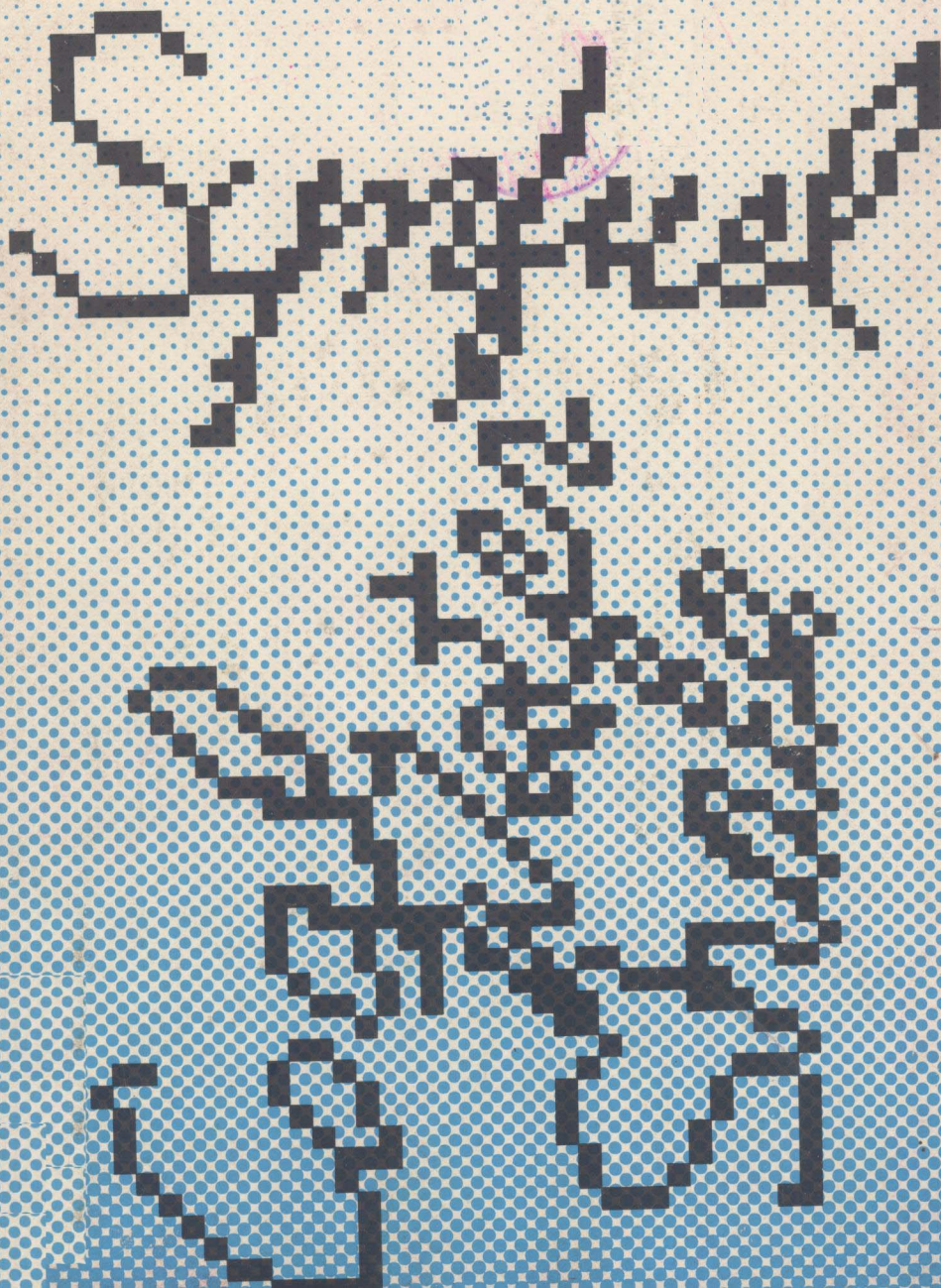


Water in Synthetic Fuel Production The Technology and Alternatives

Ronald F. Probst
and
Harris Gold



Water in Synthetic Fuel Production

The Technology and Alternatives

Ronald F. Probstein

Water Purification Associates
and

Massachusetts Institute of Technology

Harris Gold

Water Purification Associates

The MIT Press
Cambridge, Massachusetts, and London, England

Any opinions, findings, conclusions or recommendations herein are those of the authors and do not necessarily reflect the views of the National Science Foundation.

Copyright © 1978 by Water Purification Associates
Second printing, 1980

All rights reserved. No part of this book may be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording, or by any information storage and retrieval system, without permission in writing from the publisher.

This book was set in VIP Times Roman by the Composing Room of Michigan, Inc. It was printed and bound by Halliday Lithograph Corporation in the United States of America.

Library of Congress Cataloging in Publication Data

Probstein, Ronald F

Water in synthetic fuel production.

Includes bibliographies and index.

1. Synthetic fuel industry—Water supply.
2. Synthetic fuel industry—Waste disposal. I. Gold, Harris, joint author. II. Title.

TP360.P76 662'.66 78-1815

ISBN 0-262-16071-4 (hardcover)

ISBN 0-262-66039-3 (paperback)

Water in Synthetic Fuel Production

This book is dedicated to the idea that America will choose wisely to ensure the continuing availability of energy supplies.

Preface

Plants to manufacture synthetic fuels from coal and oil shale require large quantities of fresh water and produce large quantities of dirty water. In the United States this poses a problem; much of the easily mined coal and almost all of the high grade oil shale are in the arid West, and local and temporal water shortages sometimes occur where coal supplies are located in the East. In all regions the discharge of contaminated water is constrained by environmental considerations. In this book we have endeavored to present the practically achievable technology that can be incorporated in synthetic fuel plants to minimize water consumption and pollution. The book is intended to be a guide to understanding the role water plays in synthetic fuel production and includes the basic concepts underlying water usage and water treatment in this context.

Not all of the information needed for our analyses was known with certainty at the time of writing, and many estimates given will undoubtedly have to be revised. Moreover, the technologies to produce synthetic fuels should be expected to change. However, by concentrating on the fundamental principles of coal and oil shale conversion as they relate to water needs, the methodologies and results should be generally valid. Our aim was to show what can be done to minimize the water-related environmental impacts of commercial size plants before they are built and not afterward.

Although the book does try to present a reasonably comprehensive picture of synthetic fuel production, it is not a design manual nor does it attempt to examine every possible process or product fuel. For example, the conversion of tar sands is not discussed at all, while only brief note is made of underground (*in situ*) conversion technologies and physical and chemical coal cleaning.

The book is directed to a wide audience including those responsible for planning energy development, those involved with the engineering and design of synthetic fuel plants, and students and others who desire a background in synthetic fuel production. The book is formally self-contained and all the material—encompassing the disciplines of chemical, mechanical, civil, environmental, and mining engineering, water resources, and chemistry—should be accessible to anyone with an undergraduate degree in engineering or the physical sciences. For those readers without a technical background Chapters 1 to 3 and the concluding Chapter 9 can be read with little difficulty. Chapters 4 to 8 have their main results and conclusions summarized at the end of each chapter.

Through directly cited references, every effort has been made to acknowledge the work of others discussed in the book. However, the book also contains much unpublished work of the authors. Some of this work has been taken from ongoing

studies being carried out at Water Purification Associates by the authors and their colleagues.

The support of this project is an indirect expression of concern and interest in the development of a sound policy on the part of the United States toward the production of synthetic fuels as an alternative energy source. It is to this idea that the book is dedicated.

Cambridge, Massachusetts
October, 1977

Ronald F. Probstein
Harris Gold

Acknowledgments

We are deeply grateful to the National Science Foundation, which through its former program of Research Applied to National Needs sponsored the preparation of this book before the importance of the subject matter was widely appreciated. Special thanks are due Edward H. Bryan who served as the program manager of the initial grant under which the work was carried out. Much of the credit for the completion of the book goes to Richard H. Warder, Jr., who became the program manager on the continuation grants. Without his support the program might never have gone to completion because of continually altering government priorities. Donald Senich and Harold A. Spuhler shepherded the project through its final stages and for this we are grateful.

A special acknowledgment is due Sidney Johnson and J. W. (Pat) O'Meara of the former Office of Saline Water of the Department of the Interior. Both persisted throughout the fall of 1973 following the Arab oil embargo to obtain support for the work on which this book is based. At the beginning of 1974 they did succeed in having a small contract awarded to one of us (R.F.P.) to consider if future work on the problem was justified. The results of that study served as the basis for the program later undertaken by the National Science Foundation.

We are also grateful to a number of agencies and individuals from whom we have received indirect support through ongoing study contracts on the subject matter of this book. We wish in particular to thank the Industrial and Environmental Research Laboratory of the U.S. Environmental Protection Agency at Research Triangle Park, N.C., and T. Kelly Janes, James Chasse, and Dennis J. Cannon of that laboratory; the Office of Energy, Minerals and Industry of the U.S. Environmental Protection Agency and Gary Foley and Steven E. Plotkin of that office; the Division of Fossil Energy of the former U.S. Energy Research and Development Administration and Matthew J. Reilly, John H. Nardella, Hershel Jones, and Thomas Nakeley of that division. All of the individuals mentioned interacted strongly with our programs and provided much valuable advice and assistance.

A particular debt of gratitude is due David Goldstein of Water Purification Associates whose many contributions appear throughout the text. We are also grateful to all the other members of Water Purification Associates who provided us with technical assistance, comments, and reviews. R. Edwin Hicks, Li Liang, Joseph S. Shen, Irvine W. Wei, and David Yung all merit many thanks. We wish also to acknowledge Resource Analysis, Inc., and David H. Marks, Richard L. Laramie, and John H. Gerstle in particular, for supplying information on water resources that was developed under several joint programs with Water Purification Associates. This information was incorporated without

reference in Sections 9.2 and 9.3. Stone and Webster Engineering Corporation assisted Water Purification Associates in some of their sponsored studies on the subject matter of this book, and we particularly acknowledge the contributions of Winthrop D. Comley and Carl H. Jones to the discussions on cooling and on water treatment.

For her preparation of the figures we are grateful to Nancy Holbrook. For the typing of the manuscript and the handling of the numerous secretarial details we thank Christine Stilton and P. Margaret Qamoos.

Finally, our most sincere thanks and appreciation go to Debra Knopman who through her copy editing greatly improved the style of the original manuscript.

Water in Synthetic Fuel Production

Contents

| | |
|--|-----------|
| Preface | ix |
| Acknowledgments | xi |
| 1 Introduction and Summary | 1 |
| 1.1 Synthetic Fuels and Water | 1 |
| 1.2 Summary and Conclusions | 3 |
| Chapter 1. References | 12 |
| 2 General Considerations | 13 |
| 2.1 Hydrogenation and Other Process Water | 13 |
| 2.2 Cooling | 14 |
| 2.3 Mining, Fuel Preparation, and Residuals Disposal | 15 |
| 2.4 Coal and Shale Deposits | 16 |
| 2.5 Water Availability and Constraints | 19 |
| Chapter 2. References | 21 |
| 3 Coal and Shale Conversion Fundamentals | 23 |
| 3.1 Introduction | 23 |
| 3.2 Properties of Coal and Shale | 25 |
| 3.3 Pyrolysis | 29 |
| 3.4 Gasification of Coal | 31 |
| 3.5 Hydrogenation of Coal and Pyrolysis Oils | 35 |
| 3.6 Gas Purification | 37 |
| 3.7 Flue Gas Desulfurization | 40 |
| Chapter 3. References | 44 |
| 4 Cooling Fundamentals | 47 |
| 4.1 Evaporative Cooling Towers | 47 |
| 4.2 Dry and Wet/Dry Cooling Systems | 53 |
| 4.3 Cooling Ponds and the Cost of Water | 57 |
| 4.4 Cooling Process Streams and Gas Purifiers | 61 |
| 4.5 Cooling Turbine Condensers and Gas Compressors | 67 |
| 4.6 A Summary of Cooling Requirements | 78 |
| Chapter 4. References | 80 |
| 5 Gas Production | 82 |
| 5.1 Gasification Technologies | 82 |
| 5.2 Hydrogen Balance and the Synthane Process | 87 |
| 5.3 Hydrogen Balances for Other Processes | 94 |
| 5.4 Cooling Water | 107 |
| 5.5 Quality of Effluent Process Water Streams | 115 |

| | |
|---|------------|
| 5.6 A Summary of Water Stream Quantities | 122 |
| Chapter 5. References | 125 |
| 6 Liquid and Solid Fuel Production | 128 |
| 6.1 Liquefaction and Clean Coal Technologies | 128 |
| 6.2 Hydroliquefaction | 133 |
| 6.3 Solvent Extraction of Coal | 142 |
| 6.4 Shale Pyrolysis Technologies | 151 |
| 6.5 Integrated Oil Shale Plants | 163 |
| 6.6 Coal Pyrolysis | 172 |
| 6.7 Liquid Hydrocarbon Synthesis | 178 |
| 6.8 A Summary of Water Stream Quantities | 182 |
| Chapter 6. References | 186 |
| 7 Mining, Disposal, and Other Water Uses | 190 |
| 7.1 Mining and Fuel Preparation | 190 |
| 7.2 Ash Disposal, Flue Gas Scrubbing, and Reclamation | 196 |
| 7.3 Spent Shale Disposal and Revegetation | 202 |
| 7.4 Other Mine-Plant Water Needs | 206 |
| 7.5 A Summary of Water Stream Quantities | 210 |
| Chapter 7. References | 212 |
| 8 Water Treatment | 214 |
| 8.1 Water Treatment Plants | 214 |
| 8.2 Boiler Feed Water | 217 |
| 8.3 Process Condensate | 226 |
| 8.4 Cooling Water | 235 |
| 8.5 A Summary of Requirements | 239 |
| Chapter 8. References | 241 |
| 9 Resources and Water Requirements | 244 |
| 9.1 Coal and Oil Shale | 244 |
| 9.2 Western Water Resources | 249 |
| 9.3 Eastern and Central Water Resources | 257 |
| 9.4 Water Consumption and Residual Totals | 263 |
| 9.5 Water Requirements for Synthetic Fuel Production | 274 |
| Chapter 9. References | 277 |
| Appendix A. Conversion Factors | 281 |
| Appendix B. Properties of Selected Elements | 284 |
| Index | 285 |

Introduction and Summary

1.1 Synthetic Fuels and Water

The recognition of declining world reserves of petroleum and natural gas has accelerated the development of the technology to produce synthetic fuels compatible with existing equipment. Synthetic fuels are obtained by converting a carbonaceous material to another form. In the United States the most abundant naturally occurring materials suitable for this purpose are coal and oil shale. The conversion of these raw materials may also be undertaken to remove sulfur or nitrogen that would otherwise be burned, giving rise to undesirable air pollutants. Another reason for conversion is to increase the heating value of the original coal or shale by removing unwanted constituents such as ash and thereby produce a fuel which is cheaper to transport and handle.

The manufacture of synthetic fuels from coal or oil shale may be regarded as a process of hydrogenation in which water is the source of the hydrogen. A typical bituminous coal by weight contains 75 percent carbon, 5 percent hydrogen, and 20 percent inert or undesirable matter. On the other hand, for example, synthetic natural gas which is almost entirely methane contains 75 percent carbon and 25 percent hydrogen. In addition to the water required as a source of hydrogen, water is also generally needed for other process steps.

As in any real process, conversion can never be completely efficient. The available energy or heating value of the coal or shale cannot be fully recovered in the synthetic fuel. This unrecovered thermal energy must be transferred to the environment in some way. Generally, part of the unrecovered heat is disposed of by evaporating water. Finally, water is needed to mine and prepare the raw material and to dispose of the unwanted constituents removed in the process.

In the United States, the importance of water usage in synthetic fuel production lies principally in the fact that much of the easily mined coal and almost all of the high grade oil shale are found in the arid western areas of the country. The nation's richest "hydrocarbon basin" cuts a swath from Montana and the Dakotas in the north down through Wyoming, Utah, and Colorado to New Mexico in the south. The center of the coal and shale swath underlies the Upper Colorado River Basin, with the remainder encompassing part of the Missouri River Basin in the north and the Rio Grande Basin in the south. In these arid, sometimes drought-ridden areas, agricultural, industrial, municipal, recreational, and power needs compete for a limited water supply. Even now a *de facto* overcommitment of available fresh water resources exists in some portions of the hydrocarbon basin. The problem of water shortage is, however, not limited to the

West. In the humid coal areas of Illinois and Appalachia in the East, local and temporal water shortages may be a major impediment to the development of synthetic fuel facilities at coal mining sites. In all regions, the water discharge problem is constrained by the environmental limitation that the plant effluent waters may not add pollutants to the surface or ground water or otherwise disrupt the aquatic equilibrium.

Published estimates vary widely on the amount of water consumed in manufacturing synthetic fuels. Generally, the reason for this variance is the amount of water that is assumed to be evaporated for cooling in the plant, since cooling water is most often the prime determinant of total consumption. In conversion processes the heat to be removed will be less, the higher the efficiency of the conversion. For this reason, water usage in coal liquefaction will tend to be somewhat less than in coal gasification, when measured in relation to the thermal output of the product fuel.

By itself, the criterion of conversion efficiency may not suffice to characterize the water consumption. For example, one gasification process may consume considerably less water than another because the moisture in the coal is collected and used, although the utilization of such dirty water will not be without cost. To provide a reference point, consider a mine-plant complex to gasify coal. A plant that is reasonably well designed so as not to be wasteful of water, but not designed to minimize water consumption, might require about 18 gallons of water per million Btu of heating value in the gas. For a standard size plant producing 250 million cubic feet of pipeline gas per day, this amounts to about 4.5 million gallons of water per day. This value may be compared with a commonly quoted range of 9 to 40 million gallons per day.¹

If synthetic fuel development is to be a viable prospect in regions where water is in short or uncertain supply, then effluent process waters must be reused, water consumed for cooling must be minimized, and unusual water sources such as brackish groundwater and municipal effluents may have to be used. The actual amount of water consumed depends on a number of factors including the product fuel, the cooling method, the site, the process, and the methods of disposing of the residuals. However, there is no absolute water requirement but only a preference since it is at the discretion of the designer to reduce the quantity to very low levels. The preference is principally an economic one that largely depends on the site as it affects the real cost of water. Of course, the preference may also rest on social, political, or environmental grounds. In this book the technology and alternatives to minimize water consumption and pollution are described.

1.2 Summary and Conclusions

The synthetic fuel technologies examined include the conversion of coal to clean gaseous, liquid, and solid fuels, and the conversion of oil shale to clean liquid fuels. A number of processes are described for each conversion, including both above ground and *in situ* (underground) procedures. For purposes of comparing water requirements, water treatment plants, and residuals generated, detailed conceptual designs for integrated mine-plant complexes are presented for representative conversion processes. Only above ground processing is considered in detail. The processes and products chosen for purposes of comparison are shown in Table 1.1. Specific designs are based on standard size plants with the given product outputs.

The coal mining regions chosen were those where the largest and most easily and economically mined deposits are located. In the West these include the Powder River and Fort Union regions in Montana, Wyoming, and the Dakotas, and the Four Corners region where New Mexico, Arizona, Utah, and Colorado meet. In the central and eastern areas of the country, the Illinois and Appalachian basins were selected. The western coals are principally low sulfur subbituminous and lignite, while the eastern coals are mainly high sulfur bituminous. Average heating values for the different coal ranks are: bituminous 13,000 Btu/lb; subbituminous 9,800 Btu/lb; lignite 6,800 Btu/lb. Only high grade oil shale from the Green River Formation is considered. Specific design examples are restricted to shales with yields of about 30 to 35 gallons per ton, as might be found in Colorado or Utah.

The plant output measured in terms of the heating value of the product fuel

Table 1.1
Conversion processes, products, and plant sizes
compared for water requirements.

| Technology | Conversion Process | Product | Standard Size Plant Output |
|-------------------|--------------------------------------|----------------------|--------------------------------|
| Coal Gasification | Synthane, Hygas, Lurgi | Pipeline Gas | 250 × 10 ⁶ scf/day* |
| Coal Liquefaction | Synthoil | Fuel Oil | 50,000 barrels/day |
| Clean Coal | SRC | Solvent Refined Coal | 10,000 tons/day |
| Oil Shale | Paraho Direct and Indirect, TOSCO II | Synthetic Crude | 50,000 barrels/day |

*Standard cubic feet per day.

Table 1.2
Process efficiencies and mining rates for standard size synthetic fuel plants.

| Technology | Heating Value of Product Fuel (10^{11} Btu/day) | Process Conversion Efficiency (percent) | Coal or Shale Mining Rates* (10^3 tons/day) |
|-------------------|--|---|--|
| Coal Gasification | 2.4 | 65-70 | 16-30 |
| Coal Liquefaction | 3.1 | 70-75 | 16-31 |
| Clean Coal | 3.2 | 75-80 | 17-33 |
| Oil Shale | 2.9 | 57-72 | 75-100 |

*Highest coal mining rates for lignite, lowest rates for bituminous. All shale high grade (30 to 35 gal/ton); highest shale mining rate for Paraho Indirect process, lowest rate for TOSCO II process.

together with the process conversion efficiency and heating value of the raw fuel roughly define the coal and shale mining rate. Table 1.2 gives an approximate range of overall process conversion efficiencies, defined by the sum of the heating values in the product fuel and byproducts compared to the heating value in the raw coal or shale. For the coal conversion plants, Table 1.2 summarizes the plant sizes and mining rates for the range of heating values of the different rank coals. The range in shale mining rates corresponds to the different conversion efficiencies of the processes considered.

For a given size coal conversion plant, the quantity of water consumed depends mainly on four factors: the product, the fraction of unrecovered heat disposed by wet cooling, and to a lesser extent the site and specific process. In the above ground conversion of oil shale to synthetic crude there are three important factors affecting water consumption: the method of spent shale disposal, the shale retorting process, and the extent to which wet cooling is used.

Estimates of water consumption are net ones; all effluent streams are assumed to be recycled or reused within the mine or plant after any necessary treatment. These streams include the dirty waters generated in the conversion process and the highly saline water drawn off (blown down) from wet evaporative cooling towers. Water only leaves the plant as vapor, as hydrogen in the hydrocarbon products, or as occluded water in the solid residues. Dirty water is cleaned, but only for reuse and not for returning it to a receiving water.

The process water requirements relate to the fact that hydrogen is needed for the fuel conversion, and its source is water. The water consumed depends on the difference between the hydrogen to carbon ratio in the coal or shale and this same ratio in the product fuel plus byproducts. A second factor in determining net

consumed process water is the moisture present in the coal or shale, which is not treated as a water input but which may be recovered in the process. The net process water requirement is generally not large and water may even be produced; it represents the difference between the high pressure steam needed for the process and the dirty water generated in the process. However, each of these streams by themselves may be quite large. Moreover, the qualities of these streams are at opposite ends of the spectrum: to produce the steam it is necessary to treat the boiler feed water to very high purity, while the water generated by the process is highly contaminated with organic matter, ammonia, and hydrogen sulfide.

The quantity of water consumed in cooling depends principally upon the overall plant conversion efficiency. This specifies the heat that is not recovered and that must be dissipated to the environment. Not all of this unrecovered heat must be dissipated by cooling, as an appreciable fraction of it will be lost directly to the atmosphere. And disposing of all the remaining unrecovered heat by evaporating water may not be economical; some of the heat should be transferred to the atmosphere by forced air cooling. The extent to which water is evaporated to remove the rest of the heat depends upon whether the region in which the plant is located is water rich or water short, coupled with the true cost of water. Approximately 1,400 Btu's are transferred for every pound of water evaporated in a wet evaporative cooling tower. In water rich areas, typically 25 to 60 percent of the total unrecovered heat goes to evaporating water, while in arid regions or where water is expensive only 10 to 30 percent of the unrecovered heat is used to evaporate water.

The water required for mining and preparation of the coal or shale and for the disposal of ash or spent shale is a function of location, principally through the amount of material that must be mined or disposed. Sulfur removal also consumes water, and the amount depends not only on the coal but also on the conversion process. Water is also needed for a number of other purposes that depend upon climate, such as land reclamation. Generally, any one of these requirements is not large and the needs can be met with lower quality waters. Nevertheless, when the requirements are taken together they are significant and cannot be neglected in any plant water balance, although general rules for the amount consumed are not easily stated. Differences in consumption in this category for a given coal conversion process, however, do not vary by more than 15 percent between regions with the exception of the Four Corners region. The difference is somewhat greater when this region is compared since larger amounts of water are needed there for ash handling, dust control, and revegeta-