	ASTM E
Standard Test Method for Pyrolysis Solids Content in Pyrolysis Liquids by Filtration of Solids in Methanol	ASTM D
Standard Test Method for the Determination of Acid-Insoluble Residue in Biomass	ASTM E
Standard Test Method for Total Chemically Bound Nitrogen in Water by Pyrolysis and Chemiluminescence Detection	ASTM D
Standard Test Methods for Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis (Reapproved 2005)	ASTM D

Table B.7 Pertinent ISO and ASTM standards redirected from the ÖNORM website [72] [accessed on 12.03.2013]

C

BIOMASS THERMAL CONVERSION TECHNOLOGIES

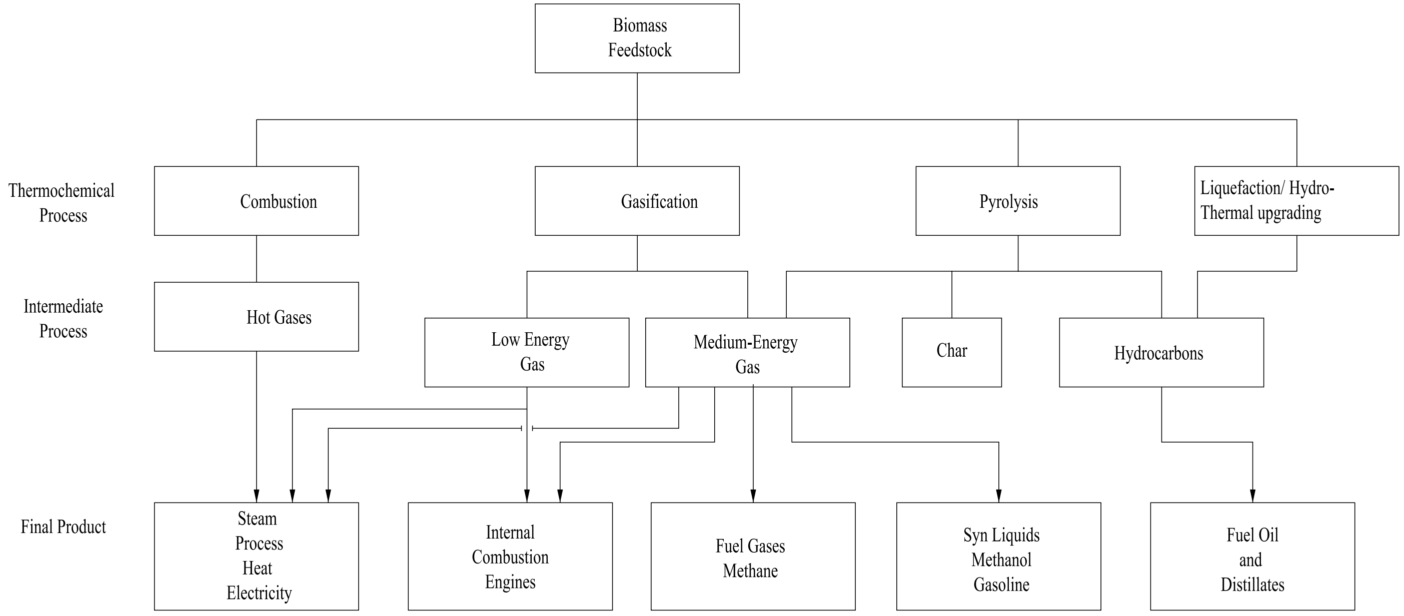

Figure C.1 Biomass thermal conversion technologies [95]

D

CERTIFIED TREE SPECIES IN AUSTRIA AND THEIR SURFACE COVERAGE

According to [52], there are 31 certified species of trees in Austria – listed in table D.1. However, based on the Austrian Forest Inventory, Hanak-Hammerl, [65], reported that, from all the aforementioned species, the Norway spruce covers approximately 59.8 % of forest surface and is only followed by Beech covering 9.5 %. The rest of the species account individually on less than 3.0 %. Additionally, in the same report, [65], it was found that the majority of the forest area is composed by coniferous trees, 74.8 %. These figures are in accordance to those presented by the *Lebensministerium*, [54].

Table D.1 Certified tree species in Austria, [52]

Id	Botanical name	German name	Abbreviation	English name (s)
1	Abies alba	Tanne	Ta	European silver fir
2	Acer platanoides	Spitzahorn	Sp.Ah	Norway maple
3	Acer pseudoplatanus	Bergahorn	B.Ah	sycamore or sycamore maple
4	Alnus glutinosa	Schwarzerle	S.Erl	black, European or common alder
5	Alnus incana	Grauerle	G.Erl	speckled or gray alder
6	Betula pendula	Weissbirke	W.Bi	silver birch
7	Betula pubescens	Moorbirke	M.Bi	downy, white, European or hairy birch
8	Carpinus betulus	Hainbuche	H.Bu	European or common hornbeam
9	Castanea sativa	Edelkastanie	E.Ka	sweet chestnut or maroon
10	Fagus sylvatica	Rotbuche	R.Bu	European or common beech
11	Fraxinus angustifolia	Quirlesche	Qu.Es	
12	Fraxinus excelsior	Esche	Es	European or common ash
13	Larix decidua	Lärche	Lae	larch
14	Picea abies	Fichte	Fi	spruce, Norway spruce
15	Pinus cembra	Zirbe	Zi	Swiss or arolla pine
16	Pinus nigra	Schwarzkiefer	S.Kie	European black pine
17	Pinus sylvestris	Weisskiefer	W.Kie	Scots pine
18	Pseudotsuga menziesii	Douglasie	Dgl	coast, common or Oregon Douglas-fir
19	Populus alba	Silberpappel	Si.Pa	white, silver, silver-leaf poplar or abele
20	Populus canescens	Graupappel	G.Pa	Grey poplar
21	Populus nigra	Schwarzpappel	S.Pa	black poplar
22	Populus tremula	Zitterpappel	Zi.Pa	aspen, common or Eurasian aspen
23	Poplar clones	Pappel-Klone	Pa	clones
24	Prunus avium	Vogelkirsche	V.Ki	wild, sweet cherry, gean
25	Quercus cerris	Zerreiche	Z.Ei	turkey oak
26	Quercus petraea	Traubeneiche	Tr.Ei	Sessile or durmast oak
27	Quercus robur	Stieleiche	St.Ei	English or penduculate oak
28	Quercus rubra	Roteiche	R.Ei	Northern red or champion oak
29	Robinia pseudoacacia	Robinie	Rob	Black Locust (false acacia)
30	Tilia cordata	Winterlinde	W.Li	small-leaved lime
31	Tilia platyphyllos	Sommerlinde	S.Li	large-leaved linden (large-leaved lime)

E

FUEL PROPERTIES OF WOODS

Table E.1 summarizes the proximate analysis of several species of woods, [44].

Since Norway spruces prevail in Austria, it is worth to mention that their average ultimate analysis is

$$\mathrm{CHONS}_{(\mathrm{daf})} = 0.513 : 0.0615 : 0.423 : 0.0016 : 0.0007\,,$$

as quoted by [44].

For comparison, the average values for coal are, [44]:

- water content (ar): 0.078,
- volatile content (daf): 0.398,
- ash yield (dry): 0.111,
- hhv kJ/kg (daf): 31733,
- that is a ratio of

$$\mathrm{CHONS}_{(\mathrm{daf})} = 0.790 : 0.0506 : 0.137 : 0.0148 : 0.0166\,.$$

In average, then, spruce has 2.179487 more water, 2.09 more volatiles content, yields 0.081 less ash than coal. It has the 0.641 (64.1%) energy than coal, in average. Coal, on the other hand, has 9.25 times more N and 23.71 times more S than spruce.

Table E.1 Proximate analysis of several species of woods (average values), [44]. (Ar: as received, daf: dry and ash-free basis. hhv: enthalpy of combustion (*aka*, high heating value))

Species	Water (ar)	Volatile matter (daf)	Ash yield (dry)	hhv_{daf}/kJ/kg
bark	0.214	0.748	0.04	20757
beech	0.123	0.831	0.007	19157
birch	0.124	0.866	0.005	19587
fir, pine, spruce	0.17	0.832	0.009	20355
leaves	0.461	0.851	0.064	20985
needles	0	0.735	0.015	20426
oak	0.134	0.841	0.01	19778
other hard wood	0.134	0.833	0.014	19923
other soft wood	0.357	0.81	0.013	20080
others	0.176	0.808	0.021	20213
park waste wood	0.296	0.803	0.131	20670
poplar	0.082	0.826	0.012	19982
tropical hard wood	0.372	0.8	0.048	19633
willow	0.109	0.835	0.019	19836
mean	0.1893	0.8155	0.0198	20126.1
standard deviation	0.1307	0.04369	0.0184	545.686

F

MATHEMATICAL TECHNIQUES

F.1 MAXWELL'S RELATIONS

Maxwell's relations are sets of partials obtained from their symmetries and from the definitions of state functions. The mathematical underpinning of such equalities is *Schwarz's theorem*:

Let $f :: \mathbb{R}^n \to \mathbb{R}$ be a function. Let a be a point in $\mathbb{R}^n$. Then, if f has continuous second partials at a, then, for all i, j running from $1, \dots, n$, we have

$$\frac{\partial^2 f}{\partial x_i \partial x_j}(a) = \frac{\partial^2 f}{\partial x_j \partial x_i}(a)\,.$$

That is, the second partials of f commute at a.

In the case of thermodynamics, f, a are state functions and points in the parameter space. Maxwell's relations thus follow, as shown in fig. F.1, where the equations at the right-hand side of the second partials come from the exterior derivatives of the corresponding state functions.

For instance, consider a system whose energy changes be given by $\mathrm{d}U = \partial_S U|_V \,\mathrm{d}S + \partial_V U|_S \,\mathrm{d}V$. Now, according to Schwarz's theorem, the second partials of the partials in $\mathrm{d}U$ must be equal:

$$\partial_V|_S \,\partial_S U|_V = \partial_S|_V \,\partial_V U|_S\,.$$

But $\partial_S U|_V$ is the system temperature and $-\partial_V U|_S$ the system pressure. Thus, the equality between second partials becomes

$$\partial_V t|_S = -\partial_S p|_V\,,$$

which is the first Maxwell's relation. A similar reasoning leads to the rest of the relations.

$$\frac{\partial^2 U}{\partial S \partial V} = \left.\frac{\partial t}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V \qquad \frac{\partial^2 H}{\partial S \partial p} = \left.\frac{\partial t}{\partial p}\right|_S = \left.\frac{\partial V}{\partial S}\right|_p$$

$$-\frac{\partial^2 F}{\partial t \partial V} = \left.\frac{\partial S}{\partial V}\right|_t = \left.\frac{\partial p}{\partial t}\right|_V \qquad \frac{\partial^2 G}{\partial t \partial p} = -\left.\frac{\partial S}{\partial p}\right|_t = \left.\frac{\partial V}{\partial t}\right|_p$$

Figure F.1 Common Maxwell's relations. The equalities come from Schwarz's theorem of second partial derivatives and from the definitions of state functions.

F.2 BRIDGMAN'S THERMODYNAMIC EQUATIONS

An alternative method to quickly develop thermodynamic equations was proposed by Bridgman. [32] His method uses the most common extensive functions (U, S, V, H, F, G), the system properties (p, t), and three material properties $(C_p, \eta_p, cf._t)$ to construct thermodynamic formulae.

In the method, a partial derivative is not interpreted entirely, but as a ratio of two partials. For instance,

$$\left.\frac{\partial S}{\partial t}\right|_p \equiv \frac{\partial S|_p}{\partial t|_p}\,.$$

Then, in existing tables, one finds the values for the interpreted quantities and finally builds the equation.

As an example, consider the system described in section 23.5. Suppose now one be interested on how temperature and pressure affect entropy changes. Thus, span the parameter space by the set $\{S, t, p\}$ and, therefore, entropy changes are found from $S(t, p)$:

$$\mathrm{d}S = \partial_t S|_p \,\mathrm{d}t + \partial_p S|_t \,\mathrm{d}p\,.$$

Then, reinterpret both partials:

$$\left.\frac{\partial S}{\partial t}\right|_p \equiv \frac{\partial S|_p}{\partial t|_p}\,, \qquad \left.\frac{\partial S}{\partial p}\right|_t \equiv \frac{\partial S|_t}{\partial p|_t}\,.$$

Next, in tables of Bridgman's thermodynamic equations, found in [32, 140], look for the values of the different ratios:

$$\frac{\partial S|_p}{\partial t|_p} = \frac{\frac{C_p}{t}}{1} = \frac{C_p}{t}\,,$$

$$\frac{\partial S|_t}{\partial p|_t} = \frac{\left.\frac{\partial V}{\partial t}\right|_p}{-1} = -\left.\frac{\partial V}{\partial t}\right|_p\,.$$

Finally, replace both partials in $\mathrm{d}S$ to have

$$\mathrm{d}S = \frac{C_p}{t}\,\mathrm{d}t - \left.\frac{\partial V}{\partial t}\right|_p \mathrm{d}p\,.$$

Note that the first partial derivative was replaced by C_p/t, a known, fixed quantity, but the second partial was replaced by another partial $\partial_t V|_p$. However, $\partial_t V|_p$ can be readily found *via* a state equation. For instance, in the case of an ideal gas:

$$\left.\frac{\partial V}{\partial t}\right|_p = \frac{n\hat{r}}{p}\,,$$

which leads to

$$\mathrm{d}S = \frac{C_p}{t}\,\mathrm{d}t - \frac{n\hat{r}}{p}\,\mathrm{d}p\,.$$

The last equation can be used to find entropy changes as a sole function of system properties.

F.3 A TECHNICALITY ON BRIDGMAN'S EQUATIONS

Bridgman's method is based on splitting partial derivatives. For instance, at the beginning of the last section, we wrote:

$$\left.\frac{\partial S}{\partial t}\right|_p \equiv \frac{\partial S|_p}{\partial t|_p}\,.$$

For the last equivalence to hold, the right-hand-side must be understood as

$$\frac{\partial S|_p}{\partial t|_p} = \frac{\partial_x S|_p}{\partial_x t|_p}\,,$$

where x is a parameter, common to S and t.

F.4 INVERSE RULE FOR PARTIAL DERIVATIVES

Consider two mutually dependent variables, x, y. Then, the *inverse rule for derivatives* states that the derivatives of x, y are related to one another by

$$\frac{\mathrm{d}y}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}y} = 1\,,$$

provided the derivatives exist.

From here, it is readily to extend the theorem to partial derivatives. Consider, for instance, the partial $\partial_t p|_V$, between a system pressure, temperature, and volume. Then, by using the inverse rule, one finds

$$\left.\frac{\partial p}{\partial t}\right|_V \left.\frac{\partial t}{\partial p}\right|_V = 1\,,$$

wherefrom

$$\left.\frac{\partial p}{\partial t}\right|_V = \left(\left.\frac{\partial t}{\partial p}\right|_V\right)^{-1}\,.$$

F.5 TRIPLE PRODUCT RULE FOR PARTIAL DERIVATIVES

Consider three mutually dependent variables, x, y, z. Then, the *triple product rule* states that the partial derivatives of the variables with respect to one another are related by

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1\,,$$

given that the partials exist.

The triple product rule is useful in combination with Bridgman's thermodynamic equations. For instance, say the partial $\partial_V U|_t$ is required. Then, we can use Bridgman's method to get

$$\begin{aligned}\left.\frac{\partial U}{\partial V}\right|_t \equiv \frac{\partial U|_t}{\partial V|_t} &= \frac{t\,\partial_t V|_p + p\,\partial_p V|_t}{-\,\partial_p V|_t}\,,\\ &= -t\left.\frac{\partial V}{\partial t}\right|_p \left.\frac{\partial p}{\partial V}\right|_t - p\,.\end{aligned}$$

The problem now is to find the product of the two partials. Here is where the triple product rule comes into handy. Looking at the first partial on second equality ($\partial_t V|_p$), we recognize the triplet $\langle V, t, p\rangle$. Then, we apply the rule to have

$$\left.\frac{\partial V}{\partial t}\right|_p \left.\frac{\partial t}{\partial p}\right|_V \left.\frac{\partial p}{\partial V}\right|_t = -1\,,$$

from where we solve for the required product of two partials:

$$\left.\frac{\partial V}{\partial t}\right|_p \left.\frac{\partial p}{\partial V}\right|_t = -\left.\frac{\partial p}{\partial t}\right|_V ,$$

thanks to the inverse rule for partials.

Finally, we replace this result in $\partial_V U|_t$ to get

$$\left.\frac{\partial U}{\partial V}\right|_t = t\left.\frac{\partial p}{\partial t}\right|_V - p\,,$$

which is our final result.