CRC

# BIOTREATMENT SYSTEMS

Volume I

Donald L. Wise

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# Biotreatment Systems

## Volume I

Editor

**Donald L. Wise, Ph.D., P.E.**

Cambridge Scientific, Inc.
Belmont, Massachusetts
and
Cabot Professor of Chemical Engineering
Northeastern University
Boston, Massachusetts

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# PREFACE

*Biotreatment Systems* is a uniquely valuable reference text consisting of contributed chapters in which are described the most insightful research and development programs around the world. The authors of these contributed chapters are those very conscientious and thoughtful technologists who are investigating pragmatic solutions to environmental problems. This important text has as the major theme the biotreatment of organic residues. This major theme primarily encompasses the field of anaerobic methane fermentation, with an emphasis on treatment of complex wastes. The text is intended to present a comprehensive overview of the most practical research programs that are being carried out in this emerging field of international significance. Due to the fact that both research and development have been carried out at major centers around the world, great care has been taken to include chapters from an international perspective. Further, as a perusal of the chapter titles will indicate, a special emphasis has been made to address both the important research aspects and the practical aspects of the work on biotreatment systems. It is to be noted that each chapter included in this text is the work of a particular individual or group. There are no multiple chapters by more than one author or group. Thus, each of the included chapters most often reflects the dedicated career efforts of these workers. Further, each contributed chapter is presented on a stand-alone basis so that the reader will find it helpful to consider only the theme of each chapter. On the other hand, there is the unifying theme with all chapters of addressing biotreatment systems research and development. A reader of this text, just entering the field, will find this text provides an excellent state-of-the-art presentation of the international import of work on biotreatment systems, with an emphasis on methane fermentation. A reader of this text, who has experience in this field, will find the text to be essential for assessment and referral of this increasingly valuable area of technology.

# THE EDITOR

**Donald L. Wise, Ph.D., P.E.,** is Founder and President of Cambridge Scientific, Inc., Belmont, Massachusetts. Dr. Wise also holds the Cabot Chair of Chemical Engineering at Northeastern University, Boston, Massachusetts. Dr. Wise received his B.S. (magna cum laude), M.S., and Ph.D. degrees in chemical engineering at the University of Pittsburgh. Dr. Wise is a specialist in process and biochemical engineering as well as advanced biomaterials development. During his career he has managed a series of programs to develop processes for production of fuel gas, liquid fuels, and organic chemicals from municipal solid waste, an array of agricultural residues, and a wide variety of crop-grown biomass, especially aquatic biomass. Dr. Wise has also been primarily responsible for the initiation of development work on fossil fuels such as peat and lignite to gaseous fuel, liquid fuels, and organic chemicals, and he also originated work on the bioconversion of coal gasifier product gases to these products. Dr. Wise initiated a program to establish the engineering feasibility of converting large-scale combined agricultural residues to fuel gas by the action of microorganisms, a project ultimately involving joint effort with research workers in fifteen countries around the world.

Dr. Wise has worked in the area of biotechnology research and development for 2 decades, has approximately 50 publications in the field, and has edited a number of reference texts. As Associate Editor of *Solar Energy,* the journal of the International Solar Energy Society, he is responsible for the review of manuscripts in the biomass/bioconversion area. Dr. Wise is also on the Editorial Board of *Resources and Conservation,* an international journal published by Elsevier, Amsterdam. He has served as an international consultant in bioconversion for the United Nations and for the U.S. Agency for International Development (AID).

A meaningful portion of these programs that Dr. Wise initiated, and has been carrying out, is his meeting with experts across the U.S. and around the world, to become familiar with both current and practical aspects of bioconversion systems.

# CONTRIBUTORS

**Ulrich Behrens**
Institute of Biotechnology
Academy of Sciences
Leipzig, German Democratic Republic

**Günter Bürger**
Institute of Biotechnology
Academy of Sciences
Leipzig, German Democratic Republic

**J. F. de Kreuk**
Division of Technology for Society
TNO
Delft, The Netherlands

**Phillip M. Fedorak**
Department of Microbiology
University of Alberta
Edmonton, Alberta, Canada

**Michael J. Hanchak**
Ecology and Environment, Inc.
Buffalo, New York

**A. O. Hanstveit**
Division of Technology for Society
TNO
Delft, The Netherlands

**Philip A. Herzbrun**
CECOS International
Buffalo, New York

**Steve E. Hrudey**
Department of Civil Engineering
University of Alberta
Edmonton, Alberta, Canada

**Robert L. Irvine**
Center for Bioengineering and
Pollution Control
and
Department of Civil Engineering
University of Notre Dame
Notre Dame, Indiana

**D. B. Janssen**
Groningen Biotechnology Center
Groningen, The Netherlands

**Iman W. Koster**
University Lecturer
Water Pollution Control Department
Wageningen Agricultural University
Wageningen, The Netherlands

**P. Kumaran**
Scientist
Environmental Microbiology Division
National Environmental Engineering
Research Institute
Nagpur, India

**Kenneth C. Malinowski**
CECOS International
Buffalo, New York

**Günther Martius**
Institute of Biotechnology
Academy of Sciences
Leipzig, German Democratic Republic

**Manfred Ringpfeil**
Institute of Biotechnology
Academy of Sciences
Leipzig, German Democratic Republic

**W. H. Rulkens**
Division of Technology for Society
TNO
Apeldoorn, The Netherlands

**N. Shivaraman**
Scientist
Environmental Microbiology Division
National Environmental Engineering
Research Institute
Nagpur, India

**Ulrich Stottmeister**
Institute of Biotechnology
Academy of Sciences
Leipzig, German Democratic Republic

**W. J. Th. van Gemert**
N.V. Nederlandse Gasunie
Groningen, The Netherlands

**H. J. van Veen**
Division of Technology for Society
TNO
Apeldoorn, The Netherlands

**Lutz Wenige**
Deceased
Dipl. Ing.
VEB Chemieanlagenbaukombinat
Leipzig, German Democratic Republic

# SERIES TABLE OF CONTENTS

## Volume I

## Volume II

## Volume III

# TABLE OF CONTENTS

### Chapter 1

# AEROBIC TREATMENT OF SEWAGE FROM LIGNITE (BROWN COAL) PROCESSING

**Manfred Ringpfeil, Ulrich Stottmeister, Ulrich Behrens, Günter Martius, Günter Bürger, and Lutz Wenige**

## TABLE OF CONTENTS

## I. INTRODUCTION

On an international scale the utilization of brown coal is only beginning. A few countries are beyond the simple use for heat production, being the lowest stage of utilization. The pressure for utilization of indigenous raw material sources in the Middle European countries led, in the first half of our century, to a highly developed industry aimed at the refinement of the products to be obtained from brown coal processing. Following this way directive and technical developments were attained. However, due to the numerous technical and economical advantages of the petrochemistry, carbochemistry based on brown coal was pushed back in these countries.

In the German Democratic Republic (G.D.R.) and Czechoslovakia carbochemistry has always been important. Newly erected, large plants in the G.D.R. were designed in the 1950s and 1960s with a fully biological waste water purification system. On the basis of some experiences of old, brown coal processing plants in the field of biological waste water purification, the necessity of an intensive research work concerning these new plants arose. Appropriate to the interest at that time the results have been published only in the German-speaking area. The mentioned turn of interest toward a more extended utilization of brown coal also in other countries challenges a summarized representation of the biological waste water purification. In this way parallel developments may possibly be avoided and new suggestions for further investigations may be stimulated.

The experiences gained from decades of operation of biological purification plants in the brown coal industry have led to industrial plants taking into account the latest knowledge of biotechnology. To recognize the features of waste waters yielding from brown coal processing and to understand the treatment technologies applied to it, a short representation of the brown coal formation as well as a compendium of processing technologies seem to be necessary.

## II. BROWN COAL FORMATION AND PROCESSING

### A. Brown Coal Formation

Formation of peat, brown coal, and hard coal from vegetable material presumed special conditions in the course of earth history. The local redox condition in connection with surface subsidence and water covering as well as the prevailing climate were fundamental for humification of the plants. The plurality of compounds included in plants can be confined to the groups celluloses, hemicelluloses, sugar, lignin, albumins, waxes, and resins. Cellulose and lignin are of importance for humus formation. Albumins are completely decomposed in the humification process. Phosphorus, nitrogen, and sulfur of the coal result from albumin compounds. Waxes and resins go scarcely altered and they provide the protobitumen.

In the process of coal formation the organic components of the plants are converted to humic acid in the primary oxidation zone with differentiated ozygen access. By means of condensation and polymerization reactions compounds with an aromatic nucleus and aliphatic side-groups are formed; for example, fulvic acid, humolignin acid, and various humic acids have been identified.

In deeper zones from the geological point of view a reduction of the humus substances takes place by microbial processes. Since no oxygen is available sulfate, nitrate, and organic compounds are used as electron acceptors (biochemical phase of coalification).

In the course of coalification the local geological conditions are leading to products of different composition. Elementary analyses of different products of the coalification process are illustrated in Figure 1 (A and B).

An elementary analysis, however, is not sufficient for the characterization and the comparison of coals summarized under the term ''brown coal''. The microscopically detectable single-constituents (macerals) are used for a classification of brown coals (e.g., humite, liptinite, and intertinite) indicating the chemical, physical, and technological properties of brown coals. To enable a more complete evaluation of coals from different fields concerning the technological properties of coals, classification characteristics have been amplified. Along with a coefficient for the coalification degree, one or two numbers have been introduced for the characterization of the technological behavior of the brown coals named ISO classification (ISO 2950 — 1974 [E]). It differentiates into six classes of freshly mined coals concerning the water content and within these five classes concerning the tar yield.[1] The technological properties of the coal determine the establishment of specific processing technologies in the vicinity of certain coal fields (e.g., in the G.D.R., brown coal coking to the west and gasification to the east of the Elbe river).

Within a deposit the different seams may show great differences with regard to composition and, regularly, only one seam is worth mining. Extraction of brown coal takes place exclusively by open-cast mining. Temporarily large influences on the cultural landscape are inevitable. An open-cast mine causes a serious engagement in the water conservation of the landscape concerned. The pit waters have to be pumped out and are partly used as industrial water. In case of a high salt load as is found in salt coal deposits, additional problems with regard to water treatment come into being which are not taken into account in the following considerations.

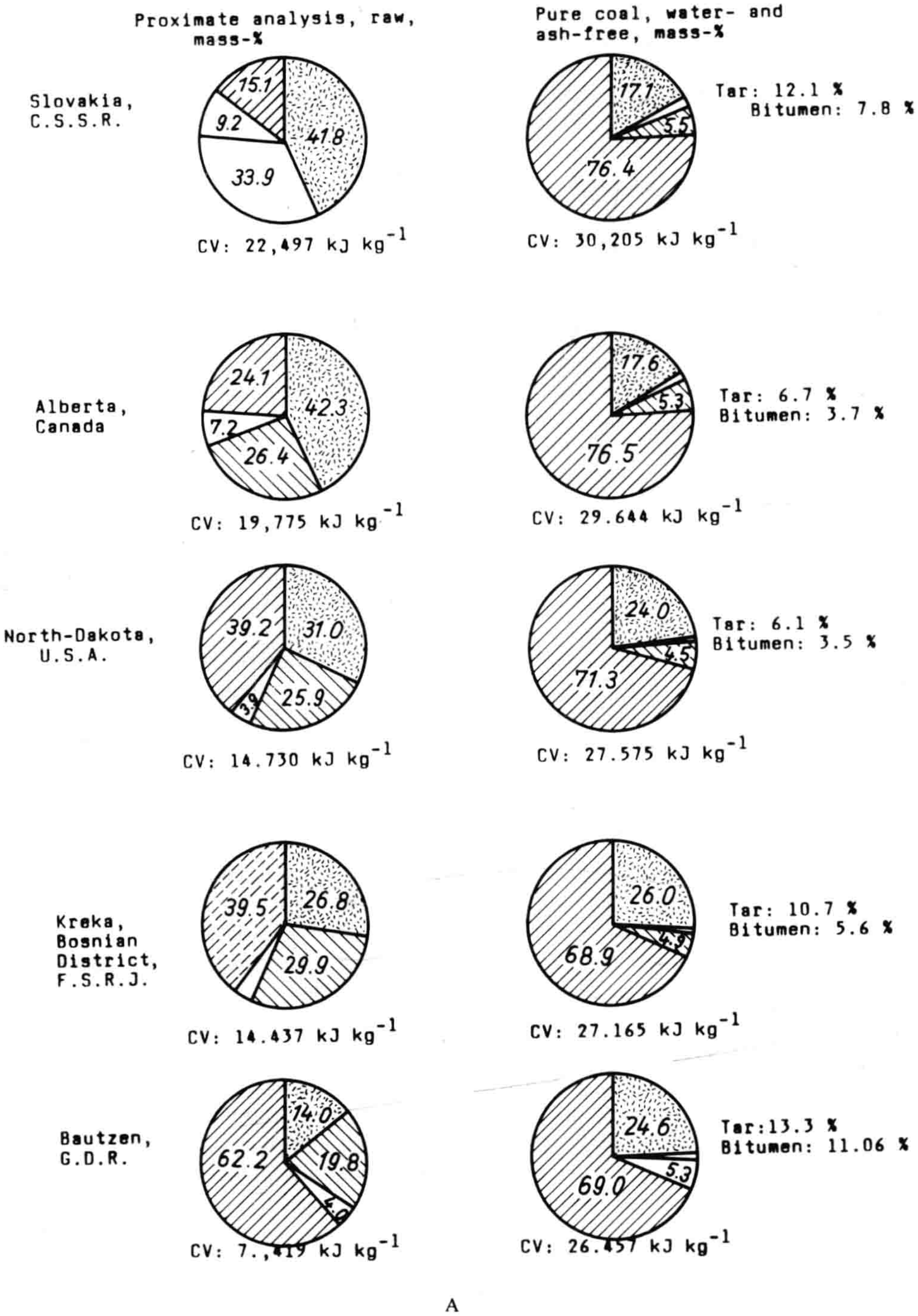

FIGURE 1 (A and B). Composition of brown coal from different fields. (According to Kurtz, R., *Ullmanns Enzyklopädie der technischen Chemie,* Vol. 14, 4th ed., Bartholomé, E., Biekert, E., Hellmann, H., Ley, H., Weigert, W. M., and Weise, E., Eds., Verlag Chemie, Weinheim, West Germany, 1977, 491.)

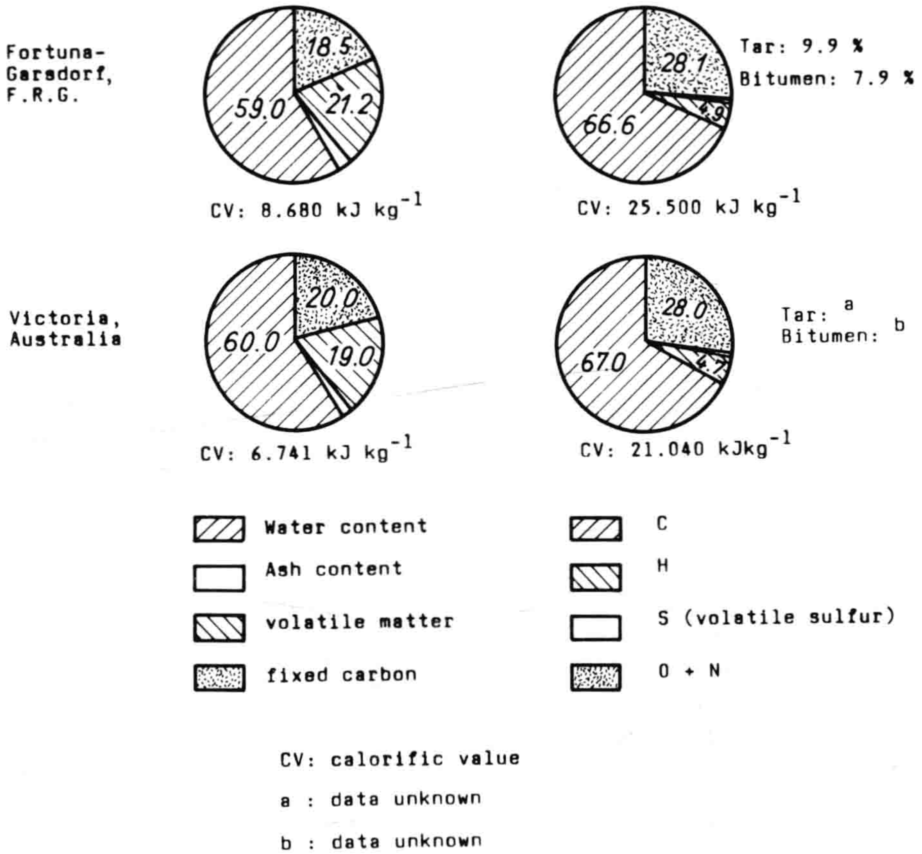

FIGURE 1B.

## B. Brown Coal Reserves of the World

In Table 1 the known brown coal reserves of the world are illustrated. Reserves and production of some countries are also shown. About 70% of the world production is realized by the G.D.R. (27.5%), West Germany (13.4%), the U.S.S.R. (17.6%), and Czechoslovakia (10.2%).

## C. Refinement of Brown Coal by Thermal Methods

Thermal refinement methods are leading to products which are energetically more favorable to use than brown coal with regard to utilization in combustion processes. Products of these refinement processes seem to be usable more favorably, e.g., as high-temperature coke, than comparable products from hard coal. For that reason brown coal refinement methods have found again an increasing interest in the last years.

### *1. Carbonization*

Low-temperature carbonization (LTC) is the heating of brown coal to a temperature of 500 to 600°C in the absence of air. High-temperature carbonization (HTC or coking) is the heating of brown coal to a temperature of about 1200°C in the absence of air. Solid bitumen-free residues as well as liquid and gaseous hydrocarbons result from these pyrolyses. LTC aims at the production of tar whose constituents are the basis of a comprehensive branch of carbochemistry.[2] Coke is the main product of HTC and the available portions of gas and liquid products are adequately modified. In principle there is no other difference between the two methods than the different heating temperatures. Heating-up velocity and size of

## Table 1
## BROWN COAL RESERVES OF THE WORLD AS WELL AS RESERVES AND PRODUCTION OF SOME COUNTRIES[6]

| | | **Reserves (metric tons, millions)** | | | | **Production (metric tons, thousands)** | | |
|---|---|---|---|---|---|---|---|---|
| | | **Known economic reserves** | | | | | | |
| **Country/area** | **Year** | **Total** | **Total known recoverable** | **Additional resources** | **Total resources** | **1970** | **1976** | **1978** |
| World | | 342,070 | 213,865 | 2,472,916 | 2,186,874 | 792,652 | 891,481 | 922,169 |
| Australia | 1977 | 68,058 | 39,000 | 54,628 | 122,686 | 24,175 | 30,939 | 32,868 |
| Bulgaria | 1972 | 4,356 | 4,356 | 840 | 5,196 | 28,854 | 25,184 | 25,531 |
| Czechoslovakia | 1966 | 8,234 | 3,870 | 1,623 | 9,857 | 81,783 | 89,468 | 94,879 |
| G.D.R. | 1966 | 30,000 | 252,000 | — | 30,000 | 261,482 | 246,879 | 253,264 |
| F.R.G. | 1977 | 55,000 | 28,890 | 6,100 | 61,100 | 108,437 | 134,535 | 123,587 |
| Hungary | 1966 | 2,900 | 1,450 | 2,779 | 5,679 | 23,679 | 22,323 | 22,716 |
| India | 1977 | 1,868 | 934 | 231 | 2,099 | 3,545 | 3,900 | 3,606 |
| Indonesia | 1974 | 1,960 | 980 | — | 1,960 | — | 1 | — |
| Poland | 1976 | 6,449 | 4,840 | 8,413 | 14,862 | 32,767 | 39,305 | 40,985 |
| Romania | 1966 | 1,367 | 1,100 | 2,533 | 3,900 | 14,129 | 18,731 | 21,845 |
| Turkey | 1977 | 2,968 | 3,575 | 1,875 | 4,843 | 4,437 | 8,252 | 9,326 |
| U.S.S.R. | 1971 | 107,402 | 53,700 | 1,612,922 | 1,720,324 | 144,745 | 160,031 | 162,871 |
| U.S. | 1977 | 30,497 | 15,249 | 764,664 | 795,161 | 5,409 | 23,101 | 32,318 |
| Yugoslavia | 1971 | 17,894 | 16,800 | 3,753 | 21,642 | 27,779 | 36,259 | 39,238 |

lumps of the feedstock have a decisive influence on the products yielding. Realizing a heating-up velocity of, for example, 2°C/min in the coke oven the vaporization of the inherent water will begin at 70°C. Within the range of 105 to 220°C the inherent moisture vaporizes almost completely, after that the formation of decomposition water begins and above 270°C the tar formation phase will follow.

In the case of carbonization involving gas recirculation, hot flue gases are used for coal heating. Therefore, using this method in addition to inherent water and decomposition water, a portion of combustion water is in the mixture of condensed waters from carbonization process. The mass portions of the waters formed in carbonization process are illustrated in Figure 3.

### 2. *Coal Gasification*

In principle coal gasification consists of a joint heating of coal with a gasification medium. The objective of the conversion is the production of combustible and reactive gases, respectively. In the case of autothermal gasification of brown coal, water vapor and oxygen or air are used. The heat necessary for the conversion is obtained by partial combustion of brown coal.

In the case of allothermal gasification the heat necessary for the conversion is generated outside of the reactor and transmitted to the reaction chamber.

A plurality of reactor types and process variants have been elaborated[3] for the technical realization of autothermal gasification. Technological innovations such as, for example, pressure gasification of pulverized coal, have been developed for the utilization of brown coals which are not suitable for processing with known technologies due to the composition of the coals (e.g., salt coal).

Relating to allothermal gasification methods, efforts can be recognized to combine nuclear energy and coal gasification in an energetically profitable way.[4] With the employment of a

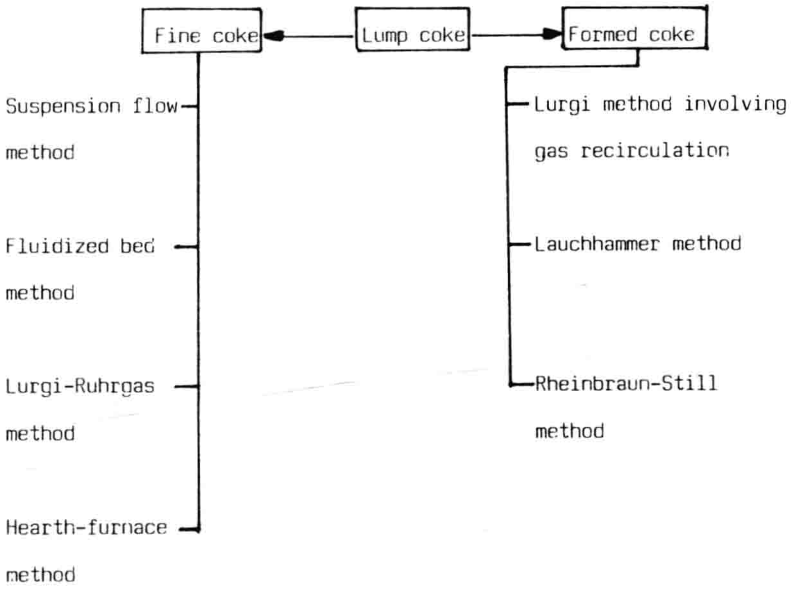

FIGURE 2. Methods of coke production from brown coal.

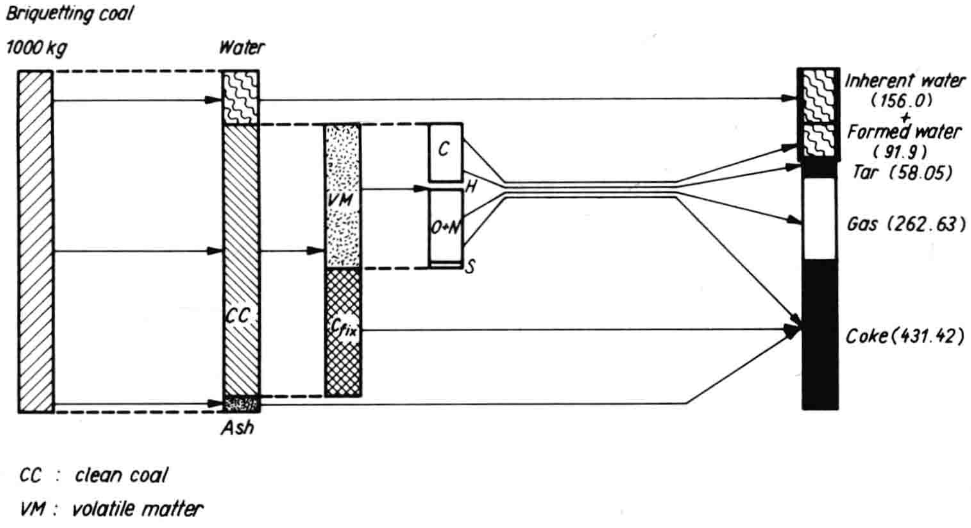

FIGURE 3. Matter and elementary balance for coking of brown coal briquette. (According to Kurtz, R., *Ullmanns Enzyklopädie der technischen Chemie*, Vol. 14, 4th ed., Bartholomé, E., Biekert, E., Hellmann, H., Ley, H., Weigert, W. M., and Weise, E., Eds., Verlag Chemie, Weinheim, West Germany, 1977, 491.)

gas-cooled high-temperature nuclear reactor, an improved utilization of brown coal connected with reduced contaminant emission as well as lower production costs are expected. Hydrogen and water vapor are used as gasification mediums.

Theoretically, a complete conversion of the carbonaceous substances of coal is possible leaving only ash as the solid phase. In practice the reactions are carried out in the way that carbonization and gasification are parallel. Reactive gases are formed containing hydrogen as well as carbon monoxide. The gases can be arranged into the following groups concerning caloric value.

1. Lean gas and water gas: 4600 to 12,500 kJ/m$^3$ (101.3 kPa; 0°C)
2. Synthesis gas and reduction gas: 3000 to 12,500 kJ/m$^3$ (101.3 kPa; 0°C)
3. Town gas and sewer gas 16,700 to 20,000 kJ/m$^3$ (101.3 kPa; 0°C)
4. Rich gas and substitute natural gas 25,000 to 37,000 kJ/m$^3$ (101.3 kPa; 0°C)

Independent of origin all these gases contain water vapor originating from coal water content and nonconverted reaction water vapor. Further, a portion of formed water originates from the partial oxidation of hydrogen in raw material. By condensation the gas waters are separated out of the gases. The composition of condensation waters may vary widely. Some examples are given in Table 2.

The composition of the condensation waters has to be regarded when technology for the coal-converting process is chosen. Particularly, the acidic waters of the east of the Elbe River (eE) coals cause corrosion problems which are harnessed by the application of suitable materials.

Contrary to hard coal condensation waters the content of cyanide and rhodanide is no object with regard to the treatment of brown coal waters.

### *3. Liquefaction of Brown Coal*

In addition to the above-mentioned methods of coal carbonization and gasification yielding mainly solid and gasified products, the processes of coal hydrogenation mainly produce liquid products as benzines and oils of different boiling ranges. At reaction temperatures of 300 to 500°C added hydrogen becomes attached under pressure to the sites of fracture of pyrolysis. As products high- and low-boiling oils and benzines are recovered.

Large coal hydrogenation plants run on a brown coal basis had been changed over to a petroleum-run basis and were put out of operation, respectively. In the case of the Bergius process pulverized coal was pasted with high-boiling oils and the suspension was pressed into reaction chambers. The pressure required for the conversion with hydrogen depends on the type of coal and is in the range of 20 to 80 mPa. The waters resulting from this process are loaded to a lower degree than the waters from coal carbonization or gasification.

The new synthesis of hydrocarbons out of synthesis gas is not often practiced due to the high energy demanded (Fischer-Tropsch synthesis). In South Africa plants are in operation based on the Sasol-process scheme (Gasol I and II). The treatment of tars and tar oils also leads to condensation waters burdened with phenolic compounds.

### *4. Summary of Processes of Brown Coal Refinement and Composition of Water*

In Table 3 the possibilities of secondary product processing with an output of phenolic waters are summarized. An example for the composition of such waters is illustrated in Table 4.

All processes of brown coal refinement are characterized by producing condensed waters which contain several volatile organic and inorganic constituents. Because of the phenolic content of these waters they are sometimes called phenolic effluents or phenolic waters. Table 3 shows a systematic overview concerning phenolic water-bearing processes and the main products of these processes. Table 4 shows some examples of typical phenolic waters from several brown coal refining processes. The values of the content of different groups change with the specific conditions of the mentioned processes as well as with the applied coal.