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SYNTHETIC FUELS

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SYNTHETIC FUELS

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TO
Irène and Maria

PREFACE

The production of synthetic fuels to replace dwindling supplies of natural fuels is already a reality in some countries, and in the United States is an urgent national priority on the verge of becoming a major industry. The scale of this development will probably be larger than any previous technological undertaking. To carry it out will require large numbers of engineers and scientists from many backgrounds to be trained in, and have an understanding of, the new field of synthetic fuels. The seeds of this field are to be found in the fact that the conversion of carbonaceous materials to synthetic fuels can be viewed as a process of hydrogenation. This can be taken to imply that the subject is built up from a limited number of fundamental chemical, physical, and engineering principles. In this book we endeavor to present synthetic fuels as a unified engineering subject, while at the same time recognizing that many of its principles are well understood aspects of various engineering fields. Although the subject is a rapidly developing one, we feel that a book which attempts its definition is needed now. We recognize that advances in the science and technology of synthetic fuels mandate future revision; however, by concentrating on what we believe to be the fundamentals, we hope that we have written a text which will be both timely and lasting.

The book is an outgrowth of a graduate course taught at M.I.T. on synthetic fuel production. The course, like the book, is directed toward beginning graduate students and advanced undergraduates, mainly, but not exclusively, in chemical and mechanical engineering. By including material on the necessary chemical and physical fundamentals, we have tried to make the text sufficiently self-contained so that it will prove of value to students from a wide variety of engineering and scientific disciplines, including environmental, mining, petroleum, and industrial engineering, as well as chemistry. It is our intention that the book also serve as a reference and guide for professionals desirous of understanding or entering this new and exciting field. In presenting the review of chemical and physical fundamentals, we have utilized examples of relevance to synthetic fuels which are applied later in the text. For those familiar with the particular subject the examples themselves will be of interest, while for those who have had only limited or no exposure, the examples provide a vehicle for understanding or reviewing the topic covered.

Synthetic fuels are generally understood to include liquid and gaseous fuels, as well as clean solid fuels, produced by the conversion of coal, oil shale, or tar sands, and various forms of biomass. The aim of the book is to provide an understanding of the methods and processes for carrying this out. Although every effort has been made to be reasonably comprehensive, the book is not a design manual, and it makes no attempt to examine every possible process and product fuel. Emphasis has been placed on the conversion of coal, oil shale, and tar sands, for which a unified picture can be developed, although biomass conversion is covered. The discussions on resources and technology development have been biased toward developed and developing technologies as seen from an American perspective. In view of the many areas encompassed by the field, the choice of material is in part dictated by the authors' preference and background. We have been helped in this regard by the fact that one of us is a chemical engineer and the other a mechanical engineer.

Wherever possible we have tried to present facts sufficient to enable the reader to draw general conclusions regarding the suitability of a process or product from rational considerations, without reliance on developers' or manufacturers' detailed design and economic studies, or empirical results. Extended or lengthy calculational details and approaches have been avoided. Where we give unit or plant mass and energy balances, they are almost always simplified and are intended to illustrate a method, a concept, or a principle, and not to replace detailed engineering calculations. Apart from pedagogical reasons, this approach is often necessary because manufacturers or developers have limited their published data for proprietary reasons. As a result we have had to fill in gaps, so that our estimates may not always conform to the latest practice or design but should be sufficient for the illustrative purposes intended.

Many times questions have arisen due to conflicting data reported in the literature. In these cases, we have never tried to sweep the problem under the rug, but have attempted to provide an answer based on the principles discussed. Occasionally we have not been successful and have been able only to ask the question. In this regard, we would note that although much of the material is drawn from published sources, much is not and represents unpublished work of the authors. Every effort has been made to acknowledge the work of others. However, because the book is intended as a text and because we do not wish to burden the reader with an overwhelming bibliography, we have often chosen not to reference an original source directly, but instead to reference books or compilations in which the original work is described and cited. Our directly cited references have been drawn mainly from the English language literature.

SI units are used consistently throughout the text. In the United States, where the transition to these units is still in progress, this may cause some moments of hesitation, particularly for professional readers in industry where British units are still prevalent in design and engineering estimations. In some cases nominal units on which plant designs are based, such as "barrels per day," are given in parentheses next to the appropriate SI unit.

Many of the disciplines on which the subject of synthetic fuels is built are applied in a number of fields, each with its own preferred terminology and nomenclature. This is most evident with thermodynamics. In view of the overall dominance of chemical processing, we have generally adopted systems used in chemistry, and they are described in context.

Problem solving is an important part of any student's learning experience, and we apologize for not having included problems in the text. This was done solely in the interest of not delaying publication of the book. However, the student will find a sufficient number of ''problems for the reader'' throughout the text to partly serve this purpose. It is our intention to prepare a problem manual within as short a time after publication of the book as is practicable.

This book is dedicated to our wives whose assistance and forbearance made it possible.

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The book owes its existence to the course on Synthetic Fuel Production taught at M.I.T. The first time the course was given, a number of individuals served as guest lecturers and contributed their ideas on the subject matter. We wish particularly to thank Lawrence E. Swabb, Jr. of Exxon Research and Engineering Co., Bernard S. Lee of the Institute of Gas Technology, Steven R. Reznek of the U.S. Environmental Protection Agency, and Sidney Katell of West Virginia University. We especially want to acknowledge Lawrence Swabb, who prepared a written set of notes on the topic of coal liquefaction from which we have benefited greatly.

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R. Edwin Hicks

SYNTHETIC FUELS

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CHAPTER

ONE

INTRODUCTION

1.1 SYNTHETIC FUELS AND THEIR MANUFACTURE

Gaseous or liquid 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. Tar sands are also suitable, and large deposits are located in Canada. The conversion of these raw materials is carried out to produce synthetic fuels to replace depleted, unavailable, or costly supplies of natural fuels. However, the conversion 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 calorific value of the original raw fuel by removing unwanted constituents such as ash, and thereby to produce a fuel which is cheaper to transport and handle.

Biomass can also be converted to synthetic fuels and the fermentation of grain to produce alcohol is a well known example. In the United States, grain is an expensive product which is generally thought to be more useful for its food value. Wood is an abundant and accessible source of bio-energy but it is not known whether its use to produce synthetic fuels is economical. The procedures for the gasification of cellulosic materials have much in common with the conversion of coal to gas. We consider the conversion of biomass in the book, but primary emphasis is placed on the manufacture of synthetic fuels from coal, oil shale, and tar sands. Most of the conversion principles to be discussed are, however, applicable to the spectrum of carbonaceous or cellulosic materials which occur naturally, are grown, or are waste.

For our purposes we regard the manufacture of synthetic fuels as a process of hydrogenation, since common fuels such as gasoline and natural gas have a higher hydrogen content than the raw materials considered. The source of the hydrogen which is added is water. The mass ratio of carbon to hydrogen for a variety of fuels is shown in Table 1.1. Generally, the more hydrogen that is added to the raw material, the lower is the boiling point of the synthesized product. Also, the more hydrogen that must be added, or alternatively the more carbon which must be removed, the lower is the overall conversion efficiency in the manufacture of the synthetic fuel.

Table 1.1 Carbon-to-hydrogen ratio for various fuels

Fuel	C/H Mass Ratio	Molar Representation
Bituminous coal	~15	$CH_{0.8}$
Benzene	12	$CH_{1.0}$
Crude oil	~ 9	$CH_{1.33}$
Gasoline	6	CH_2
Methane	3	CH_4

The organic material in both tar sands and in high-grade oil shale has a carbon-to-hydrogen mass ratio of about 8, which is close to that of crude oil and about half that of coal. For this reason, processing oil shale and tar sands to produce liquid fuels is considerably simpler than making liquid fuels from coal. However, the mineral content of rich tar sands in the form of sand or sandstone is about 85 mass percent, and the mineral content of high-grade oil shale, which is a fine-grained sedimentary rock, is about the same. Therefore, very large volumes of solids must be handled to recover relatively small quantities of organic matter from oil shale and tar sands. On the other hand, the mineral content of coal in the United States averages about 10 percent.

In any conversion to produce a fuel of lower carbon-to-hydrogen ratio, the hydrogenation of the raw fossil fuel may be direct, indirect, or by pyrolysis, either alone or in combination. Direct hydrogenation involves exposing the raw material to hydrogen at high pressure. Indirect hydrogenation involves reacting the raw material with steam, with the hydrogen generated within the system. In pyrolysis the carbon content is reduced by heating the raw hydrocarbon until it thermally decomposes to yield solid carbon, together with gases and liquids having higher fractions of hydrogen than the original material.

To obtain fuels that will burn cleanly, sulfur and nitrogen compounds must be removed from the gaseous, liquid, and solid products. As a result of the hydrogenation process, the sulfur and nitrogen originally present in the raw fuel are reduced to hydrogen sulfide and ammonia, respectively. Hydrogen sulfide and ammonia are present in the gas made from coal or released during the pyrolysis of oil shale and tar sands, and are also present in the gas generated in the hydrotreating of pyrolysis oils and synthetic crudes.

Synthetic fuels include low-, medium-, and high-calorific value gas; liquid fuels such as fuel oil, diesel oil, gasoline; and clean solid fuels. Consistent with SI units, we use the shorthand terms low-, medium-, and high-CV gas, where CV denotes calorific value, in place of the terms low-, medium-, and high-Btu gas which are appropriate to British units. Low-CV gas, often called producer or power gas, has a calorific value of about 3.5 to 10 million joules per cubic meter (MJ/m^3). This gas is an ideal turbine fuel whose greatest utility will probably be in a gas-steam combined power cycle for the generation of electricity at the location where it is produced. Medium-CV gas is loosely defined as having a calorific value of about 10–20 MJ/m^3, although the upper limit is somewhat arbitrary, with existing gasifiers yielding somewhat lower values. This gas is also termed power gas or sometimes industrial gas, as well as synthesis gas. It may be used as a fuel gas, as a source of hydrogen for the direct liquefaction of coal to liquid fuels, or for the synthesis of methanol and other liquid fuels. Medium-CV gas may also be used for the production of high-CV gas, which has a calorific value in the range of about 35 to 38 MJ/m^3, and is normally composed of more than 90 percent methane. Because of its high calorific value, this gas is a substitute for natural gas and is suitable for economic pipeline transport. For these reasons it is referred to as substitute natural gas (SNG) or pipeline gas. Lom and Williams[1] have pointed out that originally SNG stood for synthetic natural gas, but it was observed that what was natural could not very well be synthetic.

In Figure 1.1 are shown the principal methods by which the synthetic gases can be produced from coal. Gas can be manufactured by indirect hydrogenation by reacting steam with coal either in the presence of air or oxygen. When air is used, the product gas will be diluted with nitrogen and its calorific value will be low in comparison with the gas manufactured using oxygen. The dilution of the product gas with nitrogen can be avoided by supplying the heat needed for the gasification from a hot material that has been heated with air, in a separate furnace, or in the gasifier itself before gasification. In all of the cases, the gas must be cleaned prior to using it as a fuel. This purification step involves the removal of the hydrogen sulfide, ammonia, and carbon dioxide, which are products of the gasification. Medium-CV gas, consisting mainly of carbon monoxide and hydrogen, can be further upgraded by altering the carbon monoxide-to-hydrogen ratio catalytically and then, in another catalytic step, converting the resulting synthesis gas mixture to methane. A high-CV gas can be produced by direct hydrogenation, termed hydrogasification, in which hydrogen is contacted with the coal. A procedure still under development, which allows the direct production of methane, is catalytic gasification. In this method the catalyst accelerates the steam gasification of coal at relatively low temperatures and also catalyzes the upgrading and methanation reactions at the same low temperature in the same unit.

Gas can also be produced by pyrolysis, that is, by the distillation of the volatile components. Oil shale or tar sands are generally not thought of as primary raw materials for gas production, although the use of oil shale has been discussed.

Clean synthetic liquid fuels can be produced by several routes, as shown in Figures 1.2 to 1.4. For example, in indirect liquefaction (Figure 1.2), coal is first gasified and then the liquid fuel is synthesized from the gas. This procedure is not thermally efficient, relating to the fact that the carbon bonds in the coal must first be broken, as in gasification, and then in a further step some of them must be put back together again. Another procedure, illustrated in Figure 1.3, is pyrolysis, the distillation of the natural oil out of the coal, shale, or tar sands. The oil vapors are condensed, the resulting pyrolysis oil is treated with hydrogen, and the sulfur and nitrogen in it is reduced. This is similar to the procedure used in upgrading crude oil in a refinery to produce a variety of liquid fuels. Pyrolysis may also be carried out in a hydrogen atmosphere, a process termed hydropyrolysis, in order to increase the liquid and gas yield. In direct liquefaction (Figure 1.4) there are two basic procedures, hydroliquefaction and solvent extraction. In hydroliquefaction the coal is mixed with recycled coal oil and, together with hydrogen, fed to a high pressure catalytic reactor where