

GASIFICATION

Chris Higman and Maarten van der Burgt



Dipartimento Ingegneria Industriale

Inv. n. 10000495



AMSTERDAM BOSTON HEIDELBERG LONDON
NEW YORK OXFORD PARIS SAN DIEGO
SAN FRANCISCO SINGAPORE SYDNEY TOKYO

Gulf Professional Publishing is an imprint of Elsevier



Contents

Preface, vii

1 Introduction, 1

- 1.1 Historical Development of Gasification, 1
- 1.2 Gasification Today, 5

2 The Thermodynamics of Gasification, 9

- 2.1 Reactions, 10
- 2.2 Thermodynamic Modeling of Gasification, 13
- 2.3 Deductions from the Thermodynamic Model, 17
- 2.4 Optimizing Process Conditions, 23

3 The Kinetics of Gasification and Reactor Theory, 29

- 3.1 Kinetics, 29
- 3.2 Reactor Theory, 35
- 3.3 Applications to Reactor Design, 38

4 Feedstocks and Feedstock Characteristics, 41

- 4.1 Coals and Coke, 41
- 4.2 Liquid and Gaseous Feedstocks, 53
- 4.3 Biomass, 67
- 4.4 Wastes, 76

5 Gasification Processes, 85

- 5.1 Moving-Bed Processes, 87
- 5.2 Fluid-Bed Gasifiers, 98
- 5.3 Entrained-Flow Gasifiers, 109
- 5.4 Oil Gasification and Partial Oxidation of Natural Gas, 128
- 5.5 Biomass Gasification, 147
- 5.6 Gasification of Wastes, 155
- 5.7 Black Liquor Gasification, 159
- 5.8 Miscellaneous Processes, 161

6 Practical Issues, 171

- 6.1 Effect of Pressure, 171
- 6.2 Pressurization of Coal, 173
- 6.3 Coal Sizing and Drying, 183
- 6.4 Reactor Design, 184
- 6.5 Burners, 191
- 6.6 Synthesis Gas Cooling, 192
- 6.7 Particulate Removal, 200
- 6.8 Process Measurement, 201
- 6.9 Trace Components of Raw Synthesis Gas, 208
- 6.10 Choice of Oxidant, 219
- 6.11 Corrosion Aspects, 223

7 Applications, 231

- 7.1 Chemicals, 231
- 7.2 Syntfuels, 252
- 7.3 Power, 259

8 Auxiliary Technologies, 293

- 8.1 Oxygen Supply, 293
- 8.2 Synthesis Gas Treating, 298
- 8.3 Catalytic Gas Conditioning, 315
- 8.4 Sulfur Recovery, 320

9 Economics, Environmental, and Safety Issues, 329

- 9.1 Economics, 329
- 9.2 Environmental Issues, 335
- 9.3 Safety, 347

10 Gasification and the Future, 355

Appendix A Companion Website, 359

Appendix B Conversion Factors, 361

Appendix C Emissions Conversion Factors, 367

**Appendix D Guidelines for Reporting Operating Statistics for
Gasification Facilities, 369**

Appendix E Basis for Calculations, 373

Nomenclature, 375

List of Names and Abbreviations, 377

Index, 381

Preface

Gasification, at least of coal, is in one sense an old technology, having formed the heart of the town gas industry until the widespread introduction of natural gas. With the decline of the town gas industry, gasification became a specialized, niche technology with limited application. After substantial technical development, gasification is now enjoying a considerable renaissance. This is documented by the more than thirty projects that are in various stages of planning or completion at the present time. The reasons for this include the development of new applications such as gas-to-liquids (Fischer-Tropsch) projects, the prospect of increased efficiency and environmental performance including CO₂ capture through the use of integrated gasification combined-cycle (IGCC) in the power industry, as well as the search for an environmentally benign technology to process low-value or waste feedstocks, such as refinery residues, petroleum coke, or biomass or municipal waste.

The literature of gasification is extremely fragmented with almost all recent (post-1990) contributions being confined to conference papers or articles in the appropriate journals. In the coal literature it is mostly relegated to a single chapter, which is unable to do the subject proper justice.

The knowledge of gasification is mostly confined to commercial process licensors and the operators of existing plants. Therefore there is little opportunity for outsiders to acquire an independent overview before embarking on a project of their own.

In discussing these issues between ourselves, we concluded that there was a need for a book that collected and collated the vast amount of information available in the public domain and provided a “single point-of-entry” to the field of gasification without necessarily answering all the questions that might arise. In fact, we felt that the most important task is to communicate an understanding for the questions to put in a given situation. This book may supply some of those answers directly; others will require further follow-up. This approach is no doubt colored by our own professional experience, where the very flexibility of gasification technology, with its differing feedstocks, differing end products, differing economic situations, and continual development has inevitably led to project-specific solutions for certain issues. Individual solutions will, we believe, continue to prevail in gasification technology, rather than a global standard after Henry Ford’s philosophy of “any color they want, so long as it’s black.” For gasification, standardization, which is certainly an indispensable requisite to its economic competitiveness, must, in our opinion, first be introduced as a structuralized approach to the issues to be faced. And in developing this book, we have aimed at providing a structure that we hope can help in this process.

We trust that in doing so we can be of assistance to a broad audience, including

- Staff of companies who might want to build a plant and need to acquire know-how quickly in a compact form but independent of process licensors.
- Engineers of potential project financiers or insurers wanting to have an understanding of the technical risks involved in such a project, or those working for government departments and agencies involved in the licensing and permitting of gasification projects.
- People in the power industry who otherwise have little access to data on the subject of gasification.
- Established workers in the field looking for a reference work with a broad theoretical and practical overview.
- University students needing a book that combines the elements of academic theory and industrial practice.

After a brief historical introduction to gasification and its relevance to the development of our modern technological society in Chapter 1, there follow two chapters of theory. In order to have a good understanding of the practicalities of gasification, it is necessary to have a sufficient theoretical background. Chemical engineers will have this anyway, but many project engineers who become involved in gasification projects may have an educational background in mechanical or some other branch of engineering, and for such readers a brief summary is sure to be of use. The main emphasis of Chapter 2 is on thermodynamics, since this is generally sufficient for understanding and calculating the results of synthesis gas generation processes. But the development of computational fluid dynamics is beginning to make kinetics accessible to calculation in a manner hardly thinkable 20 years ago so that we have included a basic treatment of kinetic aspects of gasification in Chapter 3.

Chapter 4 reviews the wide variety of feedstocks that can be gasified, ranging from coal, through oils and gas, to biomass and waste. It discusses their properties as it affects both the gasification process itself and the downstream synthesis gas treatment and end usage.

The heart of the book lies in Chapters 5, 6, and 7. Chapter 5 discusses actual processes. The emphasis is on processes in commercial use today, such as those of Shell, Texaco, Lurgi, Noell, and others, such as the circulating fluid bed processes of Foster Wheeler and Lurgi. It includes brief mentions of some of the important forerunner processes, such as Winkler and Koppers-Totzek. A number of promising new processes, such as the Japanese CCP and EAGLE gasifiers, are also handled.

Chapter 6 looks at a broad selection of practical issues, including the drying and pressurizing of coal, syngas cooling and particulate removal, equipment issues, process control, trace components in synthesis gas, choice of oxidant, and corrosion aspects.

Typical applications are reviewed in Chapter 7. This includes the production of chemicals ranging from ammonia and methanol, through hydrogen to carbon

monoxide, and synthesis gas for the production of oxo-alcohols. The section on synfuels production covers gas-to-liquids (GTL) and substitute natural gas (SNG). The discussion on power applications includes state-of-the-art IGCCs as well as a look at the potential for increasing efficiency with advanced cycles.

No gasification plant stands alone. Most processes require a source of oxygen, and the product synthesis gas needs treating and conditioning before it can be used. The principle auxiliary technologies for these tasks and the principal issues surrounding their selection are discussed in Chapter 8.

Every project stands or falls on its economics. Gasification is no exception, and economic aspects are addressed in Chapter 9. This chapter also looks at the environmental impact of gasification, particularly its superior performance in power generation. Its innate ability to provide a means of CO₂ capture with only minor additional cost is an important aspect of this subject. This chapter also addresses those safety issues that can be considered specific to the technology.

By way of an epilogue, we have tried to look into the crystal ball to see what part gasification can play in our futures. We discuss the potential contribution that gasification of fossil fuels can make to the transition to a hydrogen economy. Even in an ideal “fully sustainable” world, gasification of biomass may help us in the provision of some of the petrochemical products we so take for granted today.

At a number of different points in the text we have deliberately questioned current practice or thinking. We hope that the one or other idea produced may stimulate others and help further the technology as a whole.

COMPANION WEBSITE

As an accompaniment to this book, we have built a website (www.gasification.higman.de), which includes a number of computer programs arising out of the work involved in preparing this book. They include a complete gasification calculation based on the content of Chapter 2 and also a literature databank with keyword search capability.

TERMINOLOGY

A preliminary word on terminology may be in order. Gasification has a place in many industries, each with its own specific linguistic tradition. Recognizing this, we have not tried to impose our own language on the reader, but have used whatever synonym appears appropriate to the context. Thus the words fuel, feed, and feedstock are used interchangeably without any attempt to distinguish between them. Similarly, oxidant, blast, or gasification agent are used with the same meaning in different places.

Chapter 1

Introduction

The manufacture of combustible gases from solid fuels is an ancient art but by no means a forgotten one. In its widest sense the term *gasification* covers the conversion of any carbonaceous fuel to a gaseous product with a useable heating value. This definition excludes combustion, because the product flue gas has no residual heating value. It does include the technologies of pyrolysis, partial oxidation, and hydrogenation. Early technologies depended heavily on pyrolysis (i.e., the application of heat to the feedstock in the absence of oxygen), but this is of less importance in gas production today. The dominant technology is partial oxidation, which produces from the fuel a synthesis gas (otherwise known as syngas) consisting of hydrogen and carbon monoxide in varying ratios, whereby the oxidant may be pure oxygen, air, and/or steam. Partial oxidation can be applied to solid, liquid, and gaseous feedstocks, such as coals, residual oils, and natural gas, and despite the tautology involved in “gas gasification,” the latter also finds an important place in this book. We do not, however, attempt to extend the meaning of gasification to include catalytic processes such as steam reforming or catalytic partial oxidation. These technologies form a specialist field in their own right. Although we recognize that pyrolysis does take place as a fast intermediate step in most modern processes, it is in the sense of partial oxidation that we will interpret the word *gasification*, and the two terms will be used interchangeably. Hydrogenation has only found an intermittent interest in the development of gasification technologies, and where we discuss it, we will always use the specific terms *hydro-gasification* or *hydrogenating gasification*.

1.1 HISTORICAL DEVELOPMENT OF GASIFICATION

The development of human history is closely related to fire and therefore also to fuels. This relationship between humankind, fire, and earth was already documented in the myth of Prometheus, who stole fire from the gods to give it to man. Prometheus was condemned for his revelation of divine secrets and bound to earth as a punishment. When we add to fire and earth the air that we need to make fire and the water to keep it under control, we have the four Greek elements that play such an important role in the technology of fuels and for that matter in gasification.

The first fuel used by humans was wood, and this fuel is still used today by millions of people to cook their meals and to heat their homes. But wood was and is also used for building and, in the form of charcoal, for industrial processes such as ore reduction. In densely populated areas of the world this led to a shortage of wood with sometimes dramatic results. It was such a shortage of wood that caused iron production in England to drop from 180,000 to 18,000 tons per year in the period of 1620 to 1720. The solution—which in hindsight is obvious—was coal.

Although the production of coal had already been known for a long time, it was only in the second half of the eighteenth century that coal production really took hold, not surprisingly starting in the home of the industrial revolution, England. The coke oven was developed initially for the metallurgical industry to provide coke as a substitute for charcoal. Only towards the end of the eighteenth century was gas produced from coal by pyrolysis on a somewhat larger scale. With the foundation in 1812 of the London Gas, Light, and Coke Company, gas production finally became a commercial process. Ever since, it has played a major role in industrial development.

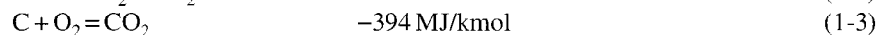
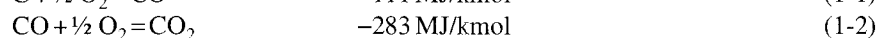
The most important gaseous fuel used in the first century of industrial development was town gas. This was produced by two processes: pyrolysis, in which discontinuously operating ovens produce coke and a gas with a relatively high heating value ($20,000\text{--}23,000\text{ kJ/m}^3$), and the water gas process, in which coke is converted into a mixture of hydrogen and carbon monoxide by another discontinuous method (approx. $12,000\text{ kJ/m}^3$ or medium Btu gas).

The first application of industrial gas was illumination. This was followed by heating, then as a raw material for the chemical industry, and more recently for power generation. Initially, the town gas produced by gasification was expensive, so most people used it only for lighting and cooking. In these applications it had the clearest advantages over the alternatives: candles and coal. But around 1900 electric bulbs replaced gas as a source of light. Only later, with increasing prosperity in the twentieth century, did gas gain a significant place in the market for space heating. The use of coal, and town gas generated from coal, for space heating only came to an end—often after a short intermezzo where heating oil was used—with the advent of cheap natural gas. But one should note that town gas had paved the way to the success of the latter in domestic use, since people were already used to gas in their homes. Otherwise there might have been considerable concern about safety, such as the danger of explosions.

A drawback of town gas was that the heating value was relatively low, and it could not, therefore, be transported over large distances economically. In relation to this problem it is observed that the development of the steam engine and many industrial processes such as gasification would not have been possible without the parallel development of metal tubes and steam drums. This stresses the importance of suitable equipment for the development of both physical and chemical processes. Problems with producing gas-tight equipment were the main reason why the production processes, coke ovens, and water gas reactors as well as the transport and storage were carried out at low pressures of less than 2 bar. This resulted in relatively voluminous equipment, to which the gasholders that were required to cope with variations in demand still bear witness in many of the cities of the industrialized world.

Until the end of the 1920s the only gases that could be produced in a continuous process were blast furnace gas and producer gas. Producer gas was obtained by partial oxidation of coke with humidified air. However, both gases have a low heating value (3500–6000 kJ/m³, or low Btu gas) and could therefore only be used in the immediate vicinity of their production.

The success of the production of gases by partial oxidation cannot only be attributed to the fact that gas is easier to handle than a solid fuel. There is also a more basic chemical reason that can best be illustrated by the following reactions:

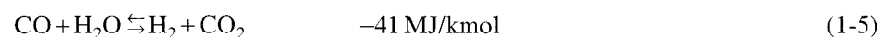


These reactions show that by “investing” 28% of the heating value of pure carbon in the conversion of the solid carbon into the gas CO, 72% of the heating value of the carbon is conserved in the gas. In practice, the fuel will contain not only carbon but also some hydrogen, and the percentage of the heat in the original fuel, which becomes available in the gas, is, in modern processes, generally between 75 and 88%. Were this value only 50% or lower, gasification would probably never have become such a commercially successful process.

Although gasification started as a source for lighting and heating, from 1900 onwards the water gas process, which produced a gas consisting of about equal amounts of hydrogen and carbon monoxide, also started to become important for the chemical industry. The endothermic water gas reaction can be written as:



By converting part or all of the carbon monoxide into hydrogen following the CO shift reaction,



it became possible to convert the water gas into hydrogen or synthesis gas (a mixture of H₂ and CO) for ammonia and methanol synthesis, respectively. Other applications of synthesis gas are for Fischer-Tropsch synthesis of hydrocarbons and for the synthesis of acetic acid anhydride.

It was only after Carl von Linde commercialized the cryogenic separation of air during the 1920s that fully continuous gasification processes using an oxygen blast became available for the production of synthesis gas and hydrogen. This was the time of the development of some of the important processes that were the forerunners of many of today's units: the Winkler fluid-bed process (1926), the Lurgi moving-bed pressurized gasification process (1931), and the Koppers-Totzek entrained-flow process (1940s).

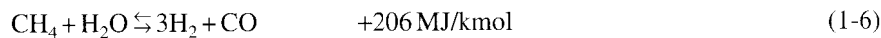
4 Gasification

With the establishment of these processes little further technological progress in the gasification of solid fuels took place over the following forty years. Nonetheless, capacity with these new technologies expanded steadily, playing their role partly in Germany's wartime synthetic fuels program and on a wider basis in the worldwide development of the ammonia industry.

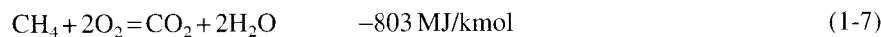
This period, however, also saw the foundation of the South African Coal Oil and Gas Corporation, known today as Sasol. This plant uses coal gasification and Fischer-Tropsch synthesis as the basis of its synfuels complex and an extensive petrochemical industry. With the extensions made in the late 1970s, Sasol is the largest gasification center in the world.

With the advent of plentiful quantities of natural gas and naphtha in the 1950s, the importance of coal gasification declined. The need for synthesis gas, however, did not. On the contrary, the demand for ammonia as a nitrogenous fertilizer grew exponentially, a development that could only be satisfied by the wide-scale introduction of steam reforming of natural gas and naphtha. The scale of this development, both in total capacity as well as in plant size, can be judged by the figures in Table 1-1. Similar, if not quite so spectacular, developments took place in hydrogen and methanol production.

Steam reforming is not usually considered to come under the heading of gasification. The reforming reaction (allowing for the difference in fuel) is similar to the water gas reaction.



The heat for this endothermic reaction is obtained by the combustion of additional natural gas:



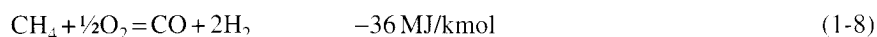
Unlike gasification processes, these two reactions take place in spaces physically separated by the reformer tube.

Table 1-1
Development of Ammonia Production Capacity 1945–1969

Year	World ammonia production (MMt/y)	Maximum converter size (t/d)
1945	5.5	100
1960	14.5	250
1964	23.0	600
1969	54.0	1400

Source: Slack and James 1973

An important part of the ammonia story was the development of the secondary reformer in which unconverted methane is processed into synthesis gas by partial oxidation over a reforming catalyst.



The use of air as an oxidant brought the necessary nitrogen into the system for the ammonia synthesis. A number of such plants were also built with pure oxygen as oxidant. These technologies have usually gone under the name of autothermal reforming or catalytic partial oxidation.

The 1950s was also the time in which both the Texaco and the Shell oil gasification processes were developed. Though far less widely used than steam reforming for ammonia production, these were also able to satisfy a demand where natural gas or naphtha were in short supply.

Then, in the early 1970s, the first oil crisis came and, together with a perceived potential shortage of natural gas, served to revive interest in coal gasification as an important process for the production of liquid and gaseous fuels. Considerable investment was made in the development of new technologies. Much of this effort went into coal hydrogenation both for direct liquefaction and also for so-called hydro-gasification. The latter aimed at hydrogenating coal directly to methane as a substitute natural gas (SNG). Although a number of processes reached the demonstration plant stage (Speich 1981), the thermodynamics of the process dictate a high-pressure operation, and this contributed to the lack of commercial success of hydro-gasification processes. In fact, the only SNG plant to be built in these years was based on classical oxygen-blown moving-bed gasification technology to provide synthesis gas for a subsequent methanation step (Dittus and Johnson 2001).

The general investment climate in fuels technology did lead to further development of the older processes. Lurgi developed a slagging version of its existing technology in a partnership with British Gas (BGL) (Brooks, Stroud, and Tart 1984). Koppers and Shell joined forces to produce a pressurized version of the Koppers-Totzek gasifier (for a time marketed separately as Prenflo and Shell coal gasification process, or SCGP, respectively) (van der Burgt 1978). Rheinbraun developed the high-temperature Winkler (HTW) fluid-bed process (Speich 1981), and Texaco extended its oil gasification process to accept a slurried coal feed (Schlinger 1984).

However, the 1980s then saw a renewed glut of oil that reduced the interest in coal gasification and liquefaction; as a result, most of these developments had to wait a further decade or so before getting past the demonstration plant stage.

1.2 GASIFICATION TODAY

The last ten years have seen the start of a renaissance of gasification technology, as can be seen from Figure 1-1. Electricity generation has emerged as a large new market for these developments, since gasification is seen as a means of enhancing the

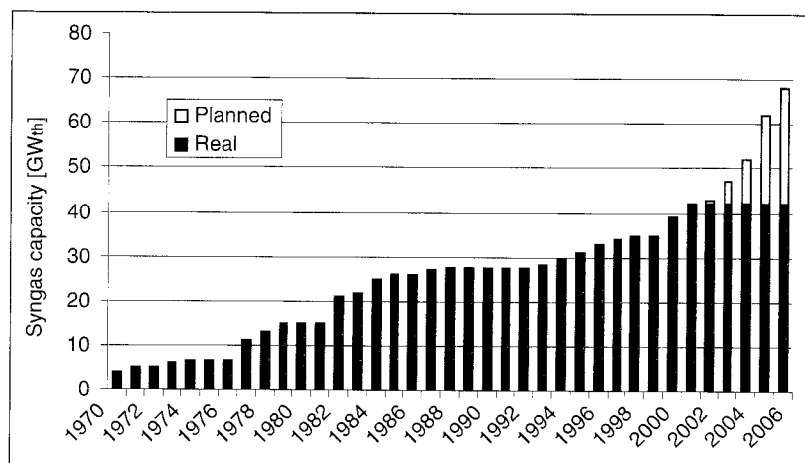


Figure 1-1. Cumulative Worldwide Gasification Capacity (Source: Simbeck and Johnson 2001)

environmental acceptability of coal as well as of increasing the overall efficiency of the conversion of the chemical energy in the coal into electricity. The idea of using synthesis gas as a fuel for gas turbines is not new. Gumz (1950) proposed this already at a time when anticipated gas turbine inlet temperatures were about 700°C. And it has largely been the development of gas turbine technology with inlet temperatures now of 1400°C that has brought this application into the realm of reality. Demonstration plants have been built in the United States (Cool Water, 100 MW, 1977; and Plaquemine, 165 MW, 1987) and in Europe (Lünen, 170 MW, 1972; Buggenum, 250 MW, 1992; and Puertollano, 335 MW, 1997).

A second development, which has appeared during the 1990s, is an upsurge in gasification of heavy oil residues in refineries. Oil refineries are under both an economic pressure to move their product slate towards lighter products, and a legislative pressure to reduce sulfur emissions both in the production process as well as in the products themselves. Much of the residue had been used as a heavy fuel oil, either in the refinery itself or in power stations and as marine bunker fuel. Residue gasification has now become one of the essential tools in addressing these issues. Although heavy residues have a low hydrogen content, they can be converted into hydrogen by gasification. The hydrogen is used to hydrocrack other heavy fractions in order to produce lighter products such as gasoline, kerosene, and automotive diesel. At the same time, sulfur is removed in the refinery, thus reducing the sulfur present in the final products (Higman 1993). In Italy, a country particularly dependent on oil for power generation, three refineries have introduced gasification technology as a means of desulfurizing heavy fuel oil and producing electric power. Hydrogen production is incorporated into the overall scheme. A similar project was realized in Shell's Pernis refinery in the Netherlands. Other European refineries have similar projects in the planning phase.

An additional driving force for the increase in partial oxidation is the development of “Gas-to-liquids” projects. For transport, liquid fuels have an undoubted advantage. They are easy to handle and have a high energy density. For the consumer, this translates into a car that can travel nearly 1000 km on 50 liters of fuel, a range performance as yet unmatched by any of the proposed alternatives. For the energy company the prospect of creating synthetic liquid fuels provides a means of bringing remote or “stranded” natural gas to the marketplace using existing infrastructure. Gasification has an important role to play in this scenario. The Shell Middle Distillate Synthesis (SMDS) plant in Bintulu, Malaysia, producing some 12,000 bbl/d of liquid hydrocarbons, is only the first of a number of projects currently in various stages of planning and engineering around the world (van der Burgt 1988).

REFERENCES

- Brooks, C. T., Stroud, H. J. F., and Tart, K. R. “British Gas/Lurgi Slagging Gasifier.” In *Handbook of Synfuels Technology*, ed. R. A. Meyers. New York: McGraw-Hill, 1984.
- Dittus, M., and Johnson, D. “The Hidden Value of Lignite Coal.” Paper presented at Gasification Technologies Conference, San Francisco, October 2001.
- Gumz, W. *Gas Producers and Blast Furnaces*. New York: John Wiley & Sons, 1950.
- Higman, C. A. A. “Partial Oxidation in the Refinery Hydrogen Management Scheme.” Paper presented at AIChE Spring Meeting, Houston, March 1993.
- Schlenger, W. G. “The Texaco Coal Gasification Process.” In *Handbook of Synfuels Technology*, ed. R. A. Meyers. New York: McGraw-Hill, 1984.
- Simbeck, D., and Johnson, H. “World Gasification Survey: Industry Trends and Developments.” Paper presented at Gasification Technologies Conference, San Francisco, October 2001.
- Slack, A. V., and James, G. R. *Ammonia, Part I* New York: Marcel Dekker, 1973.
- Speich, P. “Braunkohle—auf dem Weg zur großtechnischen Veredelung.” *VIK-Mitteilungen* 3/4 (1981).
- van der Burgt, M. J. “Shell’s Middle Distillate Synthesis Process.” Paper presented at AIChE Meeting, New Orleans, 1988.
- van der Burgt, M. J. “Technical and Economic Aspects of Shell-Koppers Coal Gasification Process.” Paper presented at AIChE Meeting, Anaheim, CA 1978.