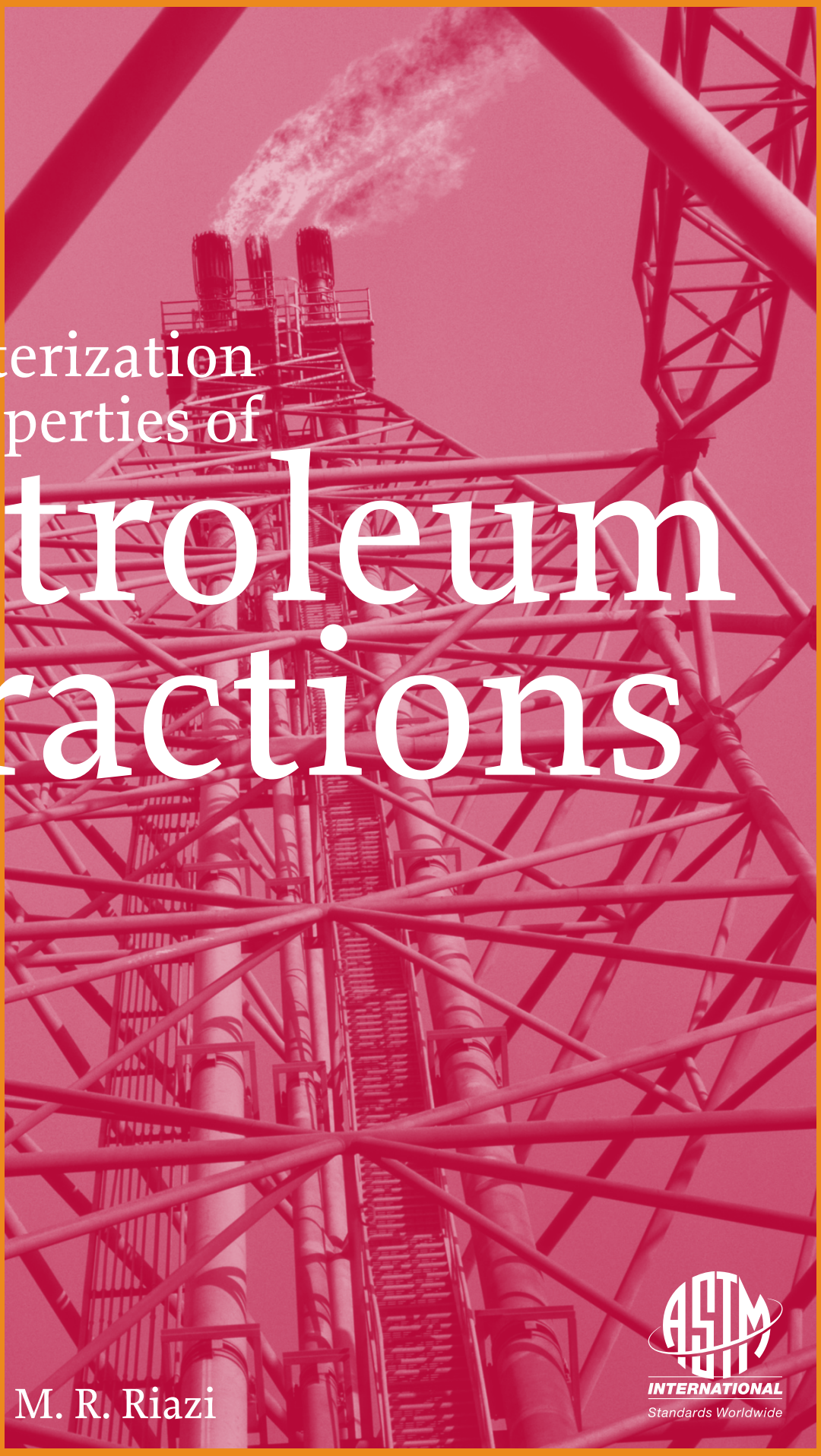
Characterization and Properties of Petroleum Fractions



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To
My family and parents

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Foreword

THIS PUBLICATION, *Characterization and Properties of Petroleum Fractions*, was sponsored by ASTM Committee D02 on Petroleum Fuels and Lubricants. The author is M. R. Riazi, Professor of Chemical Engineering, Kuwait University, Safat, Kuwait. This publication is Manual 50 of ASTM's manual series.

Preface

Scientists do not belong to any particular country, ideology, or religion, they belong to the world community

THE FIELD OF Petroleum Characterization and Physical Properties has received significant attention in recent decades with the expansion of computer simulators and advanced analytical tools and the availability of more accurate experimental data. As a result of globalization, structural changes are taking place in the chemical and petroleum industry. Engineers working in these industries are involved with process simulators to design and operate various units and equipment. Nowadays, a large number of process simulators are being produced that are equipped with a variety of thermodynamic models and choice of predictive methods for the physical properties. A person familiar with development of such methods can make appropriate use of these simulators saving billions of dollars in costs in investment, design, manufacture, and operation of various units in these industries. Petroleum is a complex mixture of thousands of hydrocarbon compounds and it is produced from an oil well in a form of reservoir fluid. A reservoir fluid is converted to a crude oil through surface separation units and then the crude is sent to a refinery to produce various petroleum fractions and hydrocarbon fuels such as kerosene, gasoline, and fuel oil. Some of the refinery products are the feed to petrochemical plants. More than half of world energy sources are from petroleum and probably hydrocarbons will remain the most convenient and important source of energy and as a raw material for the petrochemical plants at least throughout the 21st century. Other fossil type fuels such as coal liquids are also mixtures of hydrocarbons although they differ in type with petroleum oils. From 1970 to 2000, the share of Middle East in the world crude oil reserves raised from 55 to 65%, but this share is expected to rise even further by 2010–2020 when we near the peak point where half of oil reserves have been produced. The world is not running out of oil yet but the era of cheap oil is perhaps over. Therefore, economical use of the remaining oil and treatment of heavy oils become increasingly important. As it is discussed in Chapter 1, use of more accurate physical properties for petroleum fractions has a direct and significant impact on economical operation and design of petroleum processing and production units which in turn would result in a significant saving of existing petroleum reserves.

One of the most important tasks in petroleum refining and related processes is the need for reliable values of the volumetric and thermodynamic properties for pure hydrocarbons and their mixtures. They are important in the design and operation of almost every piece of processing equipment. Reservoir engineers analyze PVT and phase behavior of reservoir fluids to estimate the amount of oil or gas in a reservoir, to determine an optimum operating condition in a separator unit, or to develop a recovery process for an oil or gas field. However, the most advanced design approaches or the most sophisticated simulators cannot guarantee the optimum design or operation of a unit if required input physical properties are not accurate. A process to experimentally determine the volumetric, thermodynamic, and transport properties for all the industrially important materials would be prohibitive in both cost and time; indeed it could probably never be completed. For these reasons accurate estimations of these properties are becoming increasingly important.

Characterization factors of many types permeate the entire field of physical, thermodynamic, and transport property prediction. Average boiling points, specific gravity, molecular weight, critical temperature, critical pressure, acentric factor, refractive index, and certain molecular type analysis are basic parameters necessary to utilize methods of correlation and prediction of the thermophysical properties. For correlating physical and thermodynamic properties, methods of characterizing undefined mixtures are

necessary to provide input data. It could be imagined that the best method of characterizing a mixture is a complete analysis. However, because of the complexity of undefined mixtures, complete analyses are usually impossible and, at best, inconvenient. A predictive method to determine the composition or amount of sulfur in a hydrocarbon fuel is vital to see if a product meets specifications set by the government or other authorities to protect the environment.

My first interaction with physical properties of petroleum fluids was at the time that I was a graduate student at Penn State in the late 70s working on a project related to enhanced oil recovery for my M.S. thesis when I was looking for methods of estimation of properties of petroleum fluids. It was such a need and my personal interest that later I joined the ongoing API project on thermodynamic and physical properties of petroleum fractions to work for my doctoral thesis. Since that time, property estimation and characterization of various petroleum fluids has remained one of my main areas of research. Later in the mid-80s I rejoined Penn State as a faculty member and I continued my work with the API which resulted in development of methods for several chapters of the API Technical Data Book. Several years later in late 80s, I continued the work while I was working at the Norwegian Institute of Technology (NTH) at Trondheim where I developed some characterization techniques for heavy petroleum fractions as well as measuring methods for some physical properties. In the 90s while at Kuwait University I got the opportunity to be in direct contact with the oil companies in the region through research, consultation, and conducting special courses for the industry. My association with the University of Illinois at Chicago in early 90s was helpful in the development of equations of state based on velocity of sound. The final revision of the book was completed when I was associated with the University of Texas at Austin and McGill University in Montreal during my leave from Kuwait University.

Part of the materials in this book were prepared when I was teaching a graduate course in applied thermodynamics in 1988 while at NTH. The materials, mainly a collection of technical papers, have been continuously updated and rearranged to the present time. These notes have also been used to conduct industrial courses as well as a course on fluid properties in chemical and petroleum engineering. This book is an expansion with complete revision and rewriting of these notes. The main objective of this book is to present the fundamentals and practice of estimating the physical and thermodynamic properties as well as characterization methods for hydrocarbons, petroleum fractions, crude oils, reservoir fluids, and natural gases, as well as coal liquids. However, the emphasis is on the liquid petroleum fractions, as properties of gases are generally calculated more accurately. The book will emphasize manual calculations with practical problems and examples but also will provide good understanding of techniques used in commercial software packages for property estimations. Various methods and correlations developed by different researchers commonly used in the literature are presented with necessary discussions and recommendations.

My original goal and objective in writing this book was to provide a reference for the petroleum industry in both processing and production. It is everyone's experience that in using thermodynamic simulators for process design and equipment, a large number of options is provided to the user for selection of a method to characterize the oil or to get an estimate of a physical property. This is a difficult choice for a user of a simulator, as the results of design calculations significantly rely on the method chosen to estimate the properties. One of my goals in writing this book was to help users of simulators overcome this burden. However, the book is written in a way that it can also be used as a textbook for graduate or senior undergraduate students in chemical, petroleum, or mechanical engineering to understand the significance of characterization, property estimation and methods of their development. For this purpose a set of problems is presented at the end of each chapter. The book covers characterization as well as methods of estimation of thermodynamic and transport properties of various petroleum fluids and products. A great emphasis is given to treatment of heavy fractions throughout the book. An effort was made to write the book in a way that not only would be useful for the professionals in the field, but would also be easily understandable to those non-engineers such as chemists, physicists, or mathematicians who get involved with the petroleum industry. The word *properties* in the title refers to thermodynamic, physical, and transport properties. Properties related to the quality and safety of petroleum products are also discussed. Organization of the book, its uses, and importance of the methods are discussed in detail

in Chapter 1. Introduction of similar books and the need for the present book as well as its application in the industry and academia are also discussed in Chapter 1. Each chapter begins with nomenclature and ends with the references used in that chapter. Exercise problems in each chapter contain additional information and methods. More specific information about each chapter and its contents are given in Chapter 1. As Goethe said, "Things which matter most must never be at the mercy of things which matter least."

I am indebted to many people especially teachers, colleagues, friends, students, and, above all, my parents, who have been so helpful throughout my academic life. I am particularly thankful to Thomas E. Daubert of Pennsylvania State University who introduced to me the field of physical properties and petroleum characterization in a very clear and understandable way. Likewise, I am thankful to Farhang Shadman of the University of Arizona who for the first time introduced me to the field of chemical engineering research during my undergraduate studies. I am indebted to them for their human characters and their scientific skills. I have been fortunate to meet and discuss with many scientists and researchers from both the oil industry and academia from around the world during the last two decades whose thoughts and ideas have in many ways been helpful in shaping the book.

I am also grateful to the institutions, research centers, and oil companies that I have been associated with or that have invited me for lecturing and consultation. Thanks to Kuwait University as well as Kuwait Petroleum Corporation (KPC) and KNPC, many of whose engineers I developed working relations with and have been helpful in evaluation of many of the estimating methods throughout the years. I am thankful to all scientists and researchers whose works have been used in this book and I hope that all have been correctly and appropriately cited. I would be happy to receive their comments and suggestions on the book. Financial support from organizations such as API, NSF, GPA, GRI, SINTEF, Petrofina Exploration Norway, NSERC Canada, Kuwait University, and KFAS that was used for my research work over the past two decades is also appreciated.

I am grateful to ASTM for publishing this work and particularly to Geroge Totten who was the first to encourage me to begin writing this book. His advice, interest, support, and suggestions through the long years of writing the book have been extremely helpful in completing this project. The introductory comments from him as well as those from other experts in the field for the back cover are appreciated. I am also grateful to the four unanimous reviewers who tirelessly reviewed the entire and lengthy manuscript with their constructive comments and suggestions which have been reflected in the book. Thanks also to Kathy Dernoga, the publishing manager at ASTM, who was always cooperative and ready to answer my questions and provided me with necessary information and tools during the preparation of this manuscript. Her encouragements and assistance were quite useful in pursuing this work. She also was helpful in the design of the front and back covers of the book as well as providing editorial suggestions. I am thankful to Roberta Storer and Joe Ermigiotti for their excellent job of editing and updating the manuscript. Cooperation of other ASTM staff, especially Monica Siperko, Carla J. Falco, and Marsha Firman is highly appreciated. The art work and most of the graphs and figures were prepared by Khaled Damyar of Kuwait University and his efforts for the book are appreciated. I also sincerely appreciate the publishers and the organizations that gave their permissions to include some published materials, in particular API, ACS, AIChE, GPA, Elsevier (U.K.), editor of Oil & Gas J., McGraw-Hill, Marcel and Dekker, Wiley, SPE, IFP, and Taylor and Francis. Thanks to the manager and personnel of KISR for allowing the use of photos of their instruments in the book. Finally and most importantly, I must express my appreciation and thanks to my family who have been helpful and patient during all these years and without whose cooperation, moral support, understanding, and encouragement this project could never have been undertaken. This book is dedicated to my family, parents, teachers, and the world scientific community.

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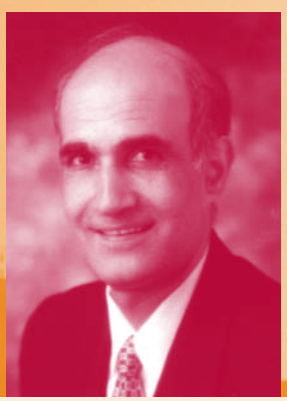

About the Author

Dr. M. R. Riazi is a professor of chemical engineering at Kuwait University. He was previously an assistant professor at Pennsylvania State University (USA), where he also received his M.S. and Ph.D. degrees. He was also a visiting professor at the following universities: Trondheim (Norway), Illinois (Chicago, USA), Wright State (Dayton, USA), Texas (Austin, USA), and McGill (Montreal, Canada). Dr. Riazi has been a consultant to several oil companies and research institutes in North America, Western Europe, North Africa, the Middle East, and Southeast Asia.

Dr. Riazi has published about 80 technical articles mainly in the fields of petroleum and chemical technology and has developed methods for three chapters of the API Data Book – *Petroleum Refining* and authored one book and four book chapters. In addition he has presented papers to more than 50 international conferences and Canadian Oil and Gas Review wrote about him. He is the Editor-in-Chief of the *International Journal of Oil, Gas and Coal Technology*. He is also on the Editorial Board of the *Journal of ASTM International* and serves as associate editor of the *Journal of Petroleum Science, Engineering and World Review of Science,Technology and Sustainable Development.*

Dr. Riazi's methods for characterization of crude oils and petroleum products have been used by oil companies and research centers worldwide and has presented about 80 invited lectures and short courses to the petroleum industry and research institutes in Canada, United States, United Kingdeom, France, Switzerland, Denmark, Holland, Norway, Poland, Malaysia, India, China, Australia, Kuwait, The Middle East and North Africa.

In 1995, he was awarded a Diploma of Honor from the American (National) Petroleum Engineering Society for his outstanding service to the petroleum industry. He was also awarded the Kuwait University outstanding research and teaching awards from the Crown Prince of Kuwait. He is a member of AIChE and the Research Society of North America.

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