

# Physicochemical Characterization of Asphalt Ridge Froth Bitumen and Petroleum Pitch

Nader Nciri, Suil Song, Namho Kim, and Namjun Cho

**Abstract**—The present paper focuses on physicochemical analysis of two different types of bitumens. These bitumen samples were chosen based on: the original crude oil (sand oil and crude petroleum), and mode of process. The aim of this study is to determine both the manufacturing effect on chemical species and the chemical organization as a function of the type of bitumen sample. In order to obtain information on bitumen chemistry, elemental analysis (C, H, N, S, and O), heavy metal (Ni, V) concentrations, IATROSCAN chromatography (thin layer chromatography-flame ionization detection), FTIR spectroscopy, and  $^1\text{H}$  NMR spectroscopy have all been used. The characterization includes information about the major compound types (saturates, aromatics, resins and asphaltenes) which can be compared with similar data for other bitumens, more importantly, can be correlated with data from petroleum samples for which refining characteristics are known. Examination of Asphalt Ridge froth bitumen showed that it differed significantly from representative petroleum pitches, principally in their nonhydrocarbon content, heavy metal concentration and aromatic compounds.

**Keywords**—Asphalt Ridge froth bitumen, Petroleum pitch, Elemental analysis, Thin Layer Chromatography-Flame Ionization Detection, Colloidal instability index, Infrared Spectroscopy,  $^1\text{H}$  Nuclear Magnetic Resonance Spectroscopy.

## I. INTRODUCTION

**I**NTEREST in tar sands as an energy source has increased significantly in recent years, and considerable effort is now being expended to determine the extent of the resource, its prospects for recovery, and the nature of the bitumen and products. Most of the known North American tar sand resource is located in Alberta, Canada, with sizeable deposits in Utah and smaller deposits scattered throughout the United States [1]-[2]. The need for additional energy sources indicates the

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need for increased development for tar-sand bitumens. The physical and chemical properties of the tar-sand bitumens ultimately determine their values because these properties influence the recovery, processing, conversion, and utilization of fossil energy resources. Asphalt Ridge near Vernal in Uintah country, Utah, is one of several bituminous sandstone deposits in the Uinta Basin that contains large amounts of bitumen from which petroleum products may be extracted [3]. Asphalt Ridge bitumen becomes gradually more important as refinery feedstock. In order to optimize quality, more information on its molecular chemistry is required.

The objective of this paper is to provide some fundamental information required on bitumen sources from Asphalt Ridge in Utah and manufactured bitumen, known as petroleum pitch for technological applications such as pavement construction or research purposes. To determine the chemical species, classical tests were conducted: Elemental analysis (EA), Thin-layer chromatography with flame ionization detection (IATROSCAN), Fourier-transformed infrared (FTIR) spectroscopy and  $^1\text{H}$  Nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy.

## II. MATERIALS AND METHOD

### A. Materials

The Asphalt Ridge froth bitumen was extracted after heating in furnace by 235 °C. The feed had the following composition: 53 wt. % bitumen; 7.5 wt. % clay and 0 wt. % moisture. Chemically, the froth bitumen comprises 93.56 wt. % of organic matters and 6.44% wt. of inorganic matters. It was black in color, semisolid liquid and sticky.

The petroleum pitches were received from two anonymous refineries companies, South Korea. The materials were labeled P-1 and P-2. The residuum derived from petroleum by a refinery distillation process was black, hard and glassy at room temperature.

### B. Elemental Analysis (EA)

The elemental compositions of Asphalt Ridge froth bitumen and petroleum pitches were acquired on a Carlo Erba NA 1500 C/N/S Analyzer.

### C. Fourier transformed-infrared spectroscopy (FT-IR)

IR spectra of bitumen were recorded on a Bruker equinox 55 spectrophotometer in the region of 4000-650  $\text{cm}^{-1}$  using KBr pellets.

### D. Thin layer chromatography-flame ionization detector (TLC-FID)

A TLC device (MK-6S, Tokyo, Japan) equipped with FID detector was used to test the TLC-FID method. The S-III chromarod (MKI, Tokyo, Japan) used in this study was 15.2 cm long and 1.0 mm in diameter and was coated with a layer of silica gel (5  $\mu\text{m}$  particle size). During experiments the chromarod was spotted with 1  $\mu\text{L}$  of extract, and subsequently was developed with the following program: n-hexane (30 min), toluene (18 min) and (95:5) (v/v) dichloromethane: methanol (4 min). The chromarod was dried at 40  $^{\circ}\text{C}$  for 2 min after each development. For the TLC-FID method, a scan rate of 40 s/scan was used. Air and hydrogen flows were 2000 mL/min and 160 mL/min respectively [4]. Results from the TLC-FID IATROSCAN served to determine the colloidal instability index ( $I_C$ ) [5], based on the colloidal model first described by Nellensteyn and enhanced by Pfeiffer to explain the difference between "sol" and "gel" bitumens [5]-[6]. In between these two extremes, a majority of bitumens were found to display an intermediate behavior due to a mixed "sol-gel" structure. To differentiate these various bitumen types, the  $I_C$  index was introduced by Gaestel et al. [7] as in (1).

$$I_C = \frac{\chi_{\text{asph}} + \chi_{\text{sat}}}{\chi_{\text{aro}} + \chi_{\text{res}}} \quad (1)$$

Where  $\chi_i$  is the weight content of the generic family ( $i = i$ -asphaltenes, resins, aromatics or saturates). The value of  $I_C$  typically ranges from 0.5 to 2.7 for road bitumens in current use [7]. A marked gel character was observed for  $I_C > 1.2$  and a typical sol behavior was found for  $I_C < 0.7$  [8].

### E. $^1\text{H}$ Nuclear magnetic resonance ( $^1\text{H}$ NMR)

A Bruker NMR Spectrometer (500 MHz) was used. Characterization was performed by dissolving each liquid fraction in  $\text{CDCl}_3$ . Tetramethyl silane (TMS) was used as internal standard.

## III. RESULTS AND DISCUSSION

### A. Feedstocks properties and elemental analysis

The knowledge of the chemical composition of the feedstocks plays a major role in predicting their behavior in terms of phase separation, coke formation, molecular interactions, and the cause of catalyst deactivation [9]. The elemental analyses and physical properties of the various samples studied are given in Table I. The elemental analyses of Asphalt Ridge bitumen and pitches are similar to values reported by other investigators [10]-[11].

### B. Hydrocarbon content

The carbon and hydrogen contents are typical of Asphalt Ridge bitumen [10] and P-1 and P-2 pitches [11]. The hydrogen content is found to be highest in Asphalt Ridge froth bitumen (10.52%) followed by P-2 pitch (9.57%) and P-1 pitch (9.19%). The carbon contents of these three feedstocks are reported to decrease from P-1 pitch (84.10%) to P-2 pitch (83.02%) ending by Asphalt Ridge froth bitumen (79.94%). This relationship was expected on the basis of organic/inorganic data. In terms of their quantity the inorganic components present in the Asphalt Ridge froth bitumen represent 6.44% of the total weight. They consist mainly of quartz and silt and the residues of salts which were emulsified in the raw Asphalt Ridge tar sand during the long history of its creation.

TABLE I  
PHYSICO-CHEMICAL PROPERTIES OF FEEDSTOCKS

Properties	Feedstocks			
	Asphalt Ridge froth bitumen	Asphalt Ridge bitumen	P-1 pitch	P-2 pitch
Carbon, wt%	79.94	85.44	84.10	83.02
Hydrogen, wt%	10.52	11.24	9.19	9.57
Nitrogen, wt%	0.96	1.02	0.43	0.49
Sulfur, wt%	0.70	0.75	5.69	5.91
Oxygen, wt%	1.44	1.54	3.24	0.97
Vanadium, ppm w/w	20.87	25	111.41	171.50
Nickel, ppm w/w	84.49	120	30.54	51.54
H/C, atomic ratio	1.57	1.57	1.31	1.38
V/Ni, atomic ratio	0.28	0.23	4.20	3.86
Penetration at 25 $^{\circ}\text{C}$ , 100 g, 5 sec, 0.01 mm	162	-	6	29
Softening point, $^{\circ}\text{C}$	39.9	-	71	61.1
Viscosity, Pa.s	135 $^{\circ}\text{C}$	295	-	2125
	180 $^{\circ}\text{C}$	55	-	235
Torsional recovery, %	135 $^{\circ}\text{C}$	5.9	-	8.5
	180 $^{\circ}\text{C}$	1.1	-	4.7
Shear stress, (G*/sin $\delta$ ), Pa	135 $^{\circ}\text{C}$	18.6	-	144.5
	180 $^{\circ}\text{C}$	-	-	-
Spindle 21, cP	135 $^{\circ}\text{C}$	21	-	27
	180 $^{\circ}\text{C}$	21	-	21
Heating value, BTU/Lb	17,4750	18,751	17,421	17,568
Undetermined				

However, in the case of petroleum pitches, the entire part of the ingredients of the pitch was made up only of organic materials (almost 100%).

### C. Heteroatom content

Table I summarizes the heteroatom compound types. The oxygen, being the critical heteroatom, content in P-1 pitch was almost three times as high as that in the Asphalt Ridge froth bitumen and P-2 pitch. This is not surprising, because when oxygen is estimated by difference the analysis is subject to the accumulation to aerial oxygen, and the oxygen content is very dependent on sample history. This unusually increase in oxygen amount may be attributed also, to the phenomenon of oxidation that takes place during the manipulation. P-1 and P-2 pitches are notably high in sulfur but low in nitrogen compared to the sample from Uinta Basin deposit (Asphalt Ridge froth bitumen). Sulfur content for the Asphalt Ridge froth bitumen (0.70%) samples represents the limits for bitumens of the Tertiary age, which typically contain 0.3-0.7% sulfur [12]. High concentration of sulfur indicates the presence of larger number of heterocyclic compound in these feeds [13]. It was suggested that the nitrogen content of petroleum is usually less than 1% by weight, but the nitrogen content of tar sand bitumen can be as high as 1.5% by weight. The presence of nitrogen complicates refining by poisoning the catalysts employed in the various processes. Nitrogen is more difficult to remove than sulfur, and there are fewer catalysts that are specific for nitrogen [14].

### D. Hydrogen-Carbon, atomic ratio

Comparison of the hydrogen/carbon ratios reveals that the high sulfur pitches are also notably more aromatic than the Uinta Basin sample. The large H/C atomic ratio means low density, low content of aromatic hydrocarbons and high cracking reactivity, resulting in high yields of light hydrocarbons and low yield of coke [15].

### E. Heating value

Heating values are typical for Asphalt Ridge froth bitumen and pitches. Heating values were calculated from elemental composition by the method of Boie [16] where for anhydrous samples the heating value in BTU/Lb is  $1.8 [8400 (C) + 27 765 (H) + 1500 (N) + 2500 (S) - 2650 (O)]$ . All feedstocks presented slight differences in heating value (Table I); this is not surprising considering that Asphalt Ridge froth bitumen and petroleum pitches may present variations in their elemental composition according to location and depth of the well as well as the process of extraction. Nevertheless, from an overall comparison the three samples seem quite similar in heating value.

### F. Vanadium & Nickel

Table I lists the Ni and V contents for the feedstocks. Results of analyses show that vanadium content is low for the low-sulfur Uintah Basin sample. Except for the correlation of vanadium content with sulfur content often observed in petroleum pitch samples, no other obvious trends exist. Nickel

and vanadium were observed as having uniform levels throughout the materials, which may indicate that they exhibit relatively strong organic associations. P-1 and P-2 samples have a higher concentration of vanadium than nickel. Vanadium is often associated with high-sulfur petroleum crude oils. Vanadium concentration was below the limits of detection in the low-sulfur bitumens of Asphalt Ridge [12].

### G. Viscosity

The viscosity property of the bitumen will influence the quantity and quality of products recovered by thermal *in situ* processes [12]. It was reported [10] that viscosities correlate with molecular weights. Because viscosities are so high, elevated temperatures are required to cause bitumens to flow. The extremely high viscosity (at 180 °C) for the P-2 pitch sample is due not only to its high molecular weight but also to the presence of higher concentrations of polar heteroatomic functional groups. As reported by Jackson and Dhir [17], at 20°C the viscosities of some types of bitumen range from  $10^3$  to  $10^8$  Poise depending on the type; compared to water  $10^{-2}$  Poise, diesel  $10^{-1}$  Poise, and engine oil 10 Poise. The viscosities however decrease with increase in temperature. This trend of behavior is also observed with Asphalt Ridge froth bitumen, P-1 pitch, and P-2 pitch as can be seen in Table I. At 135 °C, P-1 pitch is the most viscous sample, followed by P-2 pitch, and then Asphalt Ridge froth bitumen.

### H. Penetration

The penetration is very greater for Asphalt Ridge froth bitumen than the pitches. According to a research paper [18] published in 2008, it was investigated that low penetration petroleum asphalt cements is less susceptible to ageing time than soft asphalt. This is because the saturates fraction of petroleum asphalt increases the resistance to flow. Mummah and Muktar [19] have demonstrated that bitumen having penetration value above 100 mm is associated with flushing or bleeding of road surfaces whereas cracking rarely occurs with bitumen having penetration value below 80 mm. In contrast Emesiobi [20] posits that bad cracking of road pavement are also associated with bitumen having penetration values below 20 mm and for values higher than 30 mm cracking is reduced. The implication of their findings is that there is both upper and lower limit of cracking associated with bitumen in terms of penetration. The penetration values obtained for P-1 pitch fall below 20 mm, so coatings based on bitumen from the samples sources will be associated with bad cracking. However, the penetration of P-2 pitch may result in small reduction of cracking mechanism. The penetration value of Asphalt Ridge froth bitumen sample do not fall in the range of 80-120 mm as reported by Mummah and Muktar [19] and Adebayo [21] for bitumen of acceptable grades.

### I. Softening point

It is desired that bitumen should be able to resist deformations (such as boiling) resulting from incremental temperature changes; therefore the need to increase the softening point of bitumen. From Table I results revealed that

the softening point of Asphalt Ridge froth bitumen was smaller than those of P-1 and P-2 pitches. Higher amounts of saturate and naphthene aromatic fractions called plasticizing components; provide higher penetration value and lower softening point [22]. Comparison of the two pitches P-1 and P-2 and Asphalt Ridge froth bitumen reveal that sample used for characterization and those for processing were quite different. The two pitches samples came from the same core, but from separate extractions and would be expected to be nearly identical to each other. The Asphalt Ridge froth bitumen came from different location and different process and could and do differ somewhat from pitches. The difference between the petroleum pitches and tar sand bitumen may relate to differences in structure and molecular weight distribution (SARA) as discussed in the following section.

### J. FT-IR analysis

Figure 1 displays the IR spectra recorded in the ranges 4000–650  $\text{cm}^{-1}$ , obtained from Asphalt Ridge froth bitumen, P-2 and P-1 pitches respectively. All spectra in parts A, B, C of Figure 1 show similar features and contain characteristic bands for aliphatic and aromatic functions.

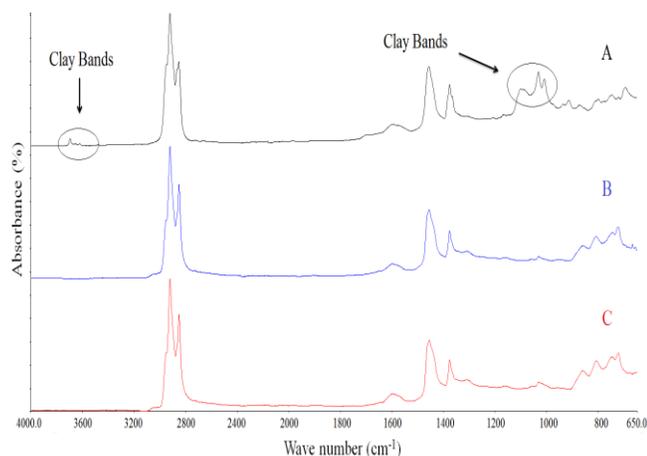


Fig. 1 FT-IR spectra of (A): Asphalt Ridge froth bitumen, (B): P-2 pitch and (C): P-1 pitch

An aliphatic signature is indicated at 2921, 2853  $\text{cm}^{-1}$ , 1456 and 1375  $\text{cm}^{-1}$ . A shoulder at approximately 3030  $\text{cm}^{-1}$  present also in all spectra is due to the stretching of olefinic C–H bonds. A weak C=O stretching band at 1702  $\text{cm}^{-1}$  was only observed in the spectrum of Asphalt Ridge froth bitumen. Which may be due to a carboxylic acid or a derivative containing C=O group such as ketones and/or quinones, based upon Bungler's report [23] of 41.3 mol % of ketones in Northwest Asphalt Ridge bitumens. Majid and Ripmeester [24] reported that hydrogens adjacent to ketones and quinones carbonyl carbons give rise to a band at this wavenumber. The IR spectra show that the Asphalt Ridge froth bitumen, as expected, consists principally of a mixture of clays. The presence of kaolinite can be discounted, at least at concentrations >1%, because of the absence of the higher-frequency member of the characteristic pair of O–H stretching bands at 3694 and 3620  $\text{cm}^{-1}$  [25]-[26]

The single band at 3620  $\text{cm}^{-1}$  is characteristic, however, of smectite and illite clays. As shown also, other typical bands of these clays are also observed. The very weak broadband at 3400  $\text{cm}^{-1}$  and the broadband at 1625  $\text{cm}^{-1}$ , which are O–H stretching and bending vibrations, respectively, are attributable to the loosely bound, interlayer water contained in smectite or hydrous illite. The very slight broad band at ~3200  $\text{cm}^{-1}$  is characteristic of water molecules tightly bonded to particle surfaces in a monolayer. Weak bands appearing at 835 and 799  $\text{cm}^{-1}$  are (Al, Mg) –O–H vibrations which can be assigned to smectite. Characteristic quartz features are moderate, two small bands at 1032 and 1008  $\text{cm}^{-1}$ , originating from siloxanes (Si–O–Si) stretching modes, as well as bands at 799, 780, and 696  $\text{cm}^{-1}$  from  $\alpha$ -SiO<sub>2</sub> bending vibrations [27].

### K. TLC-FID analysis

In Figure 2 (A), FID response is shown against Chromarod scan time representing relative mobility of sample components during Chromarod development with n-hexane, toluene and dichloromethane-methanol.

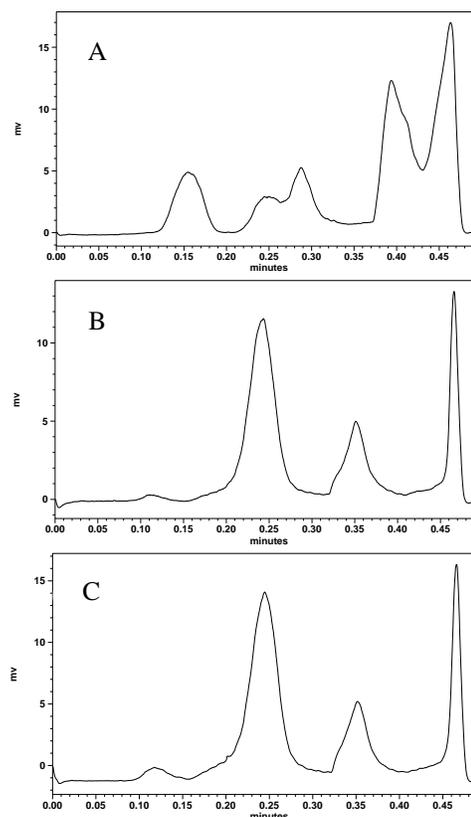


Fig. 2 Separation of Asphalt Ridge froth bitumen (A), P-1 pitch (B), and P-2 pitch (C) according to sequence 30 min n-hexane, 18 min toluene, and 4 min DCM-MeOH (95:5, v/v). The horizontal axis represents the retention time (min) and the vertical axis is the intensity (arbitrary unit).

Accordingly, saturates are resolved as a separate peak (at the scan time of 0.15 min), followed by a broad distribution of aromatics with a sequential elution of one-ring, two- and multi-ring aromatics (in the scan time range of 0.20 to 0.35 min). Finally, resins and asphaltenes are obtained at around the

scan time of 0.40 and 0.46 min respectively.

Both Figure 2 and Figure 3 show that relative amounts of resins and asphaltenes are higher in Asphalt Ridge froth bitumen compared to those in P-1 pitch and P-2 pitch. Asphaltene content is a measure of the coke-forming tendency basic to bitumen processing [28].

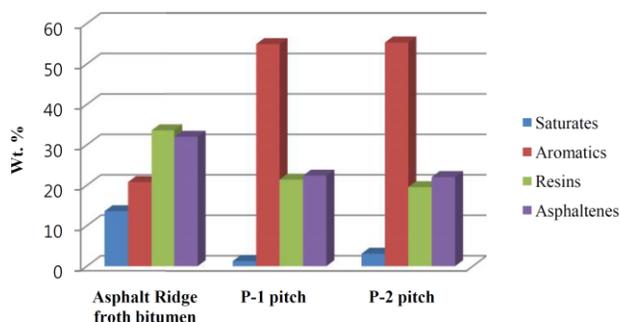


Fig.3 Schematic composition of the feedstocks fractionated by the SARA method.

Asphalt Ridge froth bitumen also shows a wide distribution of aromatics, and contains higher proportion of smaller ring aromatics than P-1 and P-2 pitches. These characteristic differences may be attributable to the origins or the degree of thermal maturation or both. Here, it should be pointed out that, two different kinds of petroleum feedstocks are advanced; one came from sand oil and the other from crude oil. The process of manufacturing of each one is somehow different. The froth bitumen has not yet undergone an intensive physicochemical treatment like the pitches. It is just fed through tubes and heated by a furnace to around 235 °C in order to break down large hydrocarbons into smaller ones and to remove the residues of water remaining in the froth. It also resembles somehow that this treatment does not affect the saturates value, which still in high level compared to the pitches. The pitches are characterized by a large amount of aromatics compared to the froth bitumen. This could be attributed to the deshydrogenative polymerization (aromatization/ condensation) and cross-linking of the pitch molecules that take place during the distillation process of crude oil [29].

As can be seen also in Figures 2 (B) and 2 (C), that the content of saturates is reduced to a lower quantities due to the process of cracking that induces dealkylation and dehydrogenation of pitch molecules [30]. In other words, the very lightest molecules are travelling through a series of trays and reaching the top of the distillation vacuum to form light petroleum products such as; light gas oil, naphtha, gasoline, and kerosene, etc. Whereas, the heaviest material are falling down from the bottom of the tower to produce the pitch [31].

It appears that the composition of both P-1 and P-2 pitches is derived from the same core and do not show any remarkable differences. The profiles of Asphalt Ridge froth bitumen and pitches chromatograms are quite different (Figure 2). In terms of aromatics, the Asphalt Ridge froth bitumen exhibits two peaks; one minor peak and one major peak. It has been reported

[32] that the former is corresponding to the alkylaromatics ranging from one to two rings and the latter is the aromatics ranging between three and  $n$  rings. However, the aromatics of pitches show just one sharp peak. This suggests that the Asphalt Ridge froth bitumen contains a large number of aromatic rings varying widely between one and  $n$  rings. Whereas, in the case of pitches, the polyaromatic rings are significantly predominant.

#### L. IC analysis

In the  $I_c$ , Colloidal instability index, the oil is considered a colloidal system consisting of the pseudocomponents saturates, aromatics, resins and asphaltenes (SARA). That index expresses the stability of asphaltenes as a function of these fractions and it is defined as the mass ratio between the sum of asphaltenes and the unfavorable components to its stability in the oil, that is, its flocculants (saturates) and the sum of its peptizer agents (aromatics and resins), which constitute the components favorable to the stability of asphaltenes present in a specific oil [33]-[35], as shown in (2).

$$I_c = \frac{\% \text{Saturates} + \% \text{Asphaltenes}}{\% \text{Resins} + \% \text{Aromatics}} \quad (2)$$

Asomaning [34] evaluated oils whose SARA contents were determined by liquid chromatography (ASTM D2007-03) [36] and by the standard method IP 143/84 [37], and experimental evidence showed that when  $I_c \geq 0.9$ , the asphaltenes are unstable in the medium; when  $0.7 \leq I_c < 0.9$ , there is uncertainty about the stability; and if  $I_c < 0.7$ , the asphaltenes are stable in the oil. Considering that percentages of saturates, aromatics, resins, and asphaltenes depend on the determination procedure, the limits of stability of this index are also susceptible to many variations. Colloidal instability index was calculated for all samples, and the values obtained are presented in Table II. The majority of the evaluated pitch samples would be stables, except the Asphalt Ridge froth bitumen, classified as uncertain. Consequently, further tests are required.

TABLE II  
CHEMICAL CHARACTERISTICS OF THE FEEDSTOCKS FROM TLC-FID

Hydrocarbon types	Asphalt Ridge froth bitumen	P-1 pitch	P-2 pitch
Saturates, wt. %	13.59	1.27	3.09
Aromatics, wt. %	20.81	54.91	55.30
Resins, wt. %	33.59	21.4	19.54
Asphaltenes, wt. %	32	22.39	22.05
Colloidal Index, $I_c$	0.83	0.31	0.33
Behavior	"sol-gel"	"sol"	"sol"
Stability	uncertain	stable	stable

It is apparent that P-1 pitch has higher peptizability of asphaltenes in oils than P-2 pitch and Asphalt Ridge froth bitumen. This observation suggests that P-1 pitch may have no tendency for separation and could be stored for years without precipitation. Another important observation is that if transport of water to the interface is across bitumen films, then the process would be easier in P-1 pitch compared to P-2 pitch and

Asphalt Ridge froth bitumen [38].

According to previous study [8], in bitumens with sufficient quantities of resins and aromatics of adequate solvating power, the asphaltenes are fully peptized and the micelles have good mobility within the bitumen. These bitumens are known as solution or "sol" type bitumens. This is the case of pitch petroleum samples where  $I_C < 0.7$ . If the quantity of the aromatic/resin fraction is insufficient to peptize the micelles or has insufficient solvating power, the asphaltenes can associate to form large agglomerations or even a continuous network throughout the bitumen. These bitumens are known as gelatinous or "gel" type bitumens, where  $I_C > 1.2$ . However, in practice most bitumens are of intermediate character "sol-gel". This is the case of Asphalt Ridge froth bitumen, where  $I_C$  is ranged between 0.7 and 1.2.

As stated previously, the value of  $I_C$  typically ranges from 0.5 to 2.7 for road bitumens [7]. According to this data, it seems that the petroleum pitches are not welcome in road construction, whereas Asphalt Ridge froth bitumen may be used without any issues. Such finding is supported by the physicochemical data listed in Table I (penetration values).

#### M. <sup>1</sup>H NMR analysis

The proton types and assignments for NMR spectra are listed in Table III. The elution method is referred to Zandar [39].

TABLE III  
POSITION AND ASSIGNMENT OF PROTON (<sup>1</sup>H) SIGNALS [39]

Parameter	Chemical shift	Type of protons
H <sub>ar</sub>	6.0-9.0	Aromatic hydrogen
H <sub>ole</sub>	4.5-6.0	Hydrogen olefinic
H <sub>α</sub>	2.0-4.0	Aliphatic hydrogen on C <sub>α</sub> to aromatic rings
H <sub>β</sub>	1.0-2.0	Aliphatic hydrogen on C <sub>β</sub> and the CH <sub>2</sub> , CH, beyond the C <sub>β</sub> to aromatic rings
H <sub>γ</sub>	0.5-1.0	Aliphatic hydrogen on C <sub>γ</sub> and the CH <sub>3</sub> beyond the C <sub>γ</sub> to aromatic rings

The hydrogen distributions based on the integrated intensities of several characteristic resonances in the aliphatic and aromatic region of feedstocks are shown in Figure 4. As seen in Figure 4, the <sup>1</sup>H NMR spectra of Asphalt Ridge froth bitumen and pitch samples showed strong peaks of methyl, methylene, and methine hydrogens of alkyl chains β or further to aromatic ring (H<sub>ali</sub>- β+γ; 2.0-1.0 ppm). The methyl hydrogens present in aliphatic compounds or attached to aromatic rings in a γ or further position (H<sub>ali</sub>-me; 1.0-0.5 ppm) are less intense in all the pitch spectra compared with high intensity for Asphalt Ridge froth bitumen. However, the hydrogens of methyl, methylene, and methine attached to aromatic rings in an α position (H<sub>sat</sub>, α; 4.0-2.0 ppm) showed very weak signals for all samples. The aromatic hydrogens (H<sub>ar</sub>; 9.0-6.0 ppm) signal is less intense in Asphalt Ridge froth bitumen as compared to P-1 and P-2 pitches. The spectrum of Asphalt Ridge froth bitumen shows that relative quantities of benzylic and aromatic hydrogens are low, and the olefinic hydrogens are not measurable. Same results have been reported by Hanks [40] with some few notable differences in the amount

of H<sub>ar</sub> and H<sub>γ</sub>.

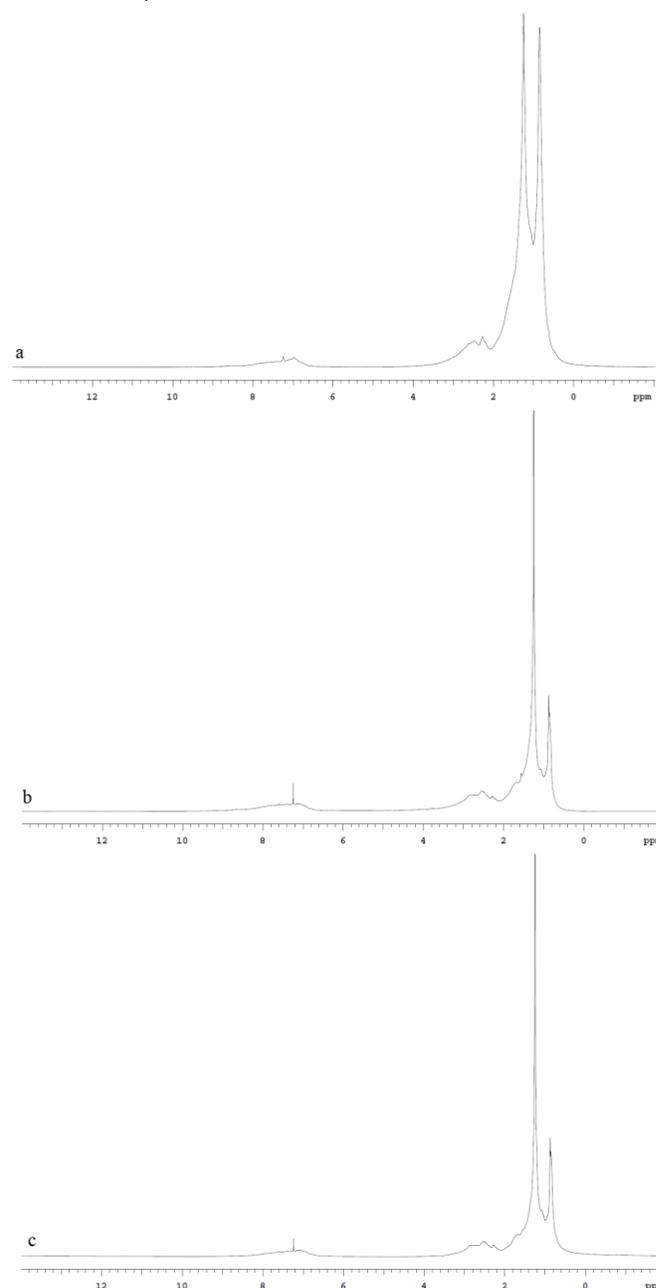


Fig. 4 <sup>1</sup>H NMR spectra for (a) Asphalt Ridge froth bitumen, (b) P-1 pitch, and (c) P-2 pitch.

Table III shows that the fractions of aromatic hydrogen (H<sub>ar</sub>) are low in all samples. The petroleum pitches have more aromatic hydrogens than the Asphalt Ridge froth bitumen. The relative decrease of aromatic hydrogen indicates that the aromatic structures were getting condensed and substituted during the thermal treatment of pitches [41]. The saturated protons (H<sub>sat</sub>) contain several types of paraffinic hydrogens, viz. H<sub>α</sub>, H<sub>β</sub> and H<sub>γ</sub>. Fractions of H<sub>α</sub> represent the least amount of aliphatic hydrogens in almost all samples which is consistent with the observation that these fractions are comprised of mostly aliphatic structures. Among H<sub>α</sub>, H<sub>β</sub> and H<sub>γ</sub> protons, the H<sub>β</sub> constitutes a major portion of the saturated protons in

Asphalt Ridge froth bitumen as well as pitches. The contents of  $H_\gamma$  protons were found decreasing in the following order: P-1 pitch < P-2 pitch < Asphalt Ridge froth bitumen. The occurrence of low contents of  $H_\gamma$  protons in asphalt was an apparent evidence of the presence of short aliphatic straight chains and increased alicyclic system.

TABLE III  
PERCENT DISTRIBUTION OF HYDROGEN OF ASPHALT SEPARATIONS

Feedstocks	Hydrogen distribution			
	$H_\alpha$	$H_\beta$	$H_\gamma$	$H_{ar}$
Asphalt Ridge froth bitumen	10.94	53.32	31.92	3.82
P-1 pitch	18.30	58.00	15.02	8.68
P-2 pitch	12.56	58.32	22.33	6.78

#### IV. CONCLUSION

The physicochemical properties of Asphalt Ridge froth bitumen from Utah in USA, and petroleum pitches from South Korea have been determined using routine physical and chemical methods. The results indicated that the Asphalt Ridge froth bitumen is found to be different from petroleum pitches. The information presented is basic and a contribution towards utilizing the abundant bitumen sources for technological applications.

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