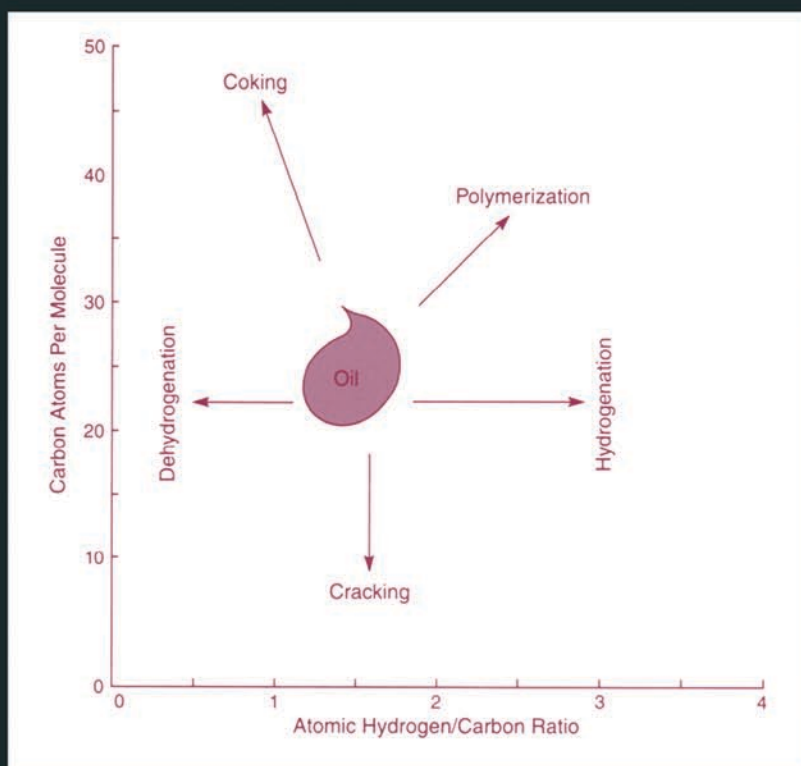


THE DESULFURIZATION OF HEAVY OILS AND RESIDUA

Second Edition, Revised and Expanded



James G. Speight

**THE DESULFURIZATION
OF HEAVY OILS
AND RESIDUA**

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James G. Speight

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Preface to the Second Edition

The sulfur content of petroleum varies from less than 0.05 to more than 14 wt% but generally falls in the range 1 to 4 wt%. Petroleum with less than 1 wt% sulfur is referred to as *low-sulfur*, and that with more than 1 wt% sulfur is referred to as *high-sulfur*. The refining industry considers heavy oils, residua, and bitumen to be high-sulfur feedstocks. Hence they are the focus of many conversion and desulfurization scenarios.

Little has changed in this respect since the publication of the first edition of this book. Indeed, there has been a tendency over the past decade for the quality of crude oil feedstocks to deteriorate—the *average* refinery feedstock is of lower API gravity and higher sulfur content than the average refinery feedstock of ten years ago. This means higher quantities of residua, more heavy oils, and higher quantities of sulfur to remove.

The success of the first edition of this text has been the primary factor in the decision to publish the second edition, which has been greatly expanded and rewritten to be more in keeping with the technological aspects of the petroleum industry. There are also expanded updates on the nature of the constituents of the asphaltene fraction of petroleum to show the means by which such constituents might influence desulfurization activity.

Since the first edition of this book, there have been many changes in the refining industry. The overall character of the feedstocks entering refineries has changed to such an extent that the difference can be measured by a decrease of several points on the API gravity scale. There is also more detailed information on the nature of the other nonhydrocarbon constituents of petroleum as well as a section on how these particular constituents behave during refinery operations. Such behavior can seriously influence the life of the catalysts that are used for desulfurization processes. One chapter deals with refining chemistry so that the reader can obtain a better understanding of the chemistry involved in the pro-

cessing of heavy feedstocks and the fate of the sulfur in these feedstocks. In addition, environmental issues have become of such importance that a chapter on the cleanup of refinery gases is included. And the environmental effects of sulfur-containing gases are also addressed.

This edition has references cited throughout the text, in contrast to the first edition, which contained a general bibliography at the end of each chapter. The cited references will guide the reader to the original article for more detail. Although there are many thousands of references in my personal files, no attempt has been made to include them all. I have selected those that might give the reader the most information.

Among other changes from the first edition, the book has been reorganized. Each chapter has been written as a standalone entity to spare the reader the inconvenience of having to refer to different parts of the book for discussions of a given topic. This has necessitated, for convenience, the duplication of some of the tables and figures. However, such duplication has been kept to a minimum.

In addition, petroleum refining has entered a significant transition period as the industry moves into the twenty-first century. Refinery operations have evolved to include a range of next-generation processes as the demand for transportation fuels and fuel oil has shown steady growth. These processes are different from one another in terms of the method and product slates and will find use in refineries according to their respective features. The primary goal of these processes is to convert the heavy feedstocks to lower-boiling products, and during the conversion there is the benefit of a reduction in sulfur content. Thus, these processes need to be given some consideration. A separate chapter is therefore included in which these more modern processes for upgrading heavy feedstocks are described.

Finally, it is time to acknowledge the organizations that have also contributed to this book. The following oil companies provided photographs of refinery operations: Phillips Petroleum, Sinclair Refinery, Shell Oil, Sun Oil, and Chevron Oil are gratefully acknowledged for their contributions. Some of these pictures have appeared in *The Chemistry and Technology of Petroleum* (Marcel Dekker, Inc.) and it is appropriate that several also appear here. I am grateful to those persons who supplied the pictures.

Finally, I am indebted to my numerous colleagues in many different countries who made constructive comments on the first edition. These comments have been of great assistance in writing this volume and I am truly grateful.

James G. Speight

Preface to the First Edition

With the inception of hydrogenation as a process by which both coal and petroleum could be converted into lighter products, it was also recognized that hydrogenation would be effective for the simultaneous removal of nitrogen, oxygen, and sulfur compounds from the feedstock. However, with respect to the prevailing context of fuel industries, hydrogenation seemed to be not economical for application to petroleum fractions. At least two factors dampened interest: (1) the high cost of hydrogen and (2) the adequacy of current practices for meeting the demand for low-sulfur products by refining *low*-sulfur crude oils, or even by alternate desulfurization techniques.

Nevertheless, it became evident that reforming processes instituted in many refineries were providing substantial quantities of by-product hydrogen, enough to tip the economic balance in favor of hydrodesulfurization processes. In fact, the need for such commercial operations has become more acute because of a shift in supply trends that has increased the amount of *high*-sulfur crude oils employed as refinery feedstocks.

There are several valid reasons for removing sulfur from petroleum fractions, including: (1) reduction, or elimination, of corrosion during refining, handling, or use of the various products; (2) production of products having an acceptable odor; (3) increasing the performance (and stability) of gasoline; (4) decreasing smoke formation in kerosene; and (5) reduction of sulfur content in other fuel oils to a level that improves burning characteristics and is environmentally acceptable. In order to accomplish sulfur removal, use is still made of extraction and chemical treatment of various petroleum fractions as a means of removing certain sulfur types from petroleum products, but hydrodesulfurization is the only method generally applicable to the removal of all types of sulfur compounds.

Overall, we have seen emerge a growing dependence on high-sulfur heavier oils and residua as a result of continuing increases in the prices of the conven-

tional crude oils coupled with the decreasing availability of these crude oils through the depletion of reserves in various parts of the world. Furthermore, the ever-growing tendency to convert as much as possible of lower-grade feedstocks to liquid products is causing an increase in the total sulfur content in refined products. Refiners must, therefore, continue to remove substantial portions of sulfur from the lighter products, but residua and the heavier crude oils pose a particularly difficult problem. Indeed, it is now clear that there are other problems involved in the processing of the heavier feedstocks and that these heavier feedstocks, which are gradually emerging as the liquid fuel supply of the future, need special attention.

The hydrodesulfurization of petroleum fractions has long been an integral part of refining operations, and in one form or another, hydrodesulfurization is practiced in every modern refinery. The process is accomplished by the catalytic reaction of hydrogen with the organic sulfur compounds in the feedstock to produce hydrogen sulfide, which can be separated readily from the liquid (or gaseous) hydrocarbon products. The technology of the hydrodesulfurization process is well established, and petroleum feedstocks of every conceivable molecular-weight range can be treated to remove sulfur. Thus, it is not surprising that an extensive knowledge of hydrodesulfurization has been acquired during the development of the process over the last few decades. Even though most of the available information pertaining to the hydrodesulfurization process has been obtained with the lighter and more easily desulfurized petroleum fractions, it is, to some degree, applicable to the hydrodesulfurization of the heavier feedstocks such as the heavy oils and residua. On the other hand, the processing of the heavy oils and residua presents several problems that are not found with distillate processing and that require process modifications to meet the special requirements of heavy feedstock desulfurization.

It is, therefore, the object of this text to indicate how the heavier feedstocks may, in the light of current technology, be treated to remove sulfur and at the same time afford maximum yields of low-sulfur liquid products.

This text is designed for scientists and engineers who wish to be introduced to desulfurization concepts and technology as well as those who wish to make more detailed studies of how desulfurization might be accomplished.

Chapters relating to the composition and evaluation of heavy oils and residua are regarded as being necessary for a basic understanding of the types of feedstock that will necessarily need desulfurization treatment.

For those readers requiring an in-depth theoretical treatment, a discussion (Chapter 3) of the chemistry and physics of the desulfurization process has been included. Attention is also given to the concept of desulfurization during the more conventional refinery operations (Chapter 4).

However, no attempt is made, at any point in the present text, to enter into discussions related to the removal of sulfur from organic materials by the various

chemical methods, such as Raney nickel desulfurization. Adequate reviews of this particular subject are available, and the minimal relevance of this aspect of desulfurization to the current text did not appear to warrant the inclusion of such a section here. Nor, for that matter, is any reference made to the desulfurization of petroleum fractions by treating in a ‘‘hydrogen-donor’’ solvent—the process itself is well known (and mature) but the commercialization (with respect to desulfurization as part of a refinery operation) has yet to be realized.

The effects of reactor type, process variables and feedstock type, catalysts, and feedstock composition (Chapters 5 and 6) on the desulfurization process provide a significant cluster of topics through which to convey the many complexities of the process. In the concluding chapters, examples and brief descriptions of commercial processes are presented (Chapter 7) and, of necessity, some indications of methods of hydrogen production (Chapter 8) are also included.

Finally, the author wishes to note that this work was completed while he was an Associate Research Officer at the Alberta Research Council, Edmonton, Alberta, Canada. In this respect the author acknowledges the valuable assistance of Mrs. Tara Emter during the preparation of the manuscript.

James G. Speight



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1

History, Definitions, and Occurrence

1. INTRODUCTION

Petroleum is scattered throughout the earth's crust, which is divided into natural groups or strata, categorized in order of their antiquity (Table 1-1) (Speight, 1999). These divisions are recognized by the distinctive systems of organic debris (as well as fossils, minerals, and other characteristics) which form a chronological time chart that indicates the relative ages of the earth's strata. It is generally acknowledged that carbonaceous materials such as petroleum occur in all these geological strata from the Precambrian to the recent, and the origin of petroleum within these formations is a question that remains open to conjecture and the basis for much research. The answer cannot be given in this text, nor for that matter can it be presented in any advanced treatise.

Petroleum is by far the most commonly used source of energy, especially as the source of liquid fuels (Table 1-2). Indeed, because of the wide use of petroleum, the past 100 years could very easily be dubbed the *Oil Century* (Ryan, 1998), the *Petroleum Era* (c.f. the *Pleistocene Era*), or the *New Rock Oil Age* (c.f. the *New Stone Age*).

At the present, the majority of the energy consumed by humans is produced from the fossil fuels with smaller amounts of energy that come from nuclear and hydroelectric sources. The continuing and expanding use of petroleum has led to various projections about its longevity. Some projections are disastrous and predict that petroleum availability is very short-lived. Others are not quite so disastrous. Nevertheless, it is becoming more and more obvious that petroleum use is increasing with the increased demand for liquid fuels and it is projected to increase into the first two decades of the twenty-first century (GRI, 1998) (Table 1-2). The interesting aspects of the projections reflect a largely stagnant nuclear energy industry in the United States. The nuclear power industry (Ze-

Table 1-1 General Description and Approximate Age of Geological Strata

Ear	Period	Epoch	Age (years $\times 10^6$)
Cenozoic	Quaternary	Recent	0.01
		Pleistocene	3
	Tertiary	Pliocene	12
		Miocene	25
		Oligocene	38
		Eocene	55
		Paleocene	65
Mesozoic	Cretaceous		135
	Jurassic		180
	Triassic		225
Paleozoic	Permian		275
	Carboniferous		
	Pennsylvanian		350
	Mississippian		
	Devonian		413
	Silurian		430
	Ordovician		500
	Cambrian		600

Table 1-2 Current and Projected Energy Consumption Scenarios (GRI, 1998)

	Energy consumption (quads)					
	1995	1996	2000	2005	2010	2015
	Actual		Projected			
Petroleum	34.7	36.0	37.7	40.4	42.6	44.1
Gas	22.3	22.6	23.9	26.3	28.8	31.9
Coal	19.7	20.8	22.3	24.1	26.2	29.0
Nuclear	7.2	7.2	7.6	7.4	6.9	4.7
Hydro	3.4	4.0	3.1	3.2	3.2	3.2
Other	3.2	3.3	3.7	4.0	4.8	5.2

broski and Levenson, 1976; Rahn, 1987) is truly an industry where the future is uncertain or, at the very least, at the crossroads. In addition, energy from hydro-sources is projected to be stable while energy from other sources (including renewable sources) is projected to show steady growth, but not sufficient to influence the consumption of petroleum as an energy source.

As a result, fossil fuels are projected to be the major sources of energy for the next fifty years. In this respect, petroleum and its associates (heavy oil and bitumen) are extremely important in any energy scenario, especially those scenarios that relate to the production of liquid fuels.

In the United States, there have been clear signs that movement away from petroleum-based fuels is a necessity. Events such as the Arab oil embargo in 1973, the natural gas shortage of 1976–1977, the gasoline lines of the summer of 1979, the potential threat to Western oil supplies posed by the Persian Gulf War, periodic blackouts, and energy shortages during cold weather have occurred. Indeed, there is a growing consensus that renewable energy sources will be a very important part of future energy scenarios. And yet, the United States and many other countries rely upon petroleum as the major source of energy. In fact, the United States currently imports more oil than it did in 1975.

For example, the United States imported approximately 6,000,000 barrels per day of petroleum and petroleum products in 1975 and now imports approximately 10,000,000 barrels per day. Approximately 90% of the products of a refinery are fuels (Pellegrino, 1998) and it is evident that this reliance on petroleum-based fuels and products will continue for several decades (Table 1-2).

The growing interest in *renewable energy sources* has been prompted, in part, by increasing concern over the pollution, resource depletion, and possible climate change (Speight, 1996a). A number of detailed studies (Boyle, 1996) suggest that *renewable energy sources* could well provide some of the world's energy by about the middle of the next century. The precise fraction of energy that will be provided by renewable energy sources beyond the year 2020 is not known and is difficult to estimate. Until that time, the world must be prepared to use available energy sources in the most efficient and environmentally acceptable manner. For example, beyond the year 2000 reformulated gasoline will be required to have a sulfur content less than 30 ppm (Absi-Halabi et al., 1997). Such energy sources are the fossil fuels. And in the context of this book, the most important energy source is petroleum.

It is a fact that in recent years, the average quality of crude oil has become worse. This is reflected in a progressive decrease in API gravity (i.e., increase in density) and a rise in sulfur content (Swain, 1991, 1993). However, it is now believed that there has been a continued tendency for the quality of crude oil feedstocks to deteriorate (Swain, 1998). Be that as it may, the nature of crude oil refining has changed considerably. This, of course, has led to the need to manage crude quality more effectively through evaluation (Chapter 2) and prod-

ucts slates (Waguespack and Healey, 1998). Indeed, the declining reserves of lighter crude oil has resulted in an increased need to develop options (Chapter 9) to desulfurize and upgrade the heavy feedstocks, specifically heavy oil and bitumen. This has resulted in a variety of process options that specialize in sulfur removal during refining (Chapter 9). It is worthy of note at this point that microbial desulfurization is becoming a recognized technology for desulfurization (Monticello, 1995; Armstrong et al., 1997) but will not be covered in this text.

The increasing supply of heavy crude oils is a matter of serious concern for the petroleum industry. In order to satisfy the changing pattern of product demand, significant investments in refining conversion processes will be necessary to profitably utilize these heavy crude oils. Although the most efficient and economical solution to this problem will depend to a large extent on individual country and company situations, the most promising technologies will likely involve the conversion of vacuum *residua* and *extra heavy crude oil* (bitumen) into light and middle distillate products.

The fuels that are derived from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. Petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry.

Petroleum is a carbon-based resource. Therefore, the geochemical carbon cycle is also of interest to fossil fuel usage in terms of petroleum formation, use, and the buildup of atmospheric carbon dioxide. Thus, the more efficient use of petroleum is of paramount importance. Petroleum technology, in one form or another, is with us until suitable alternative forms of energy are readily available (Boyle, 1996; Ramage, 1997).

Because petroleum is a carbon-based resource, the geochemical carbon cycle is also of interest to fossil fuel usage in terms of the buildup of atmospheric carbon dioxide (Berner and Lasaga, 1989). Models developed to map this phenomenon (Figure 1-1) include organic carbon but are more descriptive of the overall cycling of carbon. Such knowledge is of extreme importance in considering the so-called *greenhouse effect* that results from the burning of fossil fuels and the subsequent collection of the carbon dioxide in the atmosphere.

It is for this reason that the more efficient use of petroleum and, indeed, the conversion of petroleum to sulfur-free products is of paramount importance. Petroleum technology, in one form or another, is with us until suitable alternative forms of energy are readily available.

Therefore, a thorough understanding of the benefits and limitations of the conversion of petroleum to liquid products and desulfurization during conversion

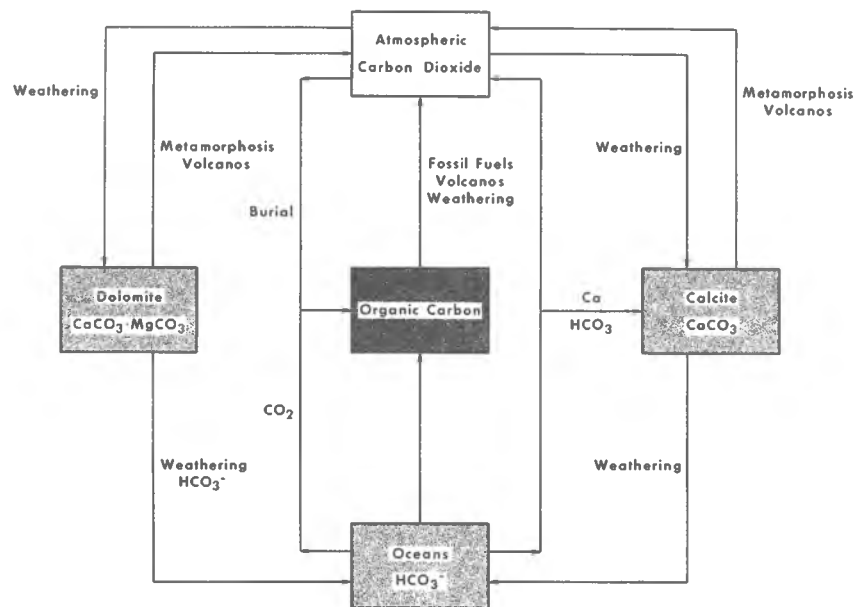


Figure 1-1 A simplified model of the carbon cycle.

is necessary and will be introduced within the pages of this book. However, the efficient conversion and desulfurization of petroleum, heavy oils, and residua is not merely a matter of passing the feedstock through a series of reactors. A thorough knowledge of the behavior of the feedstock under refinery conditions is not only beneficial but also necessary.

From a chemical standpoint petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds (Chapter 3).

Petroleum is not a uniform material. In fact, its chemical and physical (fractional) composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics. On a molecular basis, petroleum is a complex mixture of hydrocarbons with small amounts of organic compounds containing sulfur, oxygen, and nitrogen, as well as compounds containing metallic constituents, particularly vanadium nickel, iron, and copper. The hydrocarbon content may be as high as 97% w/w, for example in a light paraffinic crude oil or as low as 50% w/w in heavy crude oil and bitumen (Speight, 1999).

With the necessity of processing heavy oil, bitumen, and residua to obtain more gasoline and other liquid fuels, there has been the recognition that knowledge of the constituents of these higher boiling feedstocks is also of some importance. Indeed, the problems encountered in processing the heavier feedstocks can be equated to the *chemical character* and the *amount* of complex, higher-boiling constituents in the feedstock. Refining these materials is not just a matter of applying know-how derived from refining *conventional* crude oils but requires knowledge of the *chemical structure* and *chemical behavior* of these more complex constituents (Chapter 3).

However, heavy crude oil and bitumen are extremely complex and very little direct information can be obtained by distillation. It is not possible to isolate and identify the constituents of the heavier feedstocks using analytical techniques that rely upon volatility. Other methods of identifying the chemical constituents must be employed. Such techniques include a myriad of fractionation procedures (Chapter 3) as well methods designed to draw inferences about the hydrocarbon skeletal structures and the nature of the heteroatomic functions.

Petroleum (and the related materials *heavy oil* and *bitumen*) originate from living matter and exist in the solid, liquid, or gaseous state. Petroleum is formed in the ground by chemical and physical changes in plant (mainly) and animal residues under various conditions of temperature and pressure over long geological time periods (Speight, 1999). Carbon and hydrogen are the major elemental constituents with minor amounts of nitrogen, oxygen, sulfur, and metals. The types and relative amounts of hydrocarbons and other chemical compounds (compounds of carbon and hydrogen that also contain nitrogen, oxygen, sulfur, and/or metals) present in petroleum from different sources vary widely, but except for gasoline, the *ultimate compositions* and *heating values* fall within fairly narrow limits.

Of the data that are available (Speight, 1999), the ultimate composition of petroleum and heavy oil vary over fairly narrow limits of elemental distribution:

Carbon, 83.0–87.0%
Hydrogen, 10.0–14.0%
Nitrogen, 0.1–2.0%
Oxygen, 0.05–1.5%
Sulfur, 0.05–6.0%
Metals (Ni and V), <1000 ppm

despite the wide variation in physical properties from the lighter, more mobile crude oils at one extreme to the heavy asphaltic crude oils at the other extreme. Indeed, when the many localized or regional variations in maturation conditions are assessed it is perhaps surprising that the ultimate compositions are so similar.

Perhaps this observation, more than any other observation, is indicative of the similarity in nature of the precursors from one site to another.

Because of the narrow range of carbon and hydrogen content, it is not possible to classify petroleum or heavy oil on the basis of carbon content as coal is classified; carbon contents of coal can vary from as low as 75% w/w in lignite to 95% w/w in anthracite (Speight, 1994). Of course, other subdivisions are possible within the various carbon ranges of the coals, but petroleum is restricted to a much narrower range of elemental composition. However, it is possible to compare the atomic hydrogen-to-carbon (H/C) ratio of the heavy feedstocks with petroleum (Figure 1-2). This gives a general indication of the molar volumes of hydrogen that are required for upgrading but does not give any indication of the chemistry of upgrading.

The elemental analysis of oil sand bitumen (*extra heavy oil*) has also been widely reported (Speight, 1990), but the data suffer from the disadvantage that identification of the source is too general (i.e., Athabasca bitumen which covers several deposits) and is often not site specific. In addition, the analysis is quoted for separated bitumen, which may have been obtained by any one of several procedures and may therefore not be representative of the total bitumen on the sand. However, recent efforts have focused on a program to produce sound, reproducible data from samples for which the origin is carefully identified (Wallace et al., 1988). It is to be hoped that this program continues as it will provide a valuable database for tar sand and bitumen characterization.

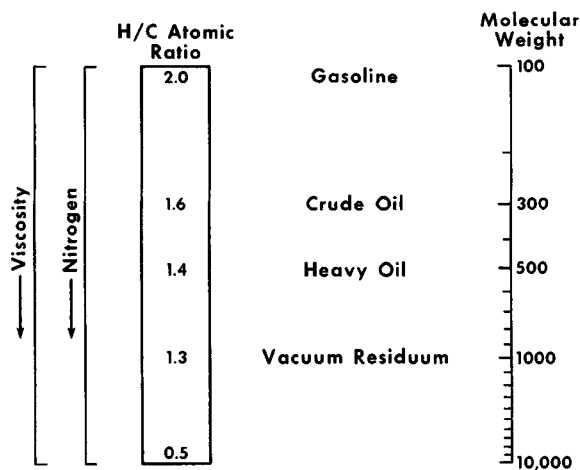


Figure 1-2 Representation of the atomic carbon/hydrogen ratio of various feedstocks.

Like conventional petroleum, of the data that are available the elemental composition of oil sand bitumen is generally constant and, like the data for petroleum, falls into a narrow range (Speight, 1999):

Carbon, $83.4 \pm 0.5\%$
Hydrogen, $10.4 \pm 0.2\%$
Nitrogen, $0.4 \pm 0.2\%$
Oxygen, $1.0 \pm 0.2\%$
Sulfur, $5.0 \pm 0.5\%$
Metals (Ni and V), >1000 ppm

The major exception to these narrow limits is the oxygen content of bitumen, which can vary from as little as 0.2% to as high as 4.5%. This is not surprising, since when oxygen is estimated by difference the analysis is subject to the accumulation of all of the errors in the other elemental data. Also, bitumen is susceptible to aerial oxygen and the oxygen content is very dependent upon the sample history. In addition, the ultimate composition of the Alberta bitumen does not appear to be influenced by the proportion of bitumen in the oil sand or by the particle size of the oil sand minerals.

The *heating values* of petroleum, heavy oil, and bitumen are measured as the *gross heats of combustion* that are given with reasonable accuracy by the equation:

$$Q = 12,400 - 2100d^2$$

where d is the 60/60°F specific gravity. Deviation is generally less than 1% although many highly aromatic crude oils show considerably higher values. The ranges for petroleum, heavy oil, and bitumen is 10,000 to 11,600 cal/gm (Speight, 1999). For comparison, the heat of combustion of gasoline is 11,000 to 11,500 cal/gm and for kerosene (and diesel fuel) the heat of combustion falls in the range 10,500 to 11,200 cal/gm. The heat of combustion for fuel oil is on the order of 9500 to 11,200 cal/gm.

With all of the scenarios in place, there is no doubt that *petroleum* and its relatives: *residua*, *heavy oil*, and *extra heavy oil (bitumen)* will be required to produce a considerable proportion of liquid fuels into the foreseeable future. Desulfurization processes will be necessary to remove sulfur in an environmentally acceptable manner to produce environmentally acceptable products. Refining strategies will focus on upgrading the heavy oils and residua and will emphasize the differences between the properties of the heavy crude feedstocks. This will dictate the choice of methods or combinations thereof for conversion of these materials to products (Schuetze and Hofmann, 1984).

Refinery processes can be categorized as *hydrogen addition processes* (e.g., hydroprocesses such as hydrotreating and hydrocracking, hydrovisbreaking, do-

nor-solvent processes) and as *carbon rejection processes* (e.g., catalytic cracking, coking, visbreaking, and other processes such as solvent deasphalting). All have serious disadvantages when applied singly to upgrading of heavy oils or residua. Removal of heteroatoms and metals by exhaustive hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodemetallization (HDM) is very expensive. The catalytic processes suffer from the disadvantage of excessive catalyst use due to metals and carbon deposition. Development of more durable and cheaper catalysts and additives to prevent coke lay-down has not yet solved the problem. The noncatalytic processes alone yield uneconomically large amounts of coke.

Both *hydrogen addition* and *carbon rejection* processes will be necessary in any realistic scheme of heavy oil upgrading (Suchanek and Moore, 1986). Most coker products require hydrogenation and most hydrotreated products require some degree of fractionation. For example, to maximize yields of transport fuels from Maya crude, efficient carbon rejection followed by hydrogenation may be necessary. There are various other approaches to the processing of other heavy oil residua (Bakshi and Lutz, 1987; Johnson et al., 1985). As of now, it is not known which combination of processes best converts a heavy feedstock into salable products.

Hydrodesulfurization and *hydrodemetallization* activities cannot be predicted by such conventional measurements as total sulfur, metals, or asphaltene content, or Conradson carbon value (Dolbear et al., 1987). To choose effective processing strategies, it is necessary to determine properties from which critical reactivity indices can be developed. Indeed, properties of heavy oil vacuum residua determined by conventional methods are not good predictors of behavior of feedstocks in upgrading processes (Dawson et al., 1989). The properties of residua vary widely and the existence of relatively large numbers of polyfunctional molecules results in molecular association that can affect reactivity. Therefore, it is evident that more knowledge is needed about the components of residua that cause specific problems in processing, and how important properties change during processing (Gray, 1990).

In summary, upgrading heavy oils and residua must, at some stage of the refinery operation utilize hydrodesulfurization. Indeed, hydrodesulfurization (HDS) processes are used at several places in virtually every refinery to protect catalysts, to meet product specifications related to environmental regulations (Table 1-3) (Speight, 1996b, 1999). Thus, several types of chemistry might be anticipated as occurring during hydrodesulfurization (Chapter 4). Similarly, hydrodenitrogenation (HDN) is commonly used only in conjunction with hydrocracking, to protect catalysts. Other hydrotreating processes are used to saturate olefins and aromatics to meet product specifications or to remove metals from residual oils.

Table 1-3 Outcome of Hydroprocesses During Refining

Reaction	Feedstock	Purpose
HDS ¹	Catalytic reformer feedstocks	Reduce catalyst poisoning
	Diesel fuel	Environmental specifications
	Distillate fuel oil	Environmental specifications
	Hydrocracker feedstocks	Reduce catalyst poisoning
	Coker feedstocks	Reduce sulfur content of coke
HDN ²	Lubricating oil	Improve stability
	Catalytic cracking feedstocks	Reduce catalyst poisoning
	Hydrocracker feedstocks	Reduce catalyst poisoning
HDM ³	Catalytic cracking feedstocks	Avoid metals deposition
		Avoid coke buildup
		Avoid catalyst destruction
		Avoid metals deposition
		Avoid coke buildup
CRR ⁴	Hydrocracker feedstocks	Avoid catalyst destruction
		Reduce coke buildup on catalyst
		Reduce coke yield
		Reduce coke yield
		Reduce coke yield

HDS¹: Hydrodesulfurization.HDN²: Hydrodenitrogenation.HDM³: Hydrodemetallization.CRR⁴: Carbon residue reduction.

2. HISTORY

The *history* of any subject is the means by which the subject is studied in the hopes that much can be learned from the events of the past. In the current context, the occurrence and use of petroleum, petroleum derivatives (naphtha), heavy oil, and bitumen is not new. The use of petroleum and its derivatives was practiced in pre-Christian times and is known largely through historical use in many of the older civilizations (Henry, 1873; Abraham, 1945; Forbes, 1958a, 1958b, 1959, 1964; James and Thorpe, 1994). Thus, the use of petroleum and the development of related technology is not such a modern subject as we are inclined to believe (Speight, 1999).

Early references to petroleum and its derivatives occur in the Bible, although by the time the various books of the Bible were written, the use of petroleum and bitumen was established. Nevertheless, these writings do offer documented examples of the use of petroleum and related materials. The caulking of a vessel with pitch is noted (Genesis 6:14) and the occurrence of *slime* (bitumen) *pits* in the Valley of Siddim (Genesis, 14:10), a valley at the southern end of the

Dead Sea, is reported. There is also reference to the use of tar as a mortar when the Tower of Babel was under construction (Genesis 11:3). Another example of the use of pitch (and slime) is given in the story of Moses (Exodus 2:3) where the basket in which he was placed to float in the river was caulked with a derivative. Perhaps the *slime* was a lower melting bitumen whereas the *pitch* was a higher melting material; the one (*slime*) acting as a flux for the other (*pitch*).

Use of asphalt by the Babylonians (1500 to 538 BC) is also documented. The Babylonians were well versed in the art of building, and each monarch commemorated his reign and perpetuated his name by construction of building or other monuments. The Egyptians were the first to adopt the practice of embalming their dead rulers and wrapping the bodies in cloth. Before 1000 BC, asphalt was rarely used in mummification, except to coat the cloth wrappings and thereby protect the body from the elements. After the viscera had been removed, the cavities were filled with a mixture of resins and spices, the corpse immersed in a bath of potash or soda, dried, and finally wrapped. From 500 to about 40 BC, asphalt was generally used both to fill the corpse cavities, as well as to coat the cloth wrappings. The word *mûmûla* first made its appearance in Arabian and Byzantine literature about 1000 AD, signifying *bitumen*.

Many other references to bitumen occur throughout the Greek and Roman empires, and from then to the Middle Ages early scientists (alchemists) frequently alluded to the use of bitumen. In later times, both Christopher Columbus and Sir Walter Raleigh (depending upon the country of origin of the biographer) have been credited with the discovery of the asphalt deposit on the island of Trinidad and apparently used the material to caulk their ships.

Approximately two thousand years ago, Arabian scientists developed methods for the distillation of petroleum and other naturally occurring organic products and these methods were introduced into Europe by way of Spain. This represents another documented use of the volatile derivatives of petroleum in addition to the nonvolatile fractions that were used as construction materials. The discovery of distillation led to an interest in the thermal product of petroleum (*nafta*; *naphtha*) when it was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare.

For example, there are records of the use of mixtures of pitch and/or *naphtha* with sulfur as a weapon of war during the Battle of Palatea, Greece, in the year 429 BC (Forbes, 1959). There are references to the use of a liquid material, *naft* (presumably the volatile fraction of petroleum which we now call *naphtha* and which is used as a solvent or as a precursor to gasoline), as an incendiary material during various battles of the pre-Christian era (James and Thorpe, 1994). This is the so-called Greek fire, a precursor and chemical cousin to napalm.

This probably represents the first documented use of the volatile derivatives of petroleum that led to a continued interest in petroleum. However, the hazards that can be imagined from such tactics could become very real, and perhaps often

fatal, to the users of what became known as *Greek fire* if any spillage occurred before ejecting the fire towards the enemy. The later technology for the use of Greek fire probably incorporated a heat-generating chemical such as quicklime (CaO) (Cobb and Goldwhite, 1995) which was suspended in the liquid and which, when coming into contact with water (to produce $[\text{Ca}(\text{OH})_2]$), released heat that was sufficient to cause the liquid to ignite. One assumes that the users of the fire were extremely cautious during periods of rain or, if at sea, during periods of turbulent weather.

The Baku region of northern Persia was also reported (by Marco Polo in 1271–1273) as having an established commercial petroleum industry producing oil *in such abundance that a hundred ships may load there at once*. It was also noted that the oil *was not good to eat but it is good for burning and as a salve for men and camels affected with itch or scab*. Polo also observed that *men come from a long distance to fetch this oil and in all the neighborhood no other oil is burned but this* (Latham, 1968). It is believed that the prime interest was in the kerosene fraction that was then known for its use as an illuminant as well as a higher-boiling fraction as the *salve*. By inference, it can be concluded that the distillation, and perhaps the thermal decomposition, of petroleum were established technologies. If not, Polo's diaries might well have contained a description of the stills or the reactors.

Recently, the issue of whether or not Polo actually made the journey to China has come under question (Wood, 1996). Be that as it may, it is interesting that Polo could have heard about the Baku petroleum operations from his far-away Venice. Or perhaps he heard the story from his father and uncle who, in turn, had heard it during a business venture to the port of Sudak (Solaia) that lay just east of Sevastopol on the northern peninsula of the Black sea. Or Polo may have heard the story personally since it is believed that he accompanied his father and uncle on at least one of their Crimean ventures. In either case, the petroleum industry in Baku seems to have been sufficiently known by merchants in the Crimea or the products of the industry were shipped to Constantinople for sale.

Bitumen was investigated in Europe during the Middle Ages (Bauer, 1546, 1556), and the separation and properties of bituminous products were thoroughly described. Other investigations continued, leading to a good understanding of the sources and use of this material even before the birth of the modern petroleum industry (Forbes, 1958a,b).

In terms of more modern bitumen use, the Cree Indians, native to the Athabasca region of northeastern Alberta, have known about the tar sands for well over 200 years. The documents by an itinerant New England fur trader note that the Indians used a sticky substance oozing from the riverbanks to waterproof their canoes.

The Canadian Government in 1890 took the first scientific interest in tar

sands. In 1897–1898, the sands were first drilled at Pelican Rapids on the Athabasca River, 80 miles southwest of Fort McMurray. Up to 1960, the development was mainly small commercial enterprises. Between 1957 and 1967, three extensive pilot-plant operations were conducted in the Athabasca region, each leading to a proposal for a commercial venture. Shell Canada, Ltd. tested in situ recovery of bitumen; a group headed by Cities Service Athabasca, Ltd. operated a pilot plant at Mildred Lake based on a hot-water extraction process; and Great Canadian Oil Sands, Ltd. operated a pilot plant at the present commercial plant site near Mildred Lake. In addition, Mobil Oil Company has conducted tests on in situ recovery, and Petrofina established a pilot facility across the Athabasca River from the site of the Great Canadian Oil Sands (GCOS, now Suncor) plant. The operations of the latter two pilot plants remain proprietary.

To continue such references is beyond the scope of this book, although they do give a flavor of the developing interest in petroleum as well as heavy oil, distillation residues (residua), and bitumen. However, it is sufficient to note that there are many other references to the occurrence and use of heavy oil and bitumen or petroleum derivatives up to the beginning of the modern petroleum industry (Cook and Despard, 1927; Mallowan and Rose, 1935; Nellensteyn and Brand, 1936; Mallowan, 1954; Marschner et al., 1978).

3. DEFINITIONS

Definitions are the means by which scientists and engineers communicate the nature of a material to each other and to the world, through either the spoken or the written word. Thus the definition of a material can be extremely important and have a profound influence on how the technical community and the public perceive that material.

Petroleum and the equivalent term *crude oil*, cover a wide assortment of materials consisting of mixtures of hydrocarbons and other compounds containing variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Speight, 1999 and references cited therein). Because petroleum is a mixture of widely varying constituents and proportions, its physical properties also vary widely (Chapter 2) and the color from colorless to black.

There are also other *types* of petroleum that are different from the conventional petroleum insofar as they are much more difficult to recover from the subsurface reservoir. These materials have a much higher viscosity (and lower API gravity) than conventional petroleum, and recovery of these petroleum types

usually requires thermal stimulation of the reservoir (Speight, 1999 *and references cited therein*).

When petroleum occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark to light colored liquid, it is often referred to as *conventional petroleum*. Heavy oils are the other *types* of petroleum that are different from conventional petroleum insofar as they are much more difficult to recover from the subsurface reservoir. The definition of heavy oils is usually based on the API gravity or viscosity, and the definition is quite arbitrary although there have been attempts to rationalize the definition based upon viscosity, API gravity, and density.

In addition to attempts to define petroleum, heavy oil, bitumen, and residua, there have been several attempts to classify these materials by the use of properties such as API gravity, sulfur content, or viscosity (Speight, 1999). However, any attempt to classify petroleum, heavy oil, and bitumen on the basis of a single property is no longer sufficient to define the nature and properties of petroleum and petroleum-related materials, perhaps even being an exercise in futility.

Classification will not be discussed in this text, having been described in more detail elsewhere (Speight, 1999). Let it suffice to use general definitions for the purposes of this text.

For many years, petroleum and heavy oil were very generally defined in terms of physical properties. For example, heavy oils were considered to be those crude oils that had gravity somewhat less than 20°API with the heavy oils falling into the API gravity range 10–15°. For example, Cold Lake heavy crude oil has an API gravity equal to 12° and extra heavy oils, such as tar sand bitumen, usually have an API gravity in the range 5–10° (Athabasca bitumen = 8°API). Residua would vary depending upon the temperature at which distillation was terminated but usually vacuum residua were in the range 2–8°API.

The definition of *heavy oil* is usually based on the API gravity or viscosity, and the definition is quite arbitrary although there have been attempts to rationalize the definition based upon viscosity, API gravity, and density (Chapter 2).

In a more general sense, the generic term *heavy oil* is often applied to a petroleum that has an API gravity of less than 20 degrees and usually, but not always, a sulfur content higher than 2% by weight. In contrast to conventional crude oils, heavy oils are darker in color and may even be black.

The term *heavy oil* has also been arbitrarily used to describe both the heavy oils that require thermal stimulation of recovery from the reservoir and the bitumen in bituminous sand (tar sand, *q.v.*) formations from which the heavy bituminous material is recovered by a mining operation. However, the term *extra heavy oil* is used to define the sub-category of petroleum that occurs in the near-solid state and is incapable of free flow under ambient conditions. *Bitumen* from tar sand deposits is often termed as *extra heavy oil*.

The term *bitumen* (also, on occasion, referred to as *native asphalt*, and *extra heavy oil*) includes a wide variety of naturally occurring reddish brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight. Bitumen is frequently found filling pores and crevices of sandstone, limestone, or argillaceous sediments, in which case the organic and associated mineral matrix is known as *rock asphalt* (Abraham, 1945; Hoiberg, 1964). Tar sand bitumen is a high-boiling material with little, if any, material boiling below 350°C (660°F) and the boiling range is close to the boiling range of an atmospheric residuum.

It is incorrect to refer to bitumen as *tar* or *pitch*. Although the word *tar* is somewhat descriptive of the black bituminous material, it is best to avoid its use with respect to natural materials. More correctly, the name *tar* is usually applied to the heavy product remaining after the destructive distillation of coal or other organic matter. *Pitch* is the distillation residue of the various types of tar.

Thus, alternative names, such as *bituminous sand* or *oil sand*, are gradually finding usage, with the former name (bituminous sands) more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and these terms are used interchangeably throughout this text.

However, in order to define conventional *petroleum*, *heavy oil*, and *bitumen*, the use of a single physical parameter such as viscosity is not sufficient. Other properties such as API gravity, elemental analysis, composition, and, most of all, the properties of the bulk deposit must also be included in any definition of these materials. Only then will it be possible to classify petroleum and its derivatives (Speight, 1999).

A *residuum* (*pl. residua*, also shortened to *resid*, *pl. resids*) is the residue obtained from petroleum after nondestructive distillation has removed all the volatile materials. The temperature of the distillation is usually maintained below 350°C (660°F) since the rate of thermal decomposition of petroleum constituents is minimal below this temperature but the rate of thermal decomposition of petroleum constituents is substantial above 350°C (660°F) (Figure 1-3).

Residua are black, viscous materials and are obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum) (Figure 1-4). They may be liquid at room temperature (generally atmospheric residua) or almost solid (generally vacuum residua) depending upon the cut-point of the distillation (Table 1-4) or depending on the nature of the crude oil (Table 1-5).

When a residuum is obtained from a crude oil and thermal decomposition has commenced, it is more usual to refer to this product as *pitch*. The differences between parent petroleum and the residua are due to the relative amounts of

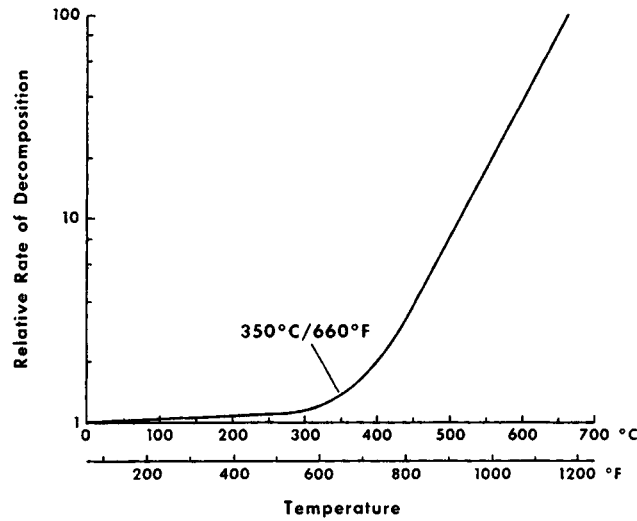


Figure 1-3 Simplified representation of the rate of thermal decomposition of petroleum constituents with temperature.

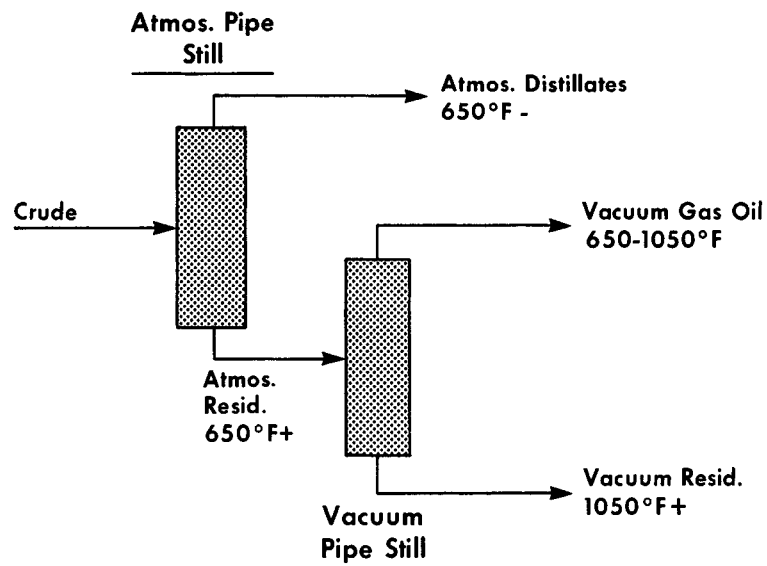


Figure 1-4 General representation of the production of residua by distillation.

Table 1-4 Properties of Tia Juana Crude Oil and its 650°F, 950°F, and 1050°F Residua (Speight, 1999)

	Whole crude	Residua		
		650°F ⁺	950°F ⁺	1050°F ⁺
Yield, vol%	100.0	48.9	23.8	17.9
Sulfur, wt%	1.08	1.78	2.35	2.59
Nitrogen, wt%		0.33	0.52	0.60
API gravity	31.6	17.3	9.9	7.1
Carbon residue, wt%				
Conradson		9.3	17.2	21.6
Metals				
vanadium, ppm		185		450
nickel, ppm		25		64
Viscosity				
Kinematic				
at 100°F	10.2	890		
at 210°F		35	1010	7959
Furol				
at 122°F		172		
at 210°F			484	3760
Pour point, °F	-5	45	95	120

various constituents present, which are removed or remain by virtue of their relative volatility (Figure 1-5).

The chemical composition of a residuum from an asphaltic crude oil is complex. Physical methods of fractionation usually indicate high proportions of asphaltenes and resins, even in amounts up to 50% (or higher) of the residuum. In addition, the presence of ash-forming metallic constituents, including such organometallic compounds as those of vanadium and nickel, is also a distinguishing feature of residua and heavy oils. Furthermore, the deeper the *cut* into the crude oil the greater is the concentration of sulfur and metals in the residuum and the greater the deterioration in physical properties (Table 1-4; Figures 1-6, 1-7, and 1-8).

Historically, there may be the impression that the industry is coming full circle. The early use of petroleum focused on the use of the heavier derivatives that remained after the more volatile fractions had evaporated under the prevailing conditions. This is illustrated in the next section. But first, a series of definitions by which petroleum and its reserves are defined.

The definitions that are used to describe petroleum *reserves* are often misunderstood because they are not adequately defined at the time of use. Therefore,

Table 1-5 Miscellaneous Properties of Heavy Oils and Residua

Crude oil origin	Kuwait ^a		Kuwait		Venezuela (east)		Burzurgan		Boscan		Khafji		California		Cabimas	
	gas oil	Vacuum	Atmospheric	Vacuum	Atmospheric	Vacuum	—	—	—	—	Atmospheric	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum
Fraction of crude, vol%	—	—	42	21	74	52	78	—	—	—	—	—	23	34	—	—
Gravity, °API	22.4	—	13.9	5.5	9.6	3.1	5.0	—	—	—	14.4	6.5	43	6.8	—	—
Viscosity SUS, 210°F	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SFS, 122°F	—	—	553	500,000	27,400	—	—	—	—	—	—	—	—	—	—	—
SFS, 210°F	—	—	—	—	—	—	—	—	—	—	429	—	—	—	—	—
cSt, 100°F	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
cSt, 210°F	—	—	55	1900	—	3355	5250	—	—	—	—	—	15,000	7800	—	—
Pour point, °F	—	—	65	—	95	—	—	—	—	—	—	—	—	162	—	—
Sulfur, wt%	2.97	—	4.4	5.45	2.6	6.2	5.9	—	—	—	4.1	5.3	2.3	3.26	—	—
Nitrogen, wt%	0.12	—	0.26	0.39	0.61	0.45	0.79	—	—	—	—	—	0.98	0.62	—	—
Metals, ppm																
Nickel	0.2	—	14	32	94	76	133	—	—	—	37	53	120	76	—	—
Vanadium	0.04	—	50	102	218	233	1264	—	—	—	89	178	180	614	—	—
Asphaltenes, wt%																
Pentane insolubles	0	—	—	11.1	—	—	—	—	—	—	—	12.0	19.0	12.9	—	—
Hexane insolubles	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heptane insolubles	0	—	2.4	7.1	9	18.4	15.3	—	—	—	—	—	—	10.5	—	—
Resins, wt%	0	—	—	39.4	—	—	—	—	—	—	—	—	—	—	—	—
Carbon residue, wt%																
Ramsbottom	<0.1	—	9.8	—	14.5	—	—	—	—	—	—	—	—	—	—	—
Conradson	0.09	—	12.2	23.1	—	22.5	18.0	—	—	—	21.4	—	24.0	18.7	—	—

Crude oil origin	Residuum type	Arabian light	Louisiana	Saudi Arabia	Alaska (North Slope)		Boscan	Tar Sand Triangle	P.R. Spring	N.W. Asphalt Ridge
					Atmospheric	Vacuum				
Fraction of crude, vol%		—	13.1	20	58	22	100	100	100	100
Gravity, °API		16.7	11.3	5.0	15.2	8.2	10.3	11.1	10.3	14.4
Viscosity SUS, 210°F		—	—	—	1281	—	—	—	—	—
SFS, 122°F		—	—	—	—	—	—	—	—	—
SFS, 210°F		—	—	—	—	—	—	—	—	—
cSt, 100°F		—	—	—	—	—	20,000	7000 ^b	200,000 ^b	15,000 ^b
cSt, 210°F		27	700	2700	42	1950	—	—	—	—
Pour point, °F		—	—	—	75	—	37	—	—	—
Sulfur, wt%		3.00	0.93	5.2	1.6	2.2	5.6	4.38	0.75	0.59
Nitrogen, wt%		—	0.38	0.30	0.36	0.63	—	0.46	1.00	1.02
Metals, ppm										
Nickel		11	20	28	18	47	117	53	98	120
Vanadium		28	—	75	30	82	1220	108	25	25
Asphaltenes, wt%										
Pentane insolubles		—	6.5	15.0	4.3	8.0	12.6	26.0	16.0	6.3
Hexane insolubles		—	—	—	—	—	11.4	—	—	—
Heptane insolubles		2.0	—	—	31.5	—	—	—	—	—
Resins, wt%		—	—	—	—	—	24.1	—	—	—
Carbon residue, wt%										
Ramsbottom		8	12.0	20.0	8.4	17.3	14.0	—	—	—
Conradson		—	—	—	—	—	—	21.6	12.5	3.5

(continued)

Table 1-5 Continued

Crude oil origin	Athabasca	Lloyd-minster	Cold Lake	Qayarah	Jobo	Bachaquero		Heavy Arabian	West Texas	
						Atmospheric	Vacuum		Vacuum	Atmospheric
Residuum type	—	—	—	—	—	—	—	—	—	—
Fraction of crude, vol%	100	100	100	100	100	34	—	27	—	—
Gravity, °API	5.9	14.5	10.0	15.3	8.6	17	2.8	4	9.4	18.4
Viscosity SUS, 210°F	513	260	—	—	—	—	—	—	—	—
SFS, 122°F	—	294	—	—	—	—	—	—	313	86
SFS, 210°F	820	—	—	—	247	—	—	—	—	—
cSt, 100°F	—	—	—	—	—	—	—	—	—	—
cSt, 210°F	—	—	79	—	—	—	—	—	—	—
Pour point, °F	50	38	—	—	—	—	—	—	—	—
Sulfur, wt%	4.9	4.3	4.4	8.4	3.9	2.4	3.7	5.3	3.3	2.5
Nitrogen, wt%	0.41	—	0.39	0.7	0.7	0.3	0.6	0.4	0.5	0.6
Metals, ppm										
Nickel	86	40	62	60	103	450	100	230	27	11
Vanadium	167	100	164	130	460	—	900	—	57	20
Asphaltenes, wt%										
Pentane insolubles	17.0	12.9	15.9	20.4	18	10	—	25	—	—
Hexane insolubles	13.5	—	—	14.3	—	—	—	—	—	—
Heptane insolubles	11.4	—	10.8	13.5	—	—	—	—	—	—
Resin, wt%	34.0	38.4	31.2	36.1	—	—	—	—	—	—
Carbon residue, wt%										
Ramsbottom	14.9	—	—	—	—	—	—	—	—	—
Conradson	18.5	9.1	13.6	15.6	14	12	27.5	—	16.9	6.6

Crude oil origin	Tia Juana (light)		Safariya		PR Spring	Asphalt Ridge	Tar Sand Triangle	Sunnyside
	Atmospheric	Vacuum	Atmospheric	Vacuum				
Residuum type					Bitumen	Bitumen	Bitumen	Bitumen
Fraction of crude, vol%	49	18	40	22	100	100	100	100
Gravity, °API	17.3	7.1	11.1	2.6	10.3	14.4	11.1	—
Viscosity SUS, 210°F	165	—	—	—	—	—	—	—
SFS, 122°F	172	—	—	—	—	—	—	—
SFS, 210°F	—	—	—	—	—	—	—	—
cSt, 100°F	890	—	—	—	—	—	—	—
cSt, 210°F	35	7959	—	—	—	—	—	—
Pour point, °F	—	—	—	—	—	—	—	—
Sulfur, wt%	1.8	2.6	4.3	5.3	0.8	0.6	4.4	0.5
Nitrogen, wt%	0.3	0.6	0.4	0.4	1.0	1.0	0.5	0.9
Metals, ppm								
Nickel	25	64	26	46	98	120	53	—
Vanadium	185	450	109	177	25	25	108	—
Asphaltenes, wt%								
Pentane insolubles	—	—	17.0	30.9	—	—	—	—
Hexane insolubles	—	—	—	—	—	—	—	—
Heptane insolubles	—	—	—	—	—	—	—	—
Resins, wt%	—	—	—	—	—	—	—	—
Carbon residue, wt%								
Ramsbottom	—	—	—	—	12.5	3.5	21.6	—
Canradson	9.3	21.6	14.0	25.9	—	—	—	—

^a Included for comparison.^b Estimated.

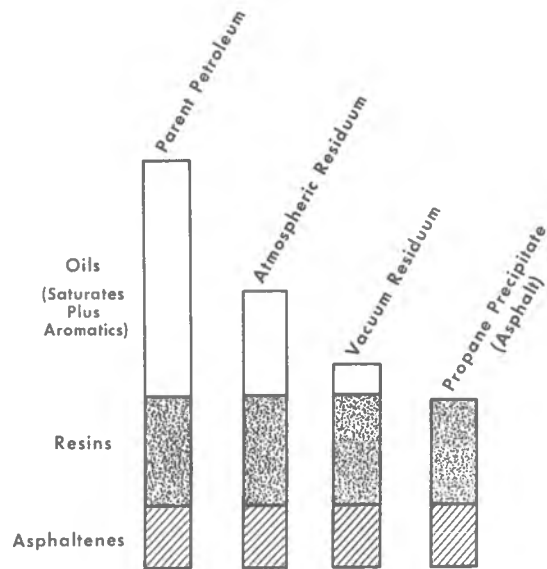


Figure 1-5 Simplified relationship between petroleum, two residua, and propane asphalt.

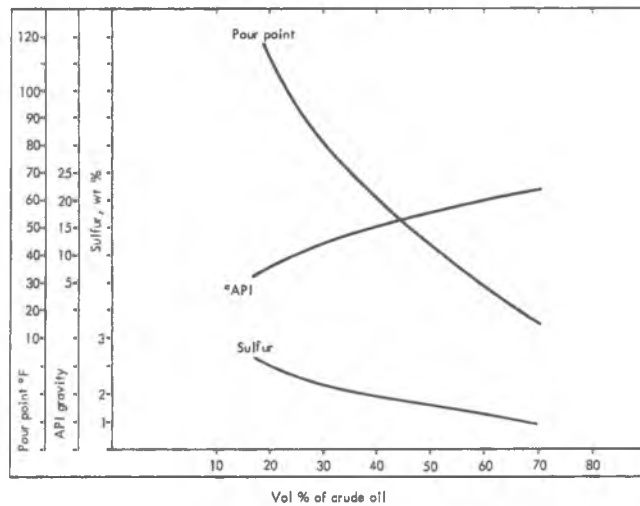


Figure 1-6 General relationship of the properties of residua from Tia Juana light crude oil with yield.

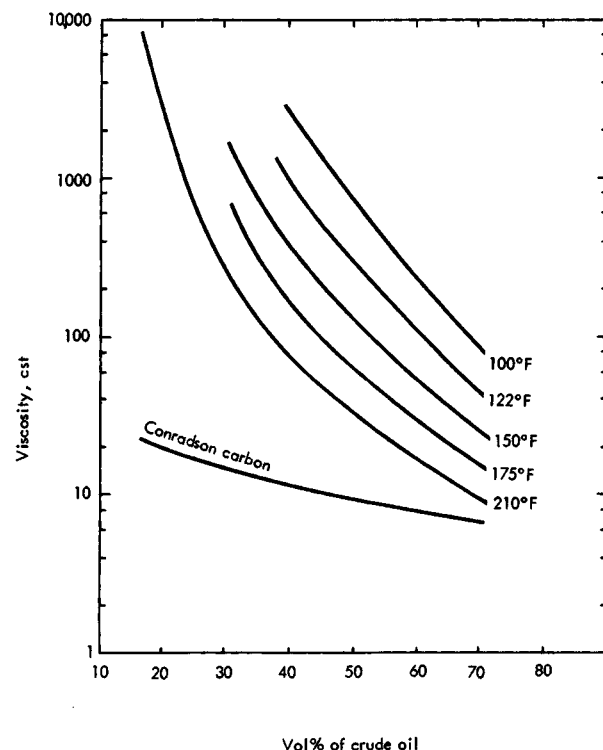


Figure 1-7 General relationship of the viscosity of residua from Tia Juana light crude oil with yield.

as a means of alleviating this problem, it is pertinent at this point to consider the definitions used to describe the amount of petroleum that remains in subterranean reservoirs (Speight, 1999).

Petroleum is a *resource*; in particular, petroleum is a *fossil fuel resource* (Speight, 1999). A *resource* is the entire commodity that exists in the sediments and strata whereas the *reserves* represent that fraction of a commodity that can be recovered economically. However, the use of the term *reserves* as being descriptive of the resource is subject to much speculation. In fact, it is subject to word variations! For example, reserves are classed as *proved*, *unproved*, *probable*, *possible*, and *undiscovered*.

Proven reserves are those reserves of petroleum that are actually found by drilling operations and are recoverable by means of current technology. They have a high degree of accuracy and are frequently updated as the recovery opera-

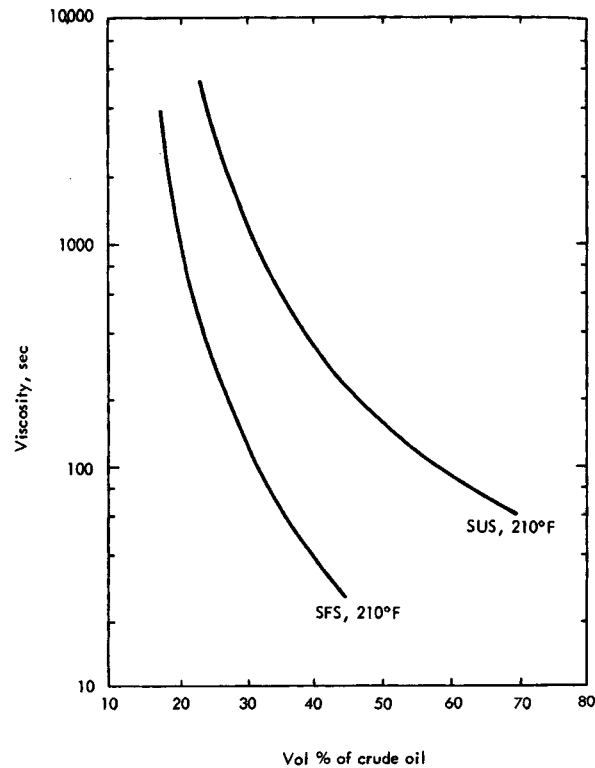


Figure 1-8 General relationship of the SUS and SFS viscosity of residua from Tia Juana light crude oil with yield.

tions proceed. They may be updated by means of reservoir characteristics, such as production data, pressure transient analysis, and reservoir modeling.

The term *inferred reserves* is also commonly used in addition to, or in place of, *potential reserves*. Inferred reserves are regarded as having a higher degree of accuracy than potential reserves, and the term is applied to those reserves that are estimated using an improved understanding of reservoir frameworks. The term also usually includes those reserves that can be recovered by further development of recovery technologies.

Probable reserves are those reserves of petroleum that are nearly certain but about which a slight doubt exists. *Possible reserves* are those reserves of petroleum with an even greater degree of uncertainty about recovery but about which there is some information. An additional term *potential reserves* is also used on occasion; these reserves are based upon geological information about

the types of sediments where such resources are likely to occur and they are considered to represent an educated guess. Then, there are the so-called *undiscovered reserves*, which are little more than figments of the imagination! The terms *undiscovered reserves* or *undiscovered resources* should be used with caution, especially when applied as a means of estimating reserves of petroleum reserves. The data are very speculative and are regarded by many energy scientists as having little value other than unbridled optimism.

The differences between the data obtained from these various estimates can be considerable, but it must be remembered that any data about the reserves of petroleum (and, for that matter, about any other fuel or mineral resource) will always be open to question about the degree of certainty. Thus, in reality, *proven reserves* may be a very small part of the total hypothetical and/or speculative amounts of a resource.

At some time in the future, certain *resources* may become *reserves*. Such a reclassification can arise as a result of improvements in recovery techniques which may either make the resource accessible or bring about a lowering of the recovery costs and render winning of the resource an economical proposition. In addition, other uses may also be found for a commodity, and the increased demand may result in an increase in price. Alternatively, a large deposit may become exhausted and unable to produce any more of the resource thus forcing production to focus on a resource that is lower grade but has a higher recovery cost.

4. OCCURRENCE

The reservoir rocks that yield crude oil range in age from Precambrian to Recent geologic time but rocks deposited during the Tertiary, Cretaceous, Permian, Pennsylvanian, Mississippian, Devonian, and Ordovician periods are particularly productive. In contrast, rocks of Jurassic, Triassic, Silurian, and Cambrian age are less productive and rocks of Precambrian age yield petroleum only under exceptional circumstances.

Most of the crude oil currently recovered is produced from underground reservoirs. However, surface seepage of crude oil and natural gas is common in many regions. In fact, it is the surface seepage of oil that led to the first use of the high boiling material (bitumen) in the Fertile Crescent. It may also be stated that the presence of active seeps in an area is evidence that oil and gas is still migrating.

The majority of crude oil reserves identified to date are located in a relatively small number of very large fields, known as *giants*. In fact, approximately three hundred of the largest oil fields contain almost seventy five percent of the available crude oil. Although most of the world's nations produce at least minor

amounts of oil, the primary concentrations are in the Persian Gulf, North and West Africa, the North Sea, and the Gulf of Mexico. In addition, of the ninety oil-producing nations, five Middle Eastern countries contain almost seventy percent of the current, known oil reserves.

4.1 Petroleum

Petroleum is by far the most commonly used source of energy, especially as the source of liquid fuels. In recent years, the average quality of crude oil has become worse. This is reflected in a progressive decrease in API gravity (i.e., increase in density) and a rise in sulfur content (Swain, 1991, 1993, 1998). Thus, the nature of crude oil refining has been changed considerably.

The declining reserves of lighter crude oil has resulted in an increasing need to develop options (Chapter 8) to upgrade the abundant supply of known heavy oil reserves. In addition, there is considerable focus and renewed efforts on adapting recovery techniques to the production of heavy oil. In fact, the occurrence of petroleum and its use as the source of much-needed liquid fuels is the key to the future of liquid fuels production (Table 1-2).

At the present, several countries are recognized as producers of petroleum and have available reserves. These available reserves have been defined (Campbell, 1997), but not quite in the manner outlined above. For example, on a worldwide basis the produced conventional crude oil is estimated to be approximately 784 billion (784×10^9) bbl with approximately 900 to 1000 billion ($900\text{--}1000 \times 10^9$) bbl remaining as reserves (Alazard and Montadert, 1993). It is also estimated that there are 180 billion bbl, which remain to be discovered with approximately 1 trillion (1×10^{12}) bbl yet-to-be-produced. The annual depletion rate is estimated to be 2.6%. However, it is believed that the apparent increase in the proven reserves of conventional crude oil is due more to revisions of previous estimates of reserves rather than to new discoveries (Alazard and Montadert, 1993). The outlook for liquid fuels into the next century and for the next several decades is believed to hinge upon the availability and conversion of heavy oils, residua, and extra heavy oils (bitumen).

There are many predictions of petroleum resource and supply models and many of these predictions have failed (Linden, 1998). However, the reality is that the United States is one of the largest importers of petroleum since domestic production is only about 64% of what it was in 1975. Domestic production of crude oil has fallen from approximately 10,000,000 barrels a day in 1975 to 6,400,000 at the end of 1998. At the same time, the total daily imports of foreign crude oil and products into the United States at the end of 1998 was approximately 10,000,000 barrels. Thus, imported crude oil and products represent approximately 61% of the daily crude oil requirements in the United States (Oil & Gas Journal, 1998; Pellegrino, 1998). These data do not include liquids produced

during domestic natural gas recovery operations that reduce the dependency on imported oil and products into the 59–60% range. Be that as it may, this is still a high dependency on imported crude oil! Thus, the imports of crude oil into the United States continue to rise and it is interesting, perhaps frightening, that projections made in 1990 (Figure 1-9) are quite close to the actual data and that the trend is for an increase in imported crude oil and products.

There seems to be little direction in terms of stability of supply or any measure of self-sufficiency in liquid fuels precursors, other than resorting to military action. This is particularly important for the United States refineries since a disruption in supply could cause major shortfalls in feedstock availability.

In addition, the crude oils available today to the refinery are quite different in composition and properties to those available some 30 years ago (Swain, 1998; Speight, 1999). The current crude oils are somewhat heavier insofar as they have higher proportions of nonvolatile (asphaltic) constituents. In fact, by the standards of yesteryear, many of the crude oils currently in use would have been classified as heavy feedstocks, bearing in mind that they may not approach the definitions used today for heavy crude oils. Changes in feedstock character, such as this tendency to heavier materials, require adjustments to refinery operations to handle these heavier crude oils to reduce the amount of coke formed during processing and to balance the overall product slate.

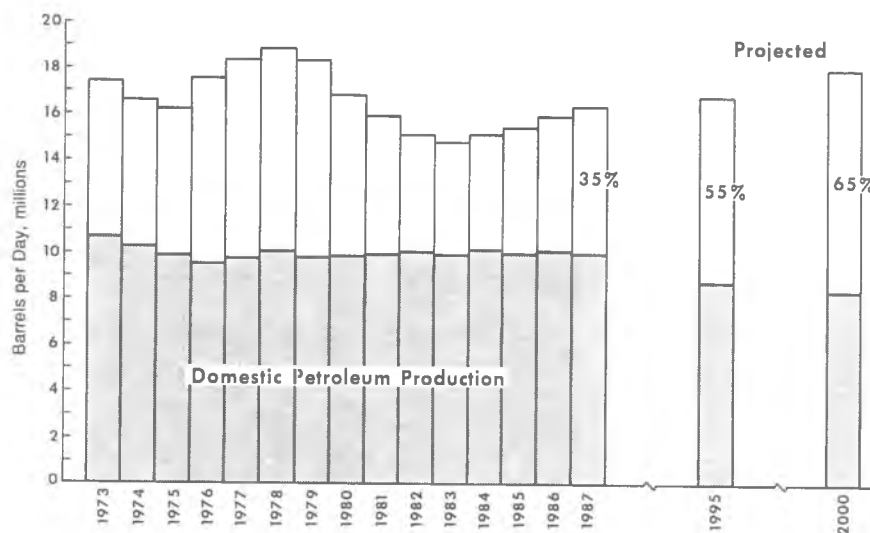


Figure 1-9 General trends of U.S. consumption and domestic production of petroleum for the past twenty-five years. (From Speight, 1991.)

4.2 Heavy Oil

When petroleum occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark to light colored liquid, it is often referred to as conventional petroleum.

Heavy oil is another *type* of petroleum that is different from conventional petroleum insofar as it is much more difficult to recover from the subsurface reservoir (Moritis, 1998). *Heavy oil* has a much higher viscosity (and lower API gravity) than conventional petroleum, and recovery of heavy oil usually requires thermal stimulation of the reservoir.

4.3 Bitumen (Extra Heavy Oil)

Bitumen in tar sand deposits represents a potentially large supply of energy. However, many of these reserves are only available with some difficulty and optional refinery scenarios will be necessary for conversion of these materials to low-sulfur liquid products (Chapter 9) because of the substantial differences in character between conventional petroleum and tar sand bitumen (Table 1-6). Bitumen recovery requires the prior application of reservoir fracturing procedures before the introduction of thermal recovery methods. Currently, commercial operations in Canada use mining techniques for bitumen recovery.

Because of the diversity of available information and the continuing attempts to delineate the various world tar sand deposits, it is virtually impossible to present accurate numbers that reflect the extent of the reserves in terms of the barrel unit. Indeed, investigations into the extent of many of the world's deposits are continuing at such a rate that the numbers vary from one year to the next. Accordingly, the data quoted here must be recognized as approximate with the potential of being quite different at the time of publication.

Throughout this text, frequent reference is made to tar sand bitumen, but because commercial operations have been in place for over 30 years (Spragins, 1978; Speight, 1990) it is not surprising that more is known about the Alberta (Canada) tar sand reserves than any other reserves in the world. Therefore, when discussion is made of tar sand deposits, reference is made to the relevant deposit, but when the information is not available, the Alberta material is used for the purposes of the discussion.

Tar sand deposits are widely distributed throughout the world (Speight, 1990, 1999 and references cited therein). The potential reserves of bitumen that occur in tar sand deposits have been variously estimated on a world basis as being in excess of 3 trillion (3×10^{12}) barrels of petroleum equivalent (Table 1-7). The reserves that have been estimated for the United States has been estimated to be in excess of 52 million (52×10^6) barrels (Table 1-8). That commercialization has taken place in Canada does not mean that commercialization is

Table 1-6 Comparison of the Properties of Conventional Petroleum with Those of Bitumen

		Bitumen	Conventional
Gravity, ° API		8.6	25–37
Distillation, °F	Vol%		
	IBP	—	
	5	430	
	10	560	—
	30	820	
	50	1,010	<650
Viscosity, SUS @ 100°F (38°C)		35,000	<30
	SUS @ 210°F (99°C)	513	
Pour point, °F		+50	
Elemental analysis, wt%			
	Carbon	83.1	86
	Hydrogen	10.6	13.5
	Sulfur	4.8	0.1–2.0
	Nitrogen	0.4	0.2
	Oxygen	1.1	
Composition, wt%			
	Asphaltenes	19	<10
	Resins	32	
	Oils	49	>60
Metals, ppm			
	Vanadium	250	
	Nickel	100	
	Iron	75	2–10
	Copper	5	
Ash, wt%		0.75	0
Conradson carbon, wt%		13.5	1–2
Net heating value, Btu/pound		17,500	~19,500

imminent for other tar sands deposits. There are considerable differences between the Canadian and the U.S. deposits that could preclude across-the-board application of the Canadian principles to the U.S. sands (Speight, 1990). The key is accessibility and recoverability.

Various definitions have been applied to energy reserves (*q.v.*) but the crux of the matter is the amount of a resource that is recoverable using current technology. And although tar sands are not a principal energy reserve, they certainly are significant with regard to projected energy consumption over the next several generations.