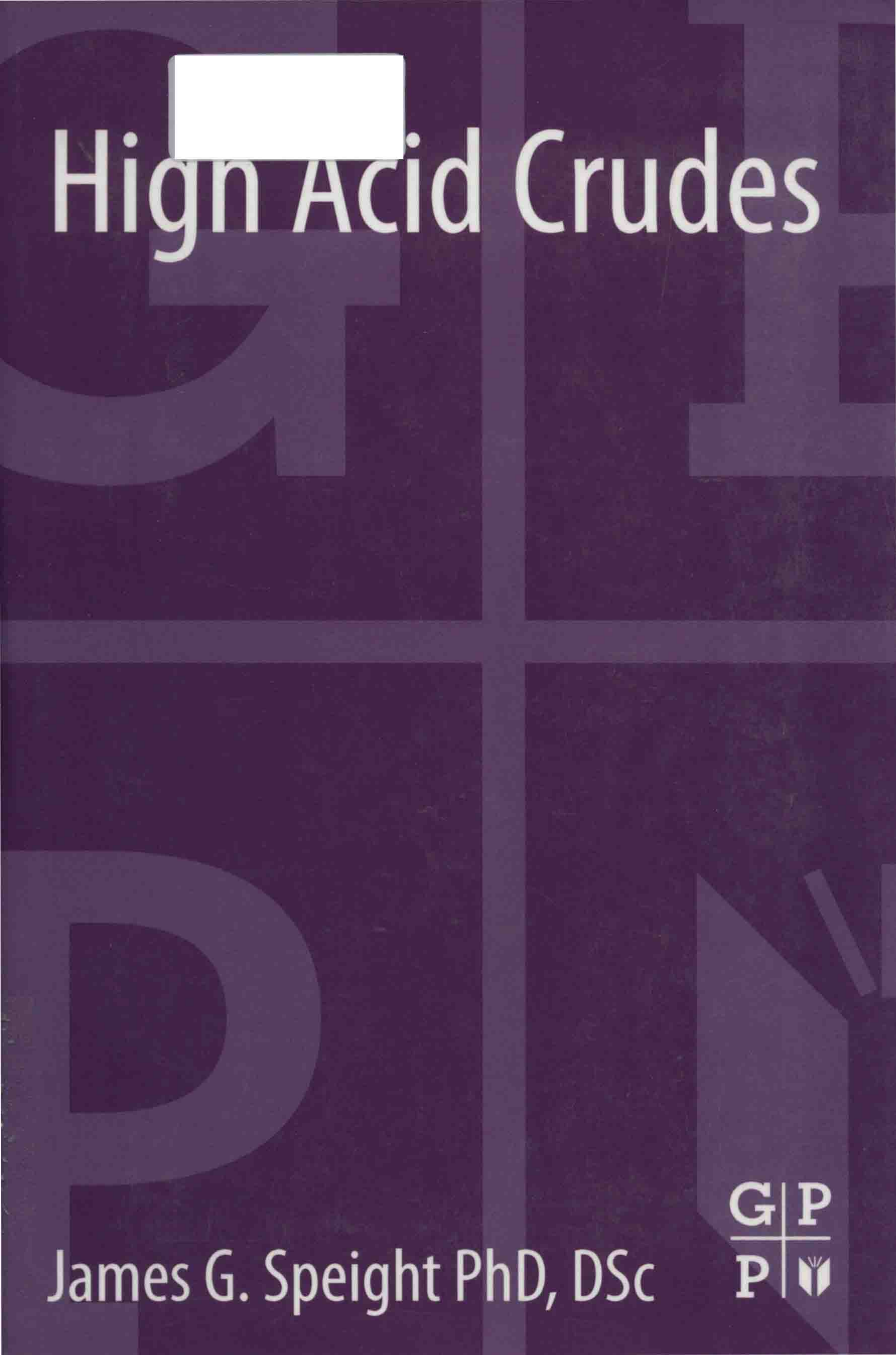

High Acid Crudes

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High Acid Crudes

PREFACE

Naphthenic acids confer acidic properties on crude oil and the extent of the acidity is expressed as the *total acid number* (TAN), which is the number of milligrams of potassium hydroxide required to neutralize one gram of crude oil. Conversely, the *total base number* (TBN) is determined by titration with acids and is a measure of the amount of basic substances in the oil always under the conditions prescribed by the test method.

High acid crude oils represent the fastest growing segment of global crude oil production. California, Brazil, North Sea, Russia, China, India, and West Africa are known to supply high acid crudes—synthetic crude oil derived from tar sand bitumen is often deemed highly acidic. Due to the overall shortage of processing capacity for high acid crude oil by many refineries and the need to produce low boiling (light) products, high quality crudes are often in high demand, resulting in abundant supply and significant discounts for opportunity crude oils.

The book provides an overview with some degree of detail of the identification of naphthenic acids and their influence on refinery process units. There are process descriptions with a focus on the examination and identification of corrosion and metallurgical problems that occur in process units caused by high acid crude oils.

Laramie, WY

March 15, 2014

CONTENTS

CHAPTER 1

Naphthenic Acids in Petroleum

1.1 INTRODUCTION

Crude oil (and the interchangeable term *petroleum*) is a highly complex mixture and typically contains thousands of components (Speight and Ozum, 2002; Hsu and Robinson, 2006; Gary et al., 2007; Cai and Tian, 2011; Speight, 2014a).

Within the large number of constituents of crude oil is a subclass of the oxygen-containing species known as *naphthenic acids* and the term *naphthenic acids* is commonly used to describe an isomeric mixture of carboxylic acids (*predominantly* monocarboxylic acids) containing one or several saturated fused alicyclic rings (Hell and Medinger, 1874; Lochte, 1952; Ney et al., 1943; Tomczyk, et al., 2001; Rodgers et al., 2002; Barrow et al., 2003; Clemente et al., 2003a,b; Zhao et al., 2012). However, in petroleum terminology it has become customary to use this term to describe the whole range of organic acids found in crude oils; species such as phenols and other acidic species are often included in the naphthenic acid category.

Naphthenic acids are a naturally occurring, complex mixture of cycloaliphatic carboxylic acids recovered from petroleum and from petroleum distillates and the term *naphthenic acid*—as used in the petroleum industry—refers collectively to all of the carboxylic acids present in crude oil. Naphthenic acids are classified as monobasic carboxylic acids of the general formula RCOOH, in which R represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives as well as any acyclic aliphatic acids (Brient et al, 1995; Petkova et al., 2009). Although alicyclic (naphthenic) acids appear to be the more prevalent on the naphthenic acid class, it is now well known that phenol derivatives are also present in crude oil (Speight, 2014).

It has generally been concluded that the carboxylic acids in petroleum with fewer than eight carbon atoms per molecule are almost entirely aliphatic in nature; monocyclic acids begin at

C_6 and predominate above C_{14}. This indicates that the complex structures of the carboxylic acids, which continue to offer challenges in determining these structures, are believed (with reasonable justification) to correspond with those of the hydrocarbons with which they are associated in the crude oil (Robbins, 1998; Rodgers et al., 2002). In the range in which paraffins are the prevailing type of hydrocarbon, the aliphatic acids may be expected to predominate. Similarly, in the ranges in which monocycloparaffins and dicycloparaffins prevail, it has been theorized that the prevalent species will be monocyclic and dicyclic acids, respectively.

More important in the present context, acidic species (naphthenic acids) in the crude oil become active corrosive agents in the distillation column and cause liquid phase corrosion at process temperatures of 250–400°C (480–750°F). Naphthenic acids can cause corrosion in refinery equipment, resulting in costs that are ultimately passed on to the consumer, and the corrosiveness of the acids is believed to be linked to their size and structure. The naphthenic acids content in crude oils is expressed as the total acid number (TAN), which is measured in units of milligrams of potassium hydroxide required to neutralize a gram of oil.

Acidic crude oils are grades of crude oil that contain substantial amounts of naphthenic acids or other acids. They are also called high acid crudes after the most common measure of acidity: the *TAN*. Arbitrarily, a crude oil with a TAN on the order of 0.5 mg KOH/g acid and higher usually qualifies as high acid crude. At an acid number of 1.0 mg KOH/g crude oil, crude oils begin to be heavily discounted in value. Other than acidity, there appear to be no other distinguishing properties that characterize these oils, although most high acid crude oils often have a gravity that is <29°API and are often (but not always) low in sulfur (except for Venezuelan high acid crudes) and frequently produce high yields of gas oil. Acidic oils can vary widely in most other properties.

The interest in (or willingness to accept) high acid crudes as refinery feedstocks high acid crudes is the result of these oils trading at discounts of several dollars per barrel when compared to conventional (low acid) crude oils but processing high acid crude oils (HACs) is also challenging for refineries, especially those not designed to handle crude oil containing naphthenic acids (Heller et al., 1963; Speight, 2014).

In terms of classification, which is not scientifically based, high acid crudes often fall into the subgroup of crude oils known as opportunity crudes. Generally, *opportunity crude oils* are often dirty and need cleaning before refining by removal of undesirable constituents, such as high sulfur, high nitrogen, and high aromatics (such as polynuclear aromatic) components. A controlled visbreaking treatment would *clean up* such crude oils by removing these undesirable constituents (which, if not removed, would cause problems further down the refinery sequence) as coke or sediment.

It is perhaps more correct to separate the *HACs* as a subclass of crude oil. HACs, which contain significant amounts of naphthenic acids, cause corrosion in the refinery—corrosion is predominant at temperatures in excess of 180°C (355°F) (Ghoshal and Sainik, 2013; Speight, 2014)—and occur particularly in the atmospheric distillation unit (the first point of entry of the HAC) and also in the vacuum distillation units. In addition, overhead corrosion is caused by the mineral salts, magnesium, calcium, and sodium chloride which are hydrolyzed to produce volatile hydrochloric acid, causing a highly corrosive condition in the overhead exchangers and must be removed (Erfan, 2011). Therefore, these salts present a significant contamination in opportunity crude oils. Other contaminants in opportunity crude oils which are shown to accelerate the hydrolysis reactions are inorganic clays and organic acids.

1.2 ORIGIN AND OCCURRENCE

Over the next decade (from the time of writing), it is forecast that the supply of high acid crudes (crudes having a TAN in excess of 1.0 mg KOH/g crude oil) will continue to increase significantly, with production rising across the world. All of these crude oils have significant acid numbers. Therefore, corrosion management is of vital importance to ensure that corrosion risk to the plant is minimized and an efficient inspection system must be in place to identify the corrosion which might occur and areas of the plant that might be subject to severe corrosion are identified so that the need for more corrosion resistant alloys can be predicted. In order to understand corrosion and corrosion management, it is necessary to understand the formation (origin) at the time of petroleum generation as well as the nature of naphthenic acids.

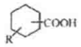
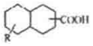
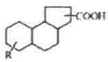
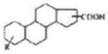
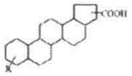
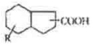
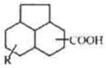
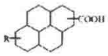
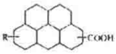
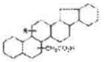
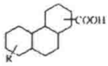
The generation of petroleum is associated with the deposition of organic detritus. The detritus deposition occurs during the development of fine-grained sedimentary rocks that occur in marine, near-marine, or even nonmarine. Petroleum is believed to be the product arising from the decay of plant and animal debris that was incorporated into sediments at the time of deposition. However, the details of this transformation and the mechanism by which petroleum is expelled from the source sediment and accumulates in the reservoir rock are still uncertain but progress has been made in environments (Speight, 2014a and references cited therein).

Nevertheless, the composition of petroleum is greatly influenced not only by the nature of the precursors that eventually form petroleum but also by the relative amounts of these precursors (that are dependent upon the local flora and fauna) that occur in the source material. Hence, it is not surprising that petroleum composition can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells are more than likely to produce petroleum with very different characteristics. The same rationale can apply to the occurrence and character of the various constituents of petroleum, not the least of which (in the current context) is the fraction known as *naphthenic acids*.

Naphthenic acid is the generic name used for all of the organic acids present in crude oils—most of the acids arise as biochemical markers of crude oil origin and maturation (Fan, 1991; Speight, 2014). Most of these acids are believed to have the chemical formula $R(CH_2)_nCOOH$, where R is a cyclopentane or cyclohexane ring and n is typically greater than 12 which can lead to the representation of structural characteristics (Tables 1.1–1.3) (Fan, 1991; Hsu et al., 2000; Barrow et al., 2003; Marshall and Rodgers, 2008; Petkova et al., 2009). In addition to $R(CH_2)_nCOOH$, a multitude of other acidic organic constituents are also present in crude oil(s) but not all of the species have been fully analyzed and identified. Although saturated carboxylic acids are the predominant compounds found in most crude oils, aromatic and even heterocyclic compounds have also been reported. For example, monoaromatics and diaromatics have also been identified within the naphthenic acid group (Derungs, 1956; Hsu at el., 2000).

Naphthenic acids are generally described by the formula $C_nH_{2n+Z}O_2$, where n is the number of carbons and Z is the *hydrogen deficiency* index.

Table 1.1 Representative Structures of Naphthenic Acids Found in Crude Oils (Fan, 1991; Hsu et al., 2000; Barrow et al., 2003; Marshall and Rodgers, 2008)

1 ring	2 rings	3 rings	4 rings	5 rings	6 rings	C22 – C33
						$C_nH_{2n-2}O_2$
						$C_nH_{2n-4}O_2$
						$C_nH_{2n-6}O_2$
						$C_nH_{2n-8}O_2$

In each case, R is an alkyl group of varying size and there may be more than one alkyl group per molecule.

Table 1.2 Predominant Naphthenic Acid Compounds Classes in a California Crude Oil (Seifert, 1973)

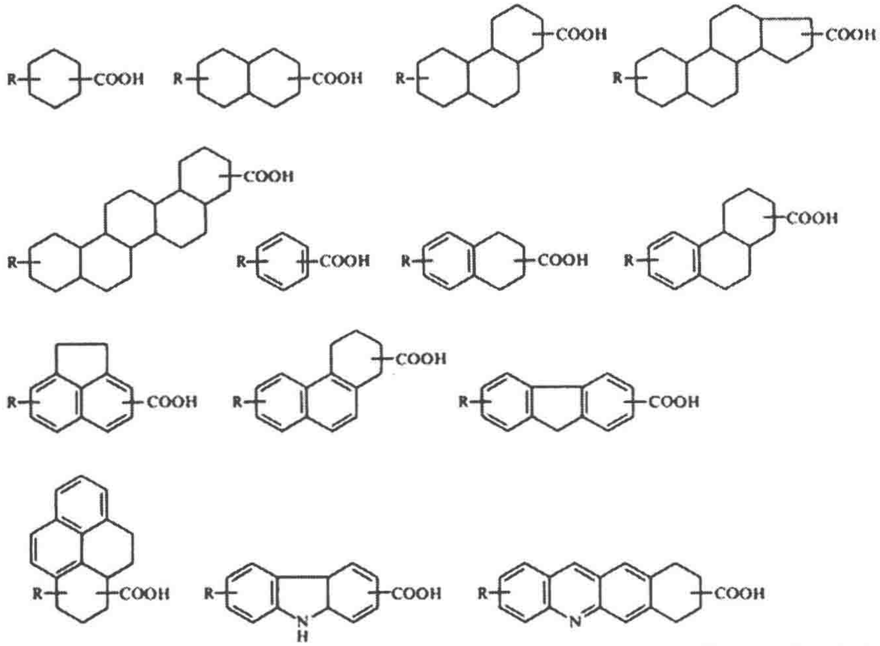
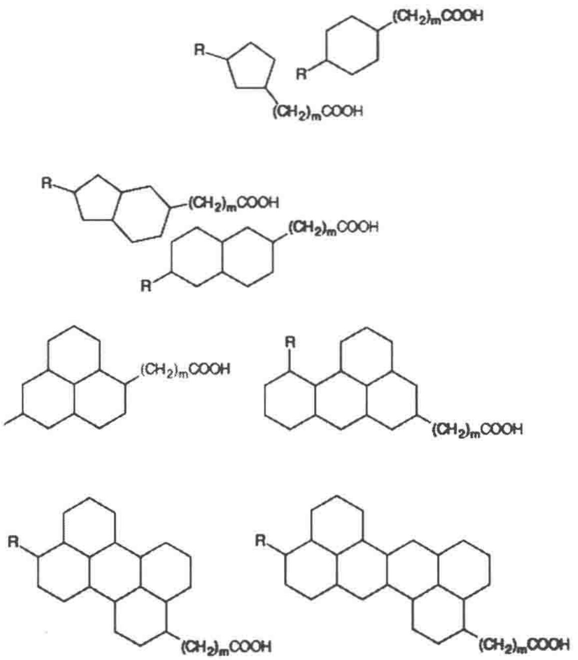


Table 1.3 Alternate Structural Types of Naphthenic Acids Where the Carboxylic Acid Function Is Attached to an Alkyl Side Chain (US EPA, 2012)



Z is either zero (for simple fatty acids with one carbon–oxygen double bond) or a negative even integer (acids with additional rings/double bonds) that specify homologous series. On a molecular basis, Z is frequently referred to as the molecular *hydrogen deficiency* (Hughey et al., 2002; Qian et al., 2001; Hughey et al., 2007).

Finally, *naphthenates* are the salts of naphthenic acids which have the formula M(naphthenate)$_2$ (M = divalent metal) or are basic oxides with the formula M_3O(naphthenate)$_6$. Naphthenate salts form when naturally occurring naphthenic acids in the crude oil come in contact with metal ions (such as calcium) in the produced water under the right conditions of pH and temperature. Naphthenates (RCOO−) are formed during crude oil production due to pressure decrease and release of carbon dioxide, which leads to increase in pH and dissociation of naphthenic acid (RCOOH). Naphthenates can precipitate with metal cations present in brine and form deposits, mainly of calcium naphthenates, which can accumulate in topside facilities, desalters, and pipelines, leading to shutdowns and other serious problems during crude refining.

The metal naphthenates are highly soluble in organic media and, with the naphthenic acids themselves, contribute to the interfacial properties of many crude oils and crude oil products (Varadaraj and Brons, 2007; Pillon, 2008).

In addition, under certain conditions, the naphthenic acids present in acidic crude oil will precipitate with calcium ions (Ca^{2+} ions) that are present in produced water and form calcium naphthenate and, to a lesser extent, other metal naphthenates. In fact, calcium naphthenate—a generic term for a deposit which usually contains calcium, sodium, magnesium, iron, and other metal naphthenates, and possibly asphaltene constituents, scale, and other solids—is a troublesome deposit that can form in oil production systems that are handling a crude oil with a high acid number (TAN). The problems caused by calcium naphthenate range from oil treating problems and poor water quality to heavy deposits that can plug lines and valves.

Thermogravimetric analysis has proved to be a suitable tool to investigate calcium naphthenate production and could be used to characterize these solids. The results showed that it is possible to distinguish the compounds produced by specific thermal stability assays. In this report, the synthetic route employed has indicated the formation of different compounds, such as calcium carbonate, calcium sulfate as gypsum, and calcium naphthenate. In the experiments, precipitation of calcium sulfate showed to be dependent on solution pH. Moreover, the reproducibility tests confirmed the qualitative significance in the formation of naphthenates (Moreira and Teixeira, 2009).

1.2.1 Origin

Naphthenic acids are natural constituents of petroleum, where they evolve through the oxidation of naphthenes (cycloalkanes). Initially, the presence of these acidic species was suggested due to process artifacts formed during refining processes, and this may still be the case in some instances. However, it was shown that only a small quantity of acids was produced during these processes (Costantinides and Arich, 1967). Currently, it is generally assumed that acids may have been incorporated into the oil from three different sources: (i) acidic compounds found in source rocks, derived from the original organic matter that created the crude oil (plants and animals), (ii) neo-formed acids during biodegradation (although the high acid concentration in biodegraded oils is believed to be related principally to the removal of nonacidic compounds, leading to a relative increase of the acid concentration levels), and (iii) acids that are derived from the bacteria themselves, e.g., from cell walls that the organisms leave behind when their life cycle is completed (Mackenzie et al., 1981; Behar and Albrecht, 1984; Thorn and Aiken, 1998; Meredith et al., 2000; Tomczyk et al., 2001; Watson et al., 2002; Wilkes et al., 2003; Barth et al., 2004; Kim et al., 2005; Fafet et al., 2008).

This diverse group of saturated monocyclic and polycyclic carboxylic acids can account for as much as 4% (w/w) of crude petroleum (Brient et al., 1995) and represents an important component of the crude oil feedstock as well as waste generated during petroleum processing in some situations (such as the desalting step). Naphthenic acids are also natural constituents of tar sand (oil sand) bitumen and, during the bitumen extraction process, when the alkalinity of the water (pH: approximately 8) promotes solubilization of naphthenic acids (pK_a: approximately 5), the acids are solubilized and concentrated in the tailings stream (Rogers et al., 2001, 2002; Headley and McMartin, 2004; Scott et al., 2005).

In terms of the origin of naphthenic acids, biodegradation of hydrocarbons and the resulting decline in crude oil quality is common in reservoirs cooler than approximately 80°C (176°F). Petroleum biodegrading organisms have a specific order of preference for compounds that they remove from oils and gases (Seifert, 1973; Speight, 2014a). Progressive degradation of crude oil tends to remove saturated hydrocarbons first, concentrating heavy polar and asphaltene components in the residual oil. This leads to decreasing oil quality reflected in a lowering of the API gravity while increasing viscosity, sulfur, and metal contents. In addition to lowering reservoir recovery efficiencies, the economic value of the oil generally decreases with biodegradation owing to a decrease in refinery distillate yields and an increase in vacuum residua yields (Wenger et al., 2001; Speight, 2014). Furthermore, biodegradation leads to the formation of naphthenic acid compounds, which increase the acidity of the oil (typically measured as *TAN*) (Speight and Arjoon, 2012). An increase in the TAN may further reduce the value of the crude oil and may contribute to production and downstream handling problems such as corrosion and the formation of emulsions (see Chapter 3).