

SPECTROMETRIC IDENTIFICATION OF NAPHTHENIC ACIDS
ISOLATED FROM CRUDE OIL

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SPECTROMETRIC IDENTIFICATION OF NAPHTHENIC ACIDS
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CHAPTER 1

INTRODUCTION

1.1 Naphthenic acids

Naphthenic acids, originally identified as carboxylic acids¹ in crude oils with single or multiple saturated ring structures, is the phrase loosely used to include all acidic components in crude oils, even including aromatic carboxylic acids.² Petroleum products have a complex composition³⁻¹⁰, most of the compounds cannot be easily characterized due to their compositional complexity, and they also have a variable range of concentration based on their geographical distribution.¹¹

Refined naphthenic acids are transparent, oily liquids. They are obtained by distilling the petroleum fractions.¹² Naphthenic acids are mainly cyclopentane derivatives with a smaller fraction based on the cyclohexane ring (Figure 1-1). In fact, naphthenic acids are a mixture of different compounds which may be polycyclic and may have unsaturated bonds, aromatic rings, and hydroxyl groups. The physical and chemical properties depend on the nature and source of the processed petroleum. As an example, Romanian naphthenic acids have a very low aromatic and phenolic compound content, usually less than 60 ppm.

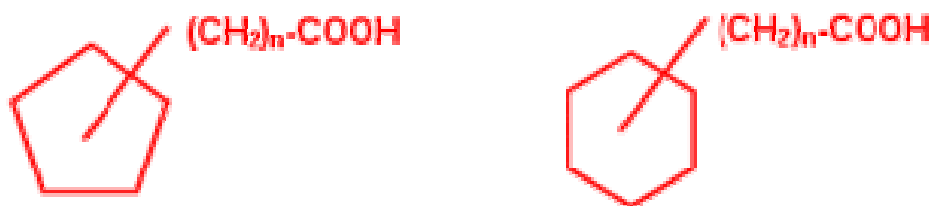
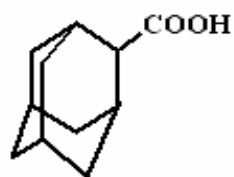


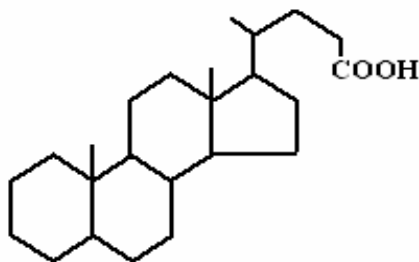
FIGURE 1-1: Cyclopentane and Cyclohexane carboxylic acids.

Empirical formula and structure of naphthenic acids are complex mixtures of alkyl-substituted acyclic and cycloaliphatic carboxylic acids. The empirical formula for the acids may be described by $C_n H_{2n+Z} O_2$ ¹³⁻¹⁷, where the Z value¹ is the “hydrogen deficiency” and is a negative, even integer, and more than one isomer will typically exist for a given Z homologue.

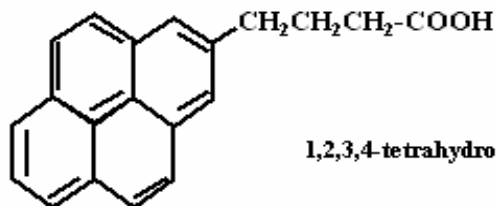
1-adamantanecarboxylic acid (180.25)



5 β -cholanic acid (360.6)



1-pyrenebutyric acid (288.35)



1,2,3,4-tetrahydro-2-naphthoic acid (176.22)

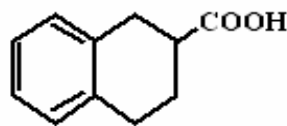


FIGURE 1-2: Aromatic naphthenic acids.

The complex composition is polydisperse with varying molecular weights and structure differences.^{11, 18-22} Examples of the types of molecular structures that are thought to comprise naphthenic acids are shown in Figure 1-2 and Figure 1-3. However individual acids are difficult to be isolated from the mixture.

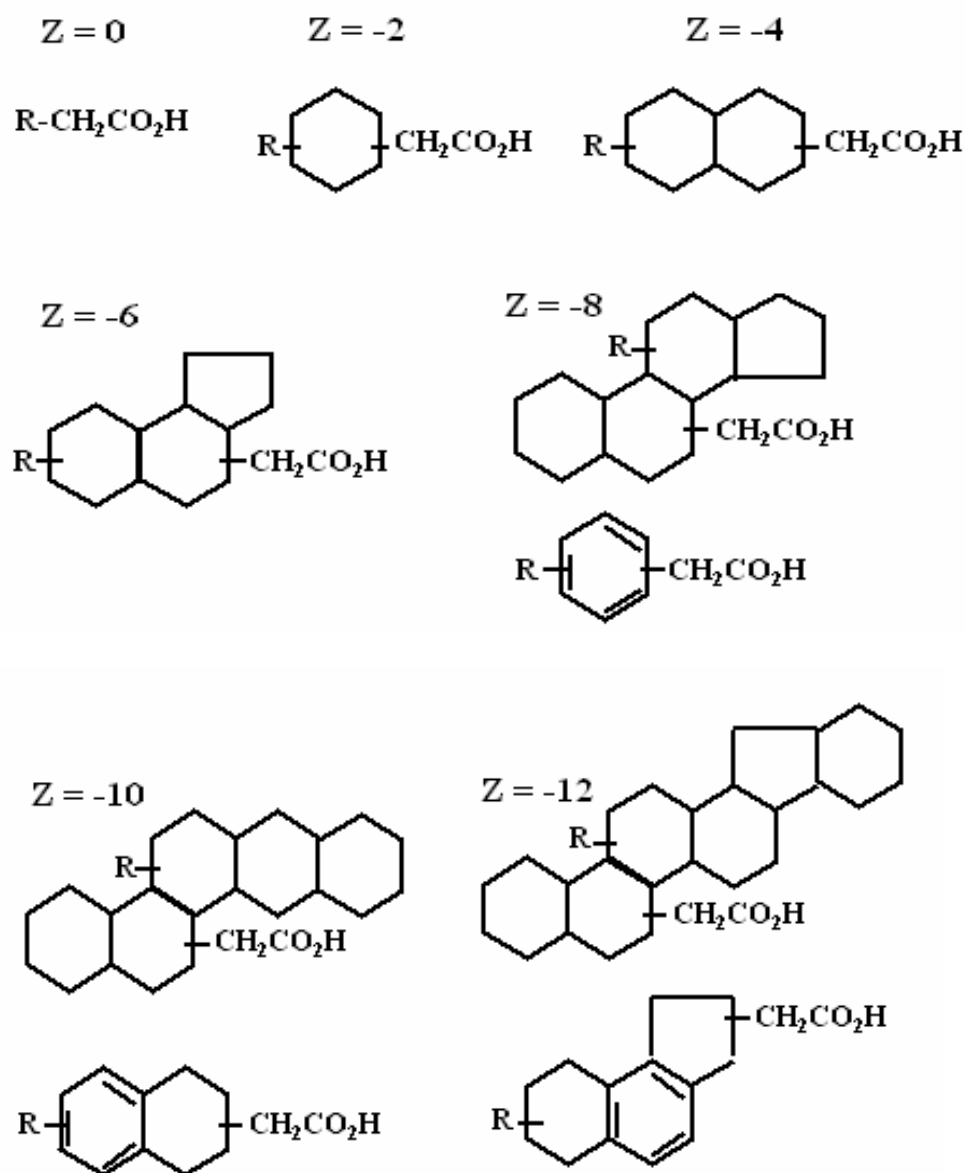


FIGURE 1-3: Z in relation to ring structure.

1.2 Problems associated with naphthenic acids

Napthenic acids in crude oils are of concern due to their corrosivity to refinery units.²³⁻²⁵ It is highly desirable to determine the ring-type distribution and the carbon number distribution of each ring type because the corrosivity of napthenic acids is dependent on their size and structure. The characterization of napthenic acids is also of interest in geochemical studies, particularly migration and biodegradation²⁶⁻²⁸, and to refinery wastewater treatment for environmental compliance.

1.3 Techniques for the isolation of naphthenic acids from crude oil

There are various chromatographic and solvent extraction methods used to isolate napthenic acids from crude oils. One of the methods of obtaining the carboxylic acid fraction from crude oil includes simple base extraction or adsorption onto a KOH impregnated silica gel.²⁹ A non-aqueous ion exchange method³⁰⁻³¹ has also been developed to separate liquid fossil fuels into acid, base, and neutral concentrates. The acid concentrate obtained in this way is then separated by HPLC into sub-fractions using tetralkylammonium hydroxide modified silica gel.³²

There are difficulties in extracting napthenic acids. For example, aqueous caustic extraction cannot be used with acids greater than C₂₀ because they form emulsions. Isolation efficiency is also difficult to assess because of the formation of salts in solution and the co-extraction of weak acids like phenol and carbazoles.

Solid phase extraction²⁹ (SPE) is a fairly recent approach for the efficient extraction of naphthenic acids. SPE is attractive because of stationary phase uniformity, low solvent consumption, and the potential to exploit specific interactions in order to separate polar hydrocarbons from non-polar hydrocarbons. The sample is absorbed on a quaternary amine ion exchange column, and then washed with hexane to remove the hydrocarbons. The aromatics and polar species are eluted with a solvent, or a mixture of solvents of higher eluotropic strength, e.g. toluene, dichloromethane, or acetone. The absorbed acids are then removed by washing with diluted acids (e.g. formic or acetic acid) and then reconstituted in an appropriate solvent.

1.4 TAN number

Crude oil typically contains naphthenic acids in quantities of up to 4 wt %. One of the important markers used to gauge the acidity of oils is the “total acid number” (TAN), which is defined as the mass of potassium hydroxide (in milligrams) required to neutralize one gram of crude oil. Crude oils are considered acidic if their TAN exceeds 0.5 mg KOH/g by non-aqueous titration³³. The TAN of oil has frequently been used to quantify the presence of naphthenic acids, because the carboxylic acid components of oils are believed to be largely responsible for oil acidity. However, more recent research has begun to highlight deficiencies in relying upon this method for such a direct correlation and the total acid number is no longer considered to be such a reliable indicator. It is therefore essential that a more reliable method should be found for isolating and

characterizing the naphthenic acids in crude oil in order for corrosion to be better understood.

1.5 Characterization of naphthenic acids using spectroscopic techniques

Fossil fuels and complex hydrocarbon mixtures have long been investigated by mass spectrometry, and various separation methods have been evaluated for general use with complex hydrocarbon mixtures. One of the greatest difficulties posed when characterizing the naphthenic acids found in crude oils is that it is not possible to extract as many naphthenic acid species as separate components for analysis, and the resulting mass spectra are, therefore, very complex.

1.5.1 MS (Mass Spectrometry)

MS is well suited for characterization of acidic components at the molecular level.^{14, 17, 22, 11, 34-37} Due to their polarity, acids are commonly converted to their corresponding esters for detailed GC/MS³⁸ analysis. However, direct acid analysis is more desirable because it can provide rapid analysis without the concern of losing material through derivatization. Several MS ionization methods have previously been developed for such purposes, including fluoride-ion chemical ionization¹³, negative-ion fast atom bombardment (FAB)¹⁴, chemical ionization (CI), and liquid secondary-ion mass spectroscopy (LSI-MS). We have evaluated alternative soft ionization techniques, including atmospheric pressure chemical ionization (APCI)¹⁷, electrospray ionization

(ESI)^{36,39}, and nanospray ionization (nanoESI)⁴⁰, which can yield molecular or pseudo-molecular ions for the determination of the molecular distribution of naphthenic acids.

When ESI coupled with a MS/MS experiment is extremely valuable in the determination of the molecular weight distribution as well as confirmation of the identity of naphthenic acid samples. Carboxylic acids generate neutral losses of 44, 28 and 18 Dalton that can be respectively attributed to M-CO₂, M-CO, and M-H₂O.³⁴ Table 1³⁴ shows an MS/MS analysis of naphthenic acids in negative ion mode. Figure1-4 and Figure1-5 show the representative spectra that illustrate the fragmentation that can be observed in MS/MS spectra.

TABLE - 1: ESI (-) ion mode MS/MS analysis of naphthenic acids standards. Table taken from reference 34.

Compound	Parent m/z [M-H] ⁻	Daughter (m/z) ^a	Mass loss	Neutral loss fragment
cyclohexylacetic acid	141	97	44	CO ₂
cyclohexanecarboxylic acid	169	125, 151	44, 18	CO ₂ , H ₂ O
adamantaneacetic acid	193	149, 175, 165	44, 18, 28	CO ₂ , H ₂ O, CO
5β-cholanic acid	359	341, 331, 315	18, 28, 44	H ₂ O, CO, CO ₂
2-naphthylacetic acid	185	141, 157	44, 28	CO ₂ , CO
1,2,3,4-tetrahydro-naphthoic acid	175	131, 147, 157	44, 28, 18	CO ₂ , CO, H ₂ O
benzoic acid	121	77	44	CO ₂
1-pyrenecarboxylic acid	245	201	44	CO ₂
1-pyreneacetic acid	259	215	44	CO ₂
1-pyrenecarboxylic acid	287	215	72	CO ₂ + C ₂ H ₂

^a Daughter peaks listed in order of relative abundance.

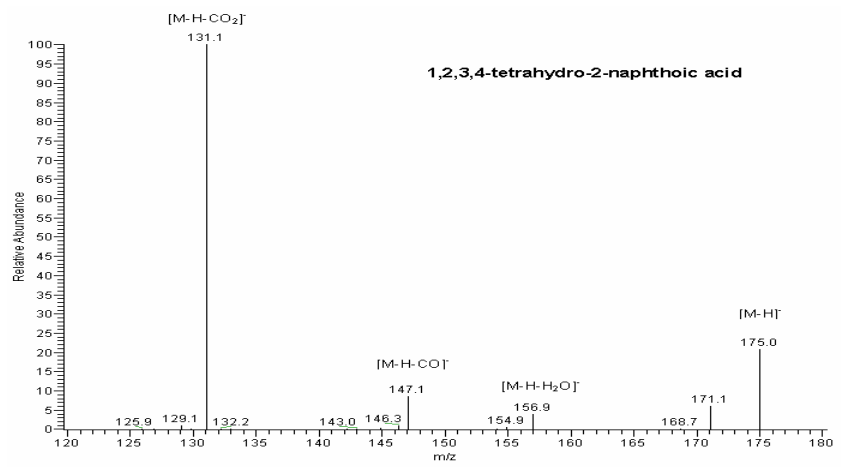


FIGURE 1-4: MS/MS of 1,2,3,4- Tetrahydro-2-naphthoic acid showing a loss of water, carbon monoxide and carbon dioxide. Figure taken from reference 34.

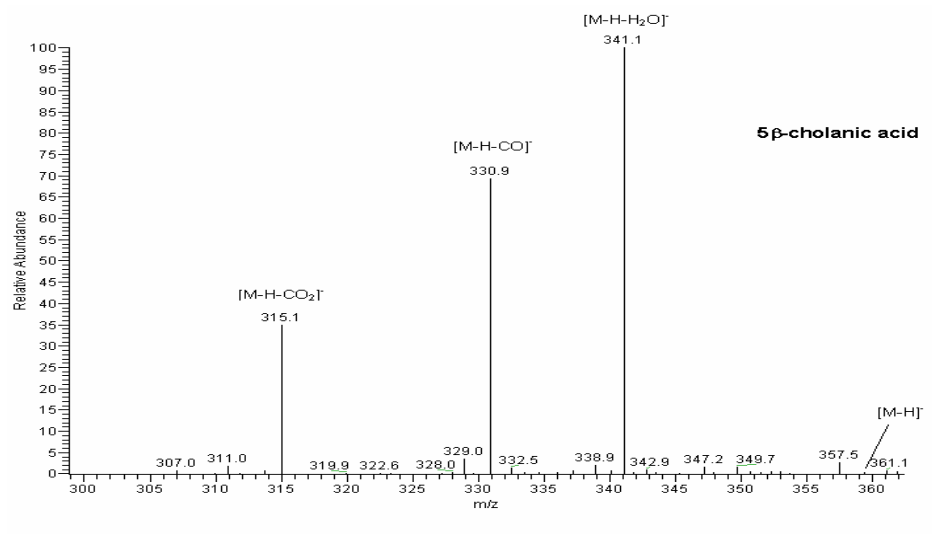


FIGURE 1-5: MS/MS of 5β-cholanic acid showing a loss of water, carbon monoxide and carbon dioxide. Figure taken from reference 34.

1.5.2 NMR (Nuclear Magnetic Resonance)

Nuclear magnetic resonance spectroscopy^{11, 42, 43} can give information about the functional groups present in a sample. In ^1H NMR, the naphthenic acids present in crude oil will exhibit a peak that can be attributed to carboxylic acid hydrogen as well as peaks that can be attributed to hydrogens in aromatic and aliphatic hydrocarbons. ^{13}C NMR can also be used to identify carbonyl, aromatic and primary, secondary and tertiary carbons associated with aliphatic hydrocarbons.⁴¹

1.5.3 IR (Infrared)

Infrared spectroscopy³¹ can also give information about the functional groups present in a sample. Naphthenic acids from crude oil should show a broad OH and a sharp C=O stretch associated with a carboxylic acid group, C-O-H out of plane and O-H out of plane bending.

1.6 Extraction of naphthenic acids with ammoniated ethylene glycol and characterization using MS, NMR and IR

Recently ammoniated ethylene glycol has been reported as an efficient extraction medium for carboxylic acids⁴⁴. Though the reported protocol seemed to extract naphthenic acids, no verification was included that naphthenic acids and only naphthenic acids were extracted. A TAN number was reported but under the conditions of titration,

acids may have been produced from esters formed during the extraction protocol. In this project the extraction efficiency of the procedure will be evaluated. A series of analytical techniques including mass spectrometry, nuclear magnetic resonance, and infrared spectroscopy will also be used to characterize the naphthenic acids extracted from ammoniated ethylene glycol.

CHAPTER 2

EXPERIMENTAL

2.0 Materials

Petroleum crude oil was obtained from Chevron Texaco, Houston. Merichem standard, and Tufflo were donated by Exxon-Mobil research and engineering (Baton Rouge, LA). Benzoic acid, butyl benzoate, 1-decane sulfonic acid, acetone, deuterated chloroform, deuterated acetone, deuterated dichloromethane were obtained from Sigma-Aldrich (St. Louis, MO) and used without further purification. Methanol, ethanol, dichloromethane, acetonitrile, acetic acid, and ammonium hydroxide were all chromatographic grade and obtained from EM Science (Gibbstown, NJ). Phenolphthalein, ethylene glycol, and petroleum ether were obtained from J T Baker (Phillipsburg, NJ), Matheson Coleman & Bell (Norwood, Ohio), and Mallinckrodt (St. Louis, MO) respectively.

2.1 Isolation of naphthenic acids

Evidence from earlier studies on crude oil indicates the presence of up to 5% naphthenic acids in crude oil samples from different parts of the world. A naphthenic acid

standard mix and a naphthenic acid extract from a crude oil have been prepared in order to evaluate the extract efficiency of ammoniated ethylene glycol. In addition, ESI/MS and tandem mass spectrometry, (MS/MS) as well as NMR and IR (when applicable), have been used to identify the classes of chemical compounds.

2.1.1 Extraction Protocol

Tufflo is a crude oil simulates (generously donated by Exxon-Mobil) that contains aliphatic and aromatic hydrocarbons in a ratio similar to that found in crude oils.

Merichem is a standard mixture of naphthenic acids. A control mixture that mimics the properties of petroleum crude oil was prepared by adding Merichem to Tufflo. 100 milligrams of Merichem was added to 1.9 grams of Tufflo, followed by sonication for 10-15 minutes to attain a uniform 5% Merichem in Tufflo solution. Tufflo is a clear viscous liquid and Merichem is a dark yellow viscous liquid; upon sonication, the whole mixture turns into a uniform light yellow liquid. Anhydrous ammonia was bubbled at a constant flow rate through 9-10 ml of ethylene glycol in a three-necked, round bottom flask maintained at 0 °C in an ice bath. It usually takes about 1.5 - 2 hours for the solution to be saturated.

Two grams of 5% Merichem in Tufflo or 2 g of petroleum crude oil was added to 9-10 ml of ammoniated ethylene glycol and then stirred for 1 hour at 0 °C. The whole system was transferred into a single neck round bottomed flask capped with a rubber stopper, then heated at 60-65 °C for an hour. The solution was then transferred into a

separating funnel and, upon cooling in about 20-25 minutes, two layers formed: an oil phase (top layer) and an ethylene glycol phase (bottom layer). (Note: If the ammonium naphthenate salts in the ethylene glycol phase are left too long in the separation funnel, they may go back into the oil phase). The top layer was then discarded, and the ethylene glycol layer, which contains ammoniated naphthenate salts, was then transferred into a round bottom flask and heated at 130-135 °C using an oil bath for 1.5 – 2 hours or until no ammonia gas evolves; the ethylene glycol layer turns to a yellow color on heating. The heat removes the ammonia, which has a low boiling point, from the ammoniated naphthenate salt, and the naphthenic acids that have high boiling points remain undecomposed. The ethylene glycol layer was transferred to a separatory funnel while hot and left to cool to room temperature.

Five-ten ml of petroleum ether was added to the funnel and all the naphthenic acids are extracted from ethylene glycol. The suspension was left to settle for 15-20 minutes. The bottom layer (ethylene glycol) was discarded. The petroleum ether layer containing the naphthenic acids was then washed with 3-5 ml of water which removes the residual ethylene glycol from the petroleum ether. The naphthenic acids are obtained by evaporation of the solvent at 40 °C for 5-8 minutes. The end result was a dry extract of naphthenic acids. Figure 2-1 illustrates the entire sequence of steps.

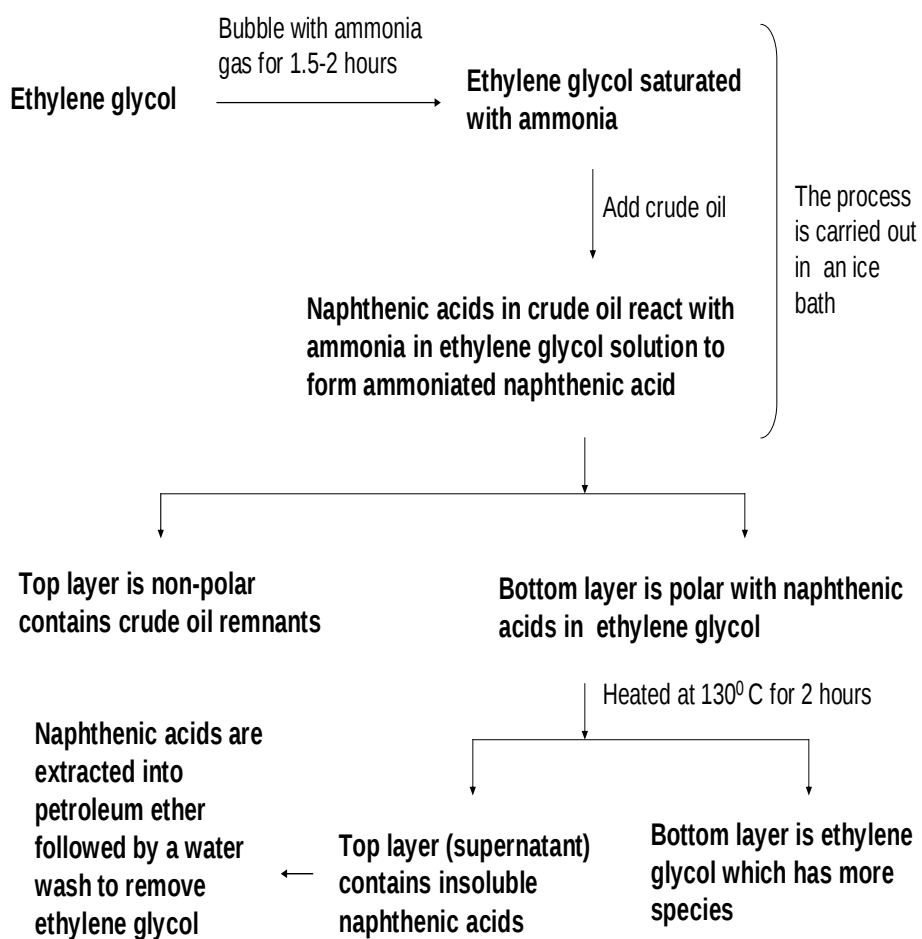


FIGURE 2-1: Overview of the extraction protocol.

2.1.2 TAN number

Naphthenic acids were extracted from either 2 g of petroleum crude oil or the 5% Merichem in Tufflo mixture using the ammoniated ethylene glycol extraction procedure. The naphthenic acids from the crude oil or the Merichem extract were titrated with 0.01 N KOH in ethanol solution using phenolphthalein indicator. The TAN number is

reported as the mass of potassium hydroxide (in milligrams) required to neutralize one gram of the 5% Merichem in Tufflo mixture or petroleum crude oil.

2.2 Mass Spectrometry (MS)

MS and MS/MS experiments were performed using a Thermo Finnigan Mass Spectrometer controlled by Tuneplus software (Excalibur), with the ESI (Electrospray Ionization) source in negative ion mode. The concentration of the sample solutions was 1-1.5 mg of naphthenic acid extract in 2 ml of solvent; which was acetonitrile, methanol or dichloromethane. The experiments were performed without 0.5% of ammonia in solution except for naphthenic acids extracted from crude oil that are run in 20% / 80% dichloromethane / acetonitrile.

2.2.1 ESI (-) MS Experiments

The sample flow rate was 4 μL – 6 $\mu\text{L}/\text{min}$; the mass scan range was between 180 to 450 m/z; mass spectra were based on 3 microscans with a 50 msec ion injection time; automatic gain control was enabled. The sheath gas was maintained at 60 psi, the temperature of the API stack at 220 ° C, the capillary voltage at 7 V, and the spray voltage at 3.15 kV.

2.2.2 ESI (-) MS/MS Experiments

For all ions, the collision activated dissociation (CAD) energy was set in such a way that the MS/MS scan of the precursor and fragment ions could both be detected. CAD energy was between 20-40 %. The optimum peak isolation width was 1 Da, (whereas a wider width (more than 1 Da) resulted in fragmentation of ions of species with m/z near that of the precursor ion.) Activation Q was 0.25 and activation time is 30 msec.

MS and MS/MS experiments were performed on a series of standards: benzoic acid, butyl benzoate, decanesulfonic acid and, a Merichem naphthenic acid standard mix.

MS and MS/MS experiments were also performed on the extract of 5% Merichem in Tufflo and the naphthenic acids extracted from crude oil.

2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

All the NMR experiments were performed on a Varian 400 MHz NMR spectrometer equipped with a Sun workstation. ^{13}C NMR spectral data were collected at a frequency of 100 MHz.

Merichem: 100 mg of Merichem was dissolved in 2ml of deuterated chloroform. ^1H and ^{13}C NMR spectra were collected.

Fractions of 5% Merichem in Tufflo: ^1H NMR experiments were performed for 5% Merichem in Tufflo after extraction, Tufflo supernatant after contact with ethylene glycol, and the ethylene glycol layer after removal of ammonia. 50 mg of each fraction was dissolved in a deuterated solvent.

Fractions of crude oil: ^1H NMR experiments were performed on naphthenic acids extracted from crude oil, crude oil supernatant after contact with ethylene glycol, and ethylene glycol after contact with crude oil after removal of ammonia. 55 mg of each fraction was dissolved in a deuterated solvent.

All the fractions were dissolved in 2ml of deuterated chloroform except for the ethylene glycol fraction which was dissolved in deuterated acetone.

2.4 Infrared Spectroscopy (IR)

Fourier transform infrared (FTIR) experiments were performed using Perkin-Elmer FTIR (model 1600) instrument controlled by Spectrum One software. All spectra were obtained in the absorbance mode with a scan range of $4000\text{--}450\text{ cm}^{-1}$ and a resolution of 4 cm^{-1} for 10 scans. Samples were prepared by dissolving 5-6 mg of Merichem standard mix, 5% Merichem in Tufflo extract, or naphthenic acid extract from petroleum crude oil in 2 mL of petroleum ether. A drop of each was placed on a polyethylene film. The petroleum ether was allowed to evaporate. Background spectra were collected for polyethylene and polyethylene and petroleum ether mix.

Petroleum ether was not used to dissolve ethylene glycol, water and crude oil samples. These samples were in the liquid state when applied to the polyethylene film.

CHAPTER 3

RESULTS

3.1 Isolation of Naphthenic acids

3.1.1 Extraction yield

The extraction yield for the 5% Merichem was determined to be 80%.

By subtracting weight of final extract from initial weight of 5% merichem in tufflo used and dividing with the initial weight of 5% merichem. There was a possibility that the extract may have impurities from crude oil and also from the chemicals used in the extraction process.

3.1.2 TAN number

7.56 mg of KOH in 0.01 N ethanol was required to neutralize 8 mg of Merichem naphthenic acid standard mix (TAN = 0.945).

3.2 Mass Spectrometry (MS)

3.2.1 MS and MS/MS of standard compounds

The MS and MS/MS study was performed on a standard carboxylic acid, an ester and a sulfonic acid to understand the characteristic fragmentation patterns of these compounds. Benzoic acid: The MS/MS experiment on a carboxylic acid (benzoic acid) was run to observe the fragmentation pattern. There is a mass loss of 44Da due to carbon dioxide loss shown by benzoate, leaving a fragment ion peak at 77 Da (benzene ring)³⁴ (Figure 3-1).

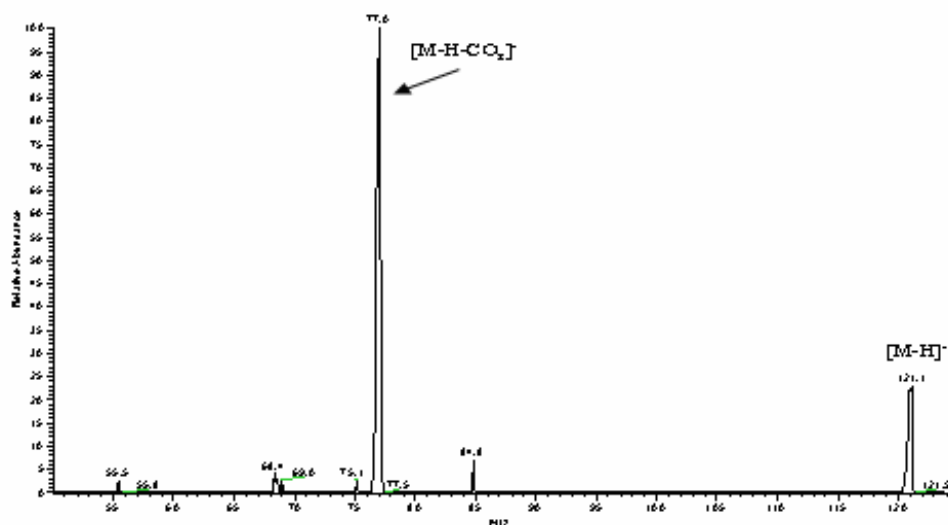


FIGURE 3-1: MS/MS of benzoic acid (122Da) in acetonitrile using ESI negative ion mode with mass range 50-125 m/z.

Ester compound: Heating an acid at high temperature (120-180 °C) in presence of a base/ water can favor the formation an ester. Our extraction procedure favors the formation of esters from acids in the crude oil. MS/MS experiments were performed on

butylbenzoate⁴⁵ with 179 m/z in acetonitrile in negative ion mode and showed a peak at 79.9m/z (Figure 3-2).

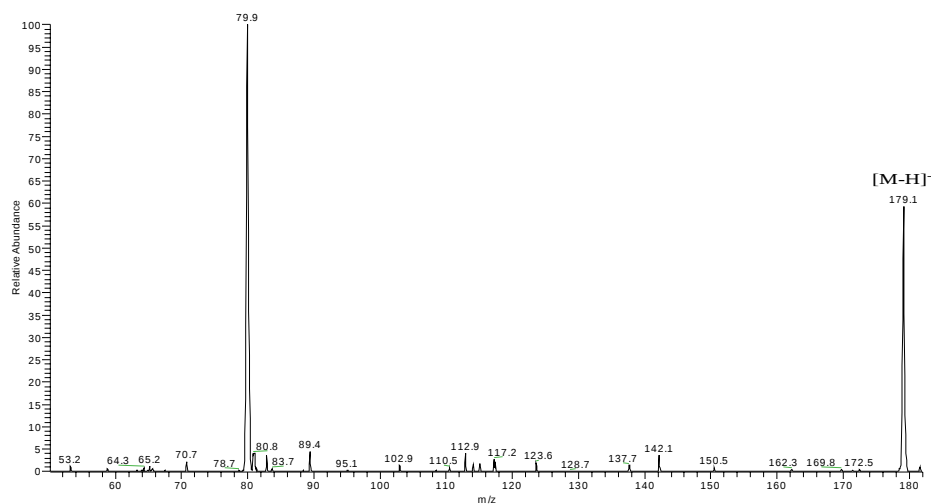


FIGURE 3-2: MS/MS of butylbenzoate (178m/z) using ESI in negative ion mode with mass range 50-182 m/z in acetonitrile.

Decanesulfonic acid: (Figure 3-3) MS/MS experiment was performed on a standard sulfur compound (1-decanesulfonic acid) in order to observe the fragmentation pattern of the precursor ion. In negative ion mode, the precursor of 1-decanesulfonic acid of molecular weight 222 (sodium salt peak with molecular mass of 244), showed a peak at 221m/z in methanol, and the MS/MS experiment showed a peak at 79.9m/z, which corresponds to SO_3 .

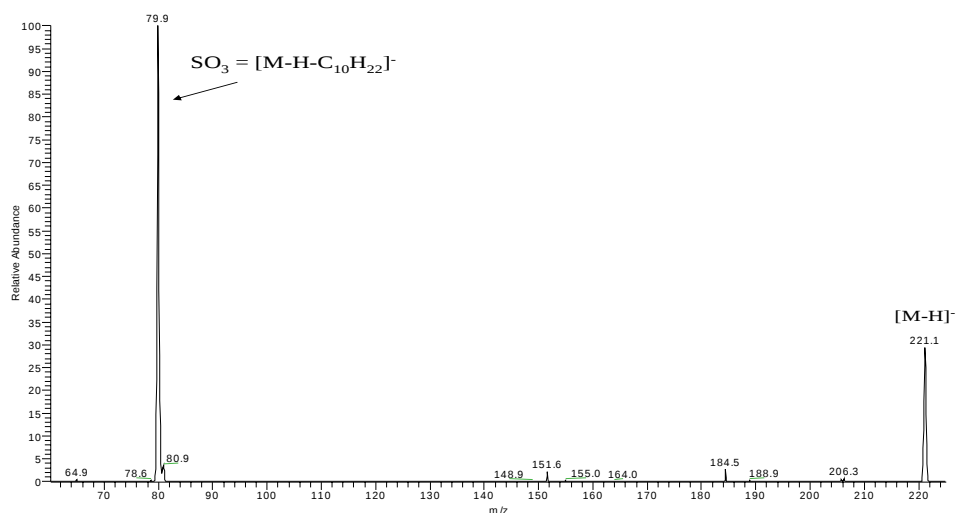


FIGURE 3-3: MS/MS of 1-decanesulfonic acid using ESI in negative ion mode in the mass range 60-225 m/z in methanol.

3.2.2 MS and MS/MS of Merichem

A number of peaks in the range of 200 to 400 m/z were found for the ESI negative ion mode mass spectrum of Merichem extract. The distribution appears very Gaussian with a maximum at around 300 and a spacing of 14 Da (due to $(-\text{CH}_2)$ between most of the large peaks. MS spectrums are shown in Figures 3-4 and 3-5.

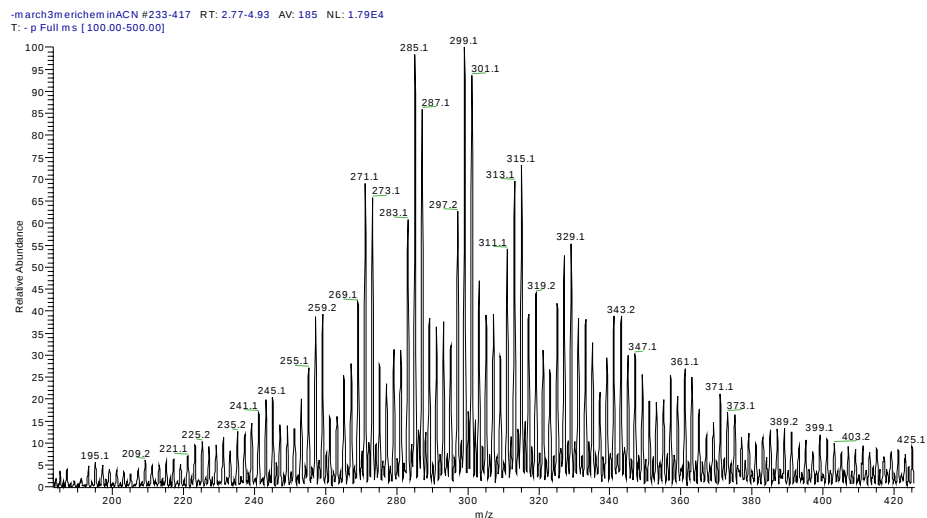


FIGURE 3-4: Merichem in ESI negative ion mode in the mass range 180-425 m/z in acetonitrile.

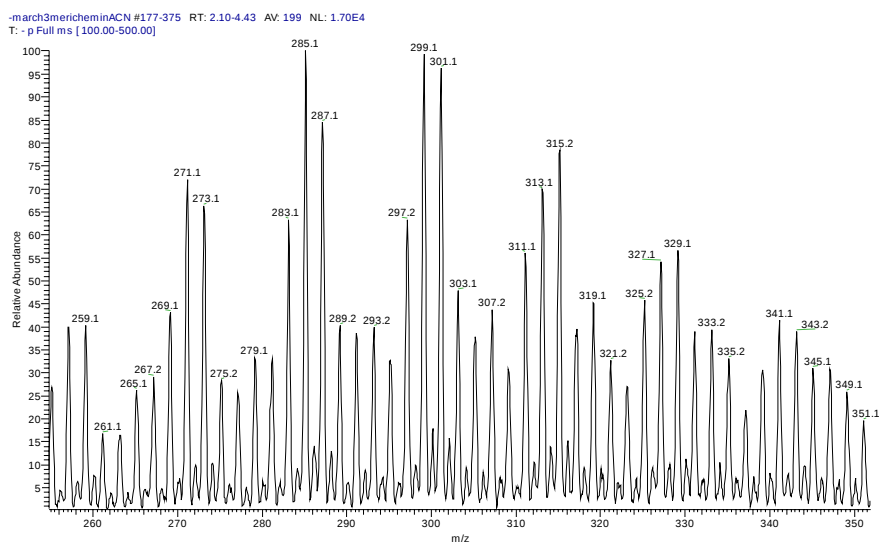


FIGURE 3-5: Merichem in ESI negative ion mode in the mass range 256-350 m/z in acetonitrile.

To identify whether the extraction of the Merichem actually yielded naphthenic acids, we performed MS/MS experiments on the Merichem naphthenic acid mix focusing

on all of the more intense common peaks. The MS/MS of Merichem peaks that were chosen for MS/MS experiments had a relative abundance of 40 and higher in the MS spectrum. The results showed mass losses of M-1, M-18, M-28, and M-44, which corresponds to a loss of hydrogen, water, carbon monoxide, and carbon dioxide.

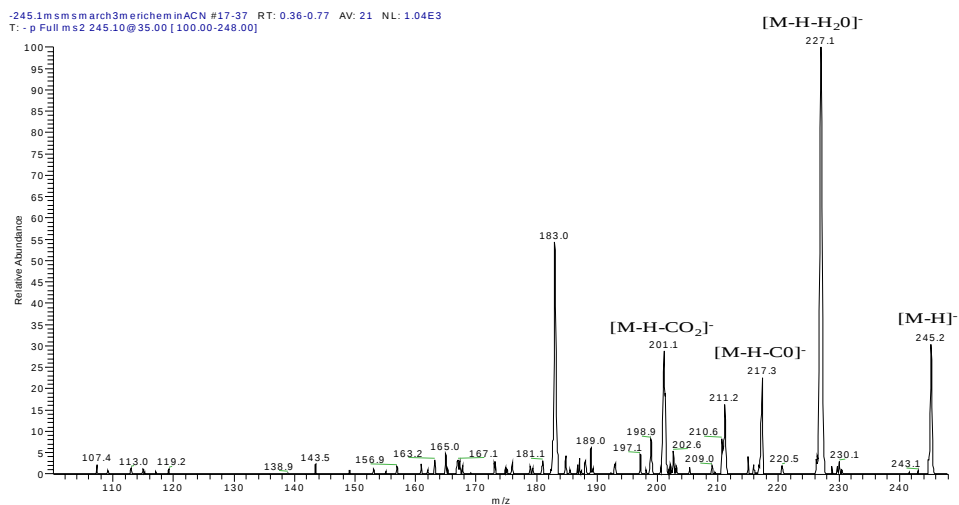


FIGURE 3-6: MS/MS of 245.1 m/z for Merichem in ESI negative ion mode within the mass range 100-248 m/z in acetonitrile.

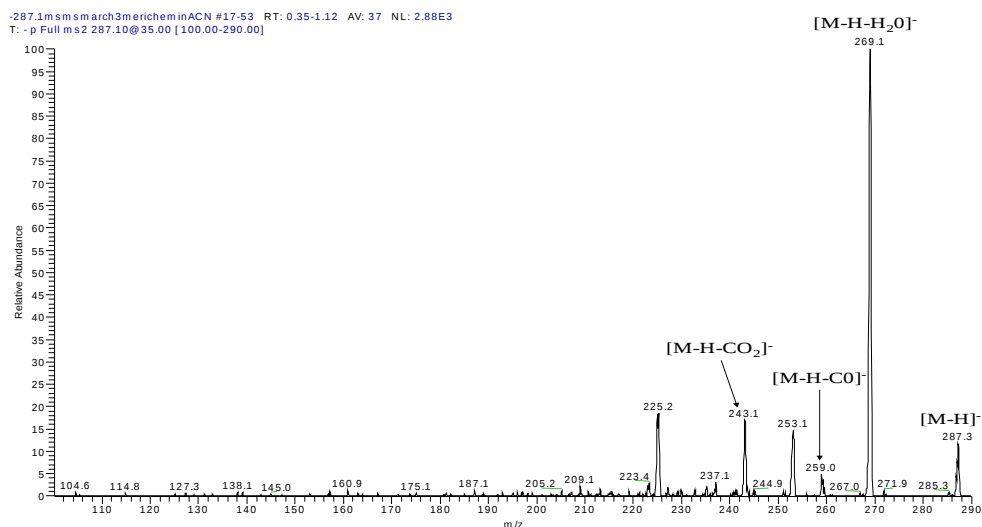


FIGURE 3-7: MS/MS of 287.1 m/z for Merichem in ESI negative ion mode with the mass range 100-290 m/z in acetonitrile.

Figures 3-6, 3-7, 3-8, and 3-9, illustrate representative MS/MS spectra for peaks at 245, 287, 301, and 313 (found in the MS spectrum), which confirm that these are due to naphthenic acids. There was a mass loss of M-34 and M-62 from the parent molecule which have not been identified. The M-1 hydrogen loss can be seen in each spectrum. The M-18 water loss was prominent and was found in all of the spectra. The mass loss of M-28 corresponding to carbon monoxide was small in some of the MS/MS spectra. All of the spectra exhibited a mass loss of M-44.

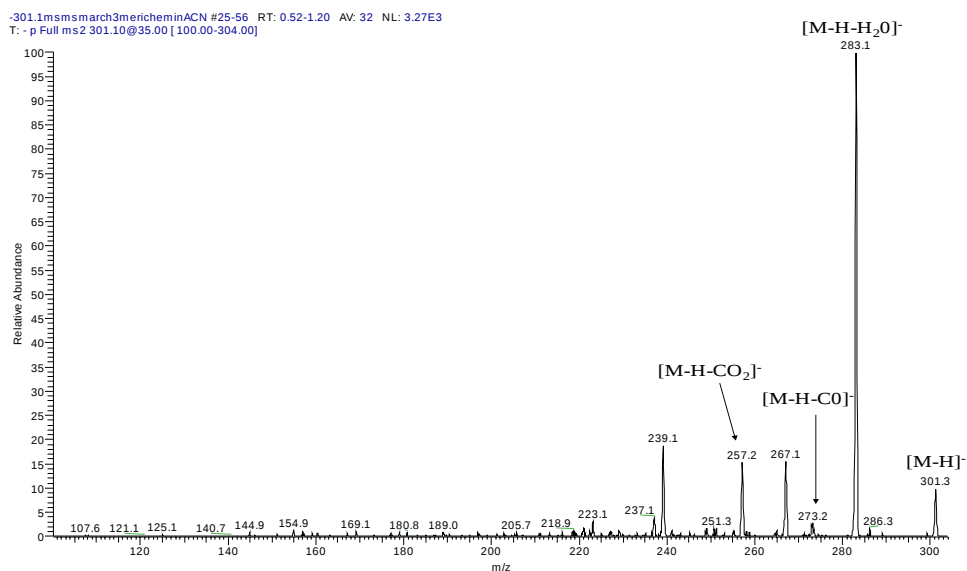


FIGURE 3-8: MS/MS of 301.1 m/z for Merichem in ESI negative ion mode with mass range 100-305 m/z in acetonitrile.

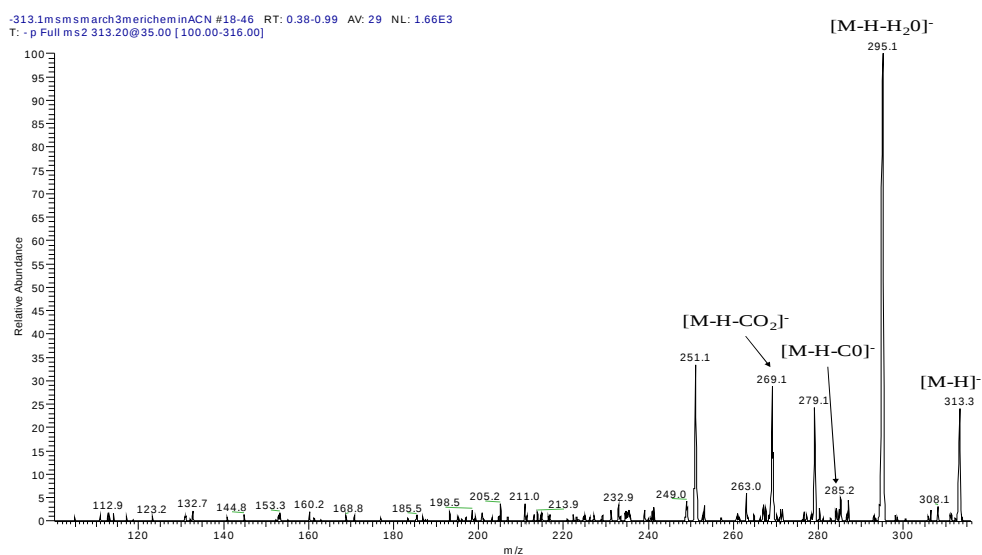


FIGURE 3-9: MS/MS of 313.2 m/z for Merichem in ESI negative ion mode with mass range 100-317 m/z in acetonitrile.

3.2.3. MS and MS/MS of naphthenic acids extracted from 5% Merichem in Tufflo

To identify whether the extraction of the Merichem actually yielded naphthenic acids, we performed MS (see Figure 3-10) and MS/MS experiments on the 5% Merichem in Tufflo extract. Merichem peaks chosen for MS/MS experiments had a relative abundance of 40 and higher in the MS spectrum.

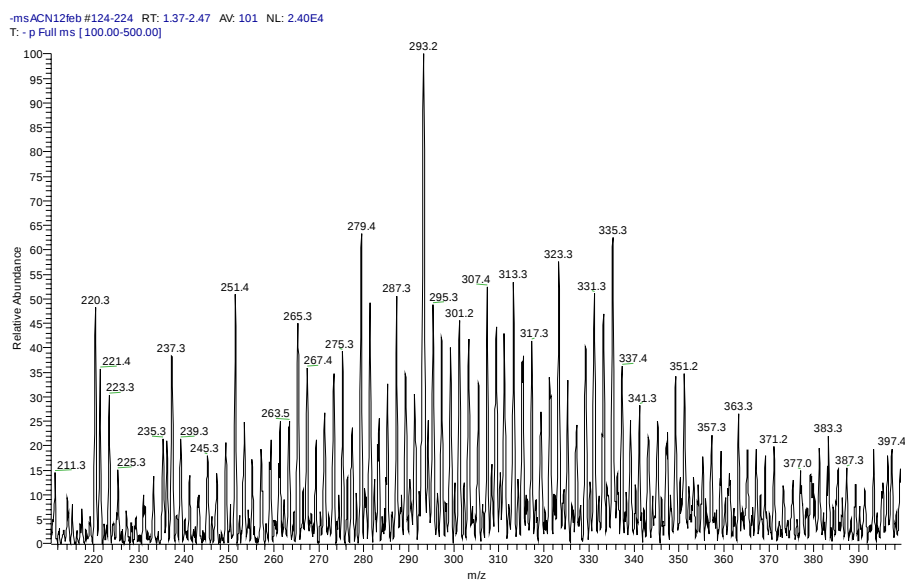


FIGURE 3-10: 5% Merichem in Tufflo Extract in ESI negative ion mode in the mass range 200-400 m/z run in acetonitrile.

A number of peaks in the range of 200 to 400 m/z were found for the ESI negative ion mode mass spectrum of 5% Merichem in Tufflo extract. The distribution no longer appears to be Gaussian. There was an underlying Gaussian distribution centered

around 300, but it was punctuated by a number of peaks with higher intensity. There was still a spacing of 14 Da (due to $(-\text{CH}_2)$) between most of the large peaks.

The results for MS/MS experiments show mass losses of M-1, M-18, M-28 and M-44, which correspond to the loss of hydrogen, water, carbon monoxide and carbon dioxide. Figures 3-11, 3-12, 3-13, and 3-14, illustrate representative MS/MS spectra for peaks at 245, 287, 301 and 313 found in the MS spectrum and confirm that these are due to naphthenic acids. The M-28 peak has a lower intensity than the other peaks. Peaks with a loss of M-34 and M-62 were also found upon fragmentation of some of the peaks in the MS spectrum.

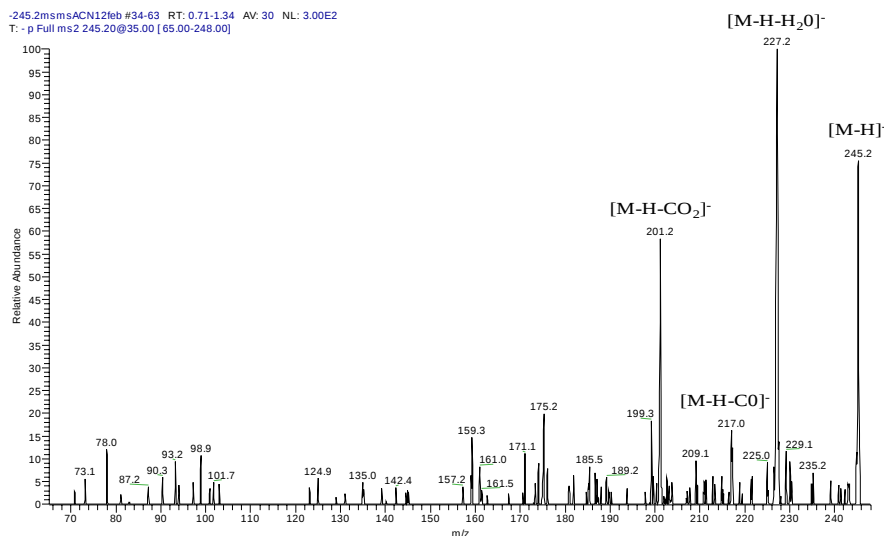


Figure 3-11 is a representative MS/MS spectrum for the peak at 245 m/z. The normal fragmentation peaks associated with a carboxylic acid are present, but there are no peaks found at M-34 and M-62. More fragmentation was observed for the extract than Merichem before extraction.

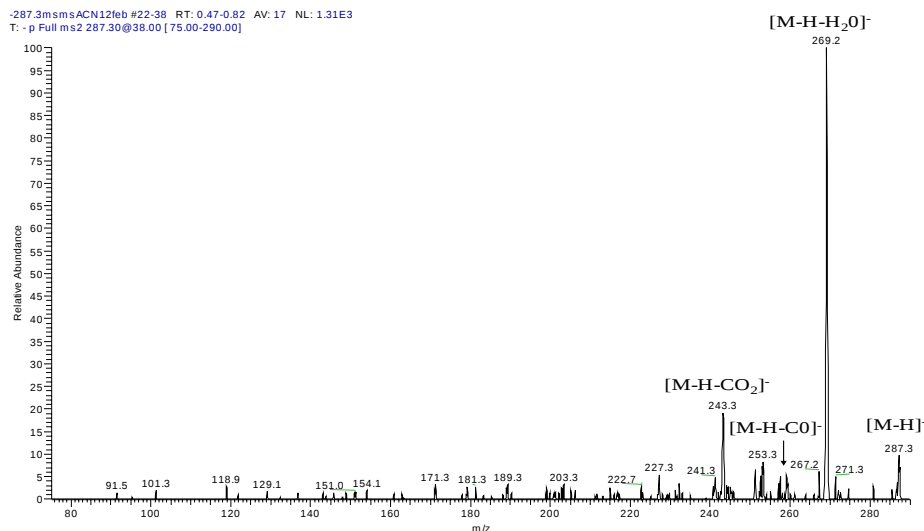


FIGURE 3-12: MS/MS of 287.3 m/z from the Merichem extract in ESI negative ion mode within a mass range of 75-290 m/z in acetonitrile.

Figure 3-12 illustrates a representative MS/MS spectrum for the peak at 287 m/z. In addition to the normal fragmentation peaks associated with a carboxylic acid, there was a peak found at M-34, but no peak was found at M-62.

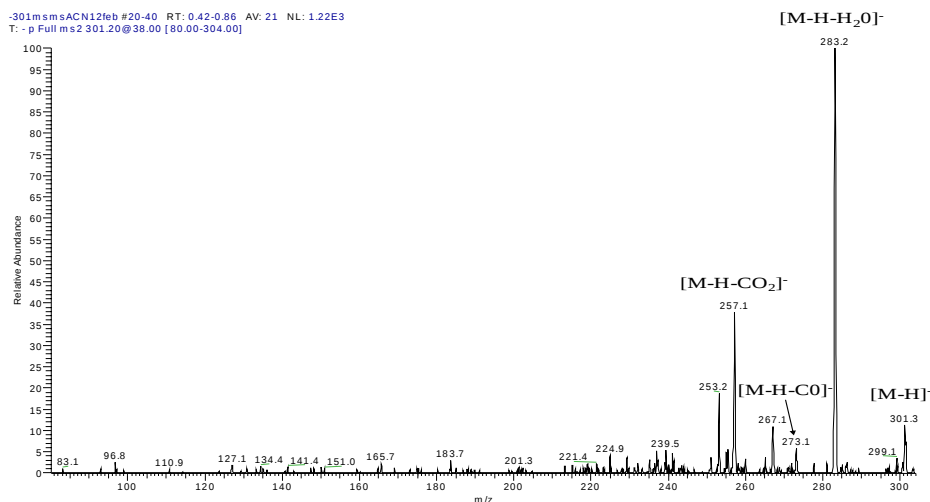


FIGURE 3-13: MS/MS of 301.2 m/z from Merichem extract in ESI negative ion mode within the mass range 80-305 m/z. in acetonitrile.

Figure 3-13 illustrates a representative MS/MS spectrum for the peak at 301 m/z.

In addition to the normal fragmentation peaks associated with a carboxylic acid, there are peaks found at M-34 and M-62.

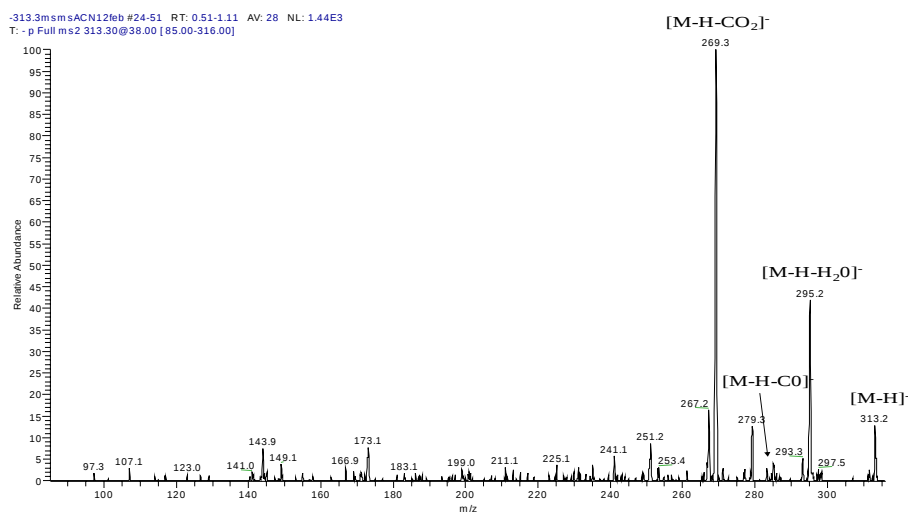


FIGURE 3-14: MS/MS of 313.2 m/z from Merichem extract in ESI negative ion mode within the mass range 85-315 m/z in acetonitrile.

Figure 3-14 illustrates a representative MS/MS spectrum for the peak at 313 m/z. In addition to the normal fragmentation peaks associated with a carboxylic acid, there are peaks found at M-34 and M-62. There are also more fragmentations.

A comparison was made between samples before and after extraction of the Merichem. The Merichem, after extraction, has a similar dispersion of peaks as Merichem before extraction, but less intense. This could be due to the extraction process and the loss of naphthenic acids; it also could be due to modification of some of the naphthenic acids.

Mass spectra of Merichem before and after extraction (indicated in parentheses) show the presence of common peaks including: 237.3 (237.3), 245.2 (245.3), 251 (251.4), 265.3 (265.3), 275.3 (275.3), 279.3 (279.4), 287.1 (287.3), 293.3 (293.2), 301.3 (301.2), 331.1 (331.3), 335.2 (335.3), and 341.3 (341.3). These provide evidence that naphthenic acids are extracted into ammoniated ethylene glycol ⁴⁴. Some of the peaks that were found in standard Merichem, before extraction, are missing after the Merichem extraction. It may be that some of the lower molecular weight naphthenic acids remained in the ethylene glycol or water used in the process of extraction. Alternatively, some of the acids may be esterified and therefore not appear in the mass spectrum.

3.2.4 MS and MS/MS of naphthenic acids extracted from crude oil

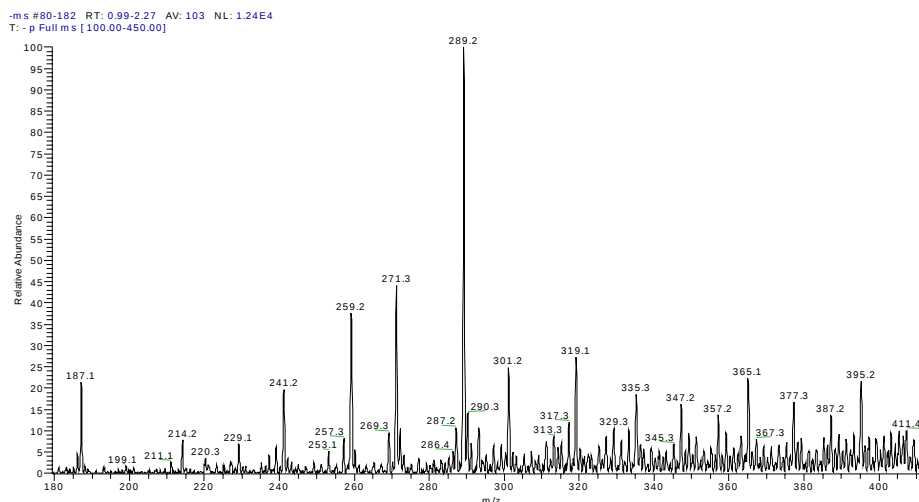


FIGURE 3-15: MS of naphthenic acids extracted from crude oil run in acetonitrile, negative ion mode within the mass range 100 m/z to 440m/z.

The MS of the naphthenic acids extracted from crude oil (Figure 3-15) does not show the diversity present in the Merichem naphthenic acid extract. Compared with Figure 3-10, only certain classes of naphthenic acids appear to be present in the extract obtained from the crude oil (Chevron Texaco Cabinda oil sample). They seem to be a homologous series (259, 289, and 319) which all lose water [$M-H_2O$], as well as a homologous series (241, 271, 301) which loses a hydride [$M-2H$] as well as water [$M-H_2O$]. Peaks chosen for MS/MS experiments have a relative abundance of 15% and higher in the MS spectrum. All peaks are reported in table 2 with decreasing intensity. There was a sulfur compound extracted from crude oil, so we may be extracting sulfur compounds along with naphthenic acids. There may be some loss of naphthenic acid from crude oil due to acids or ester derivate of acid in the extract.

TABLE - 2: MS/MS results for naphthenic acids extracted from crude oil run in acetonitrile.

Precursor	Fragment ions (Da)
187*	115, 143, 169, 159
214 #	150, 134, 71.7
241*	239, 223, 211, 197
259	241, 257, 153, 235, 123
271*	269, 253, 235, 223, 267, 241, 225, 213, 251, 227
289	271, 153, 269
301*	253, 299, 283, 237, 235, 223, 265, 199.7
319	301
335*	317, 241, 291, 273, 306.9, 350
347*	329, 239, 241, 317, 253, 303, 285, 275
365	347, 271, 335, 229, 317, 329
377*	359, 257, 269
395*	377, 351, 359, 367, 380, 241, 271

* Shows mass loss of 44 Da that was attributed to the loss of CO₂

A sulfur compound with a mass loss of 64, which was attributed to SO₂.

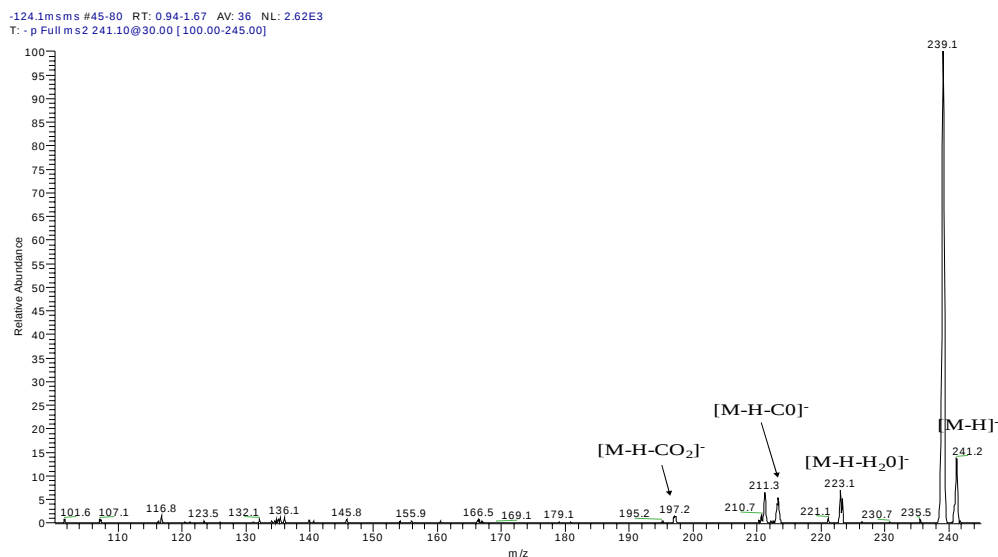


FIGURE 3-16: MS/MS of 241.2 m/z of naphthenic acid extract from crude oil with a mass range 100-245 m/z.

Figures 3-16 and 3-17, demonstrate MS/MS of the parent peak shows less fragmentation. There was low peak signal intensity for M-CO₂, M-CO, and M-H₂O mass loss. An intense peak found at 239.1 m/z and 115.1 m/z for the parent peaks 241 m/z and 187.2 m/z respectively.

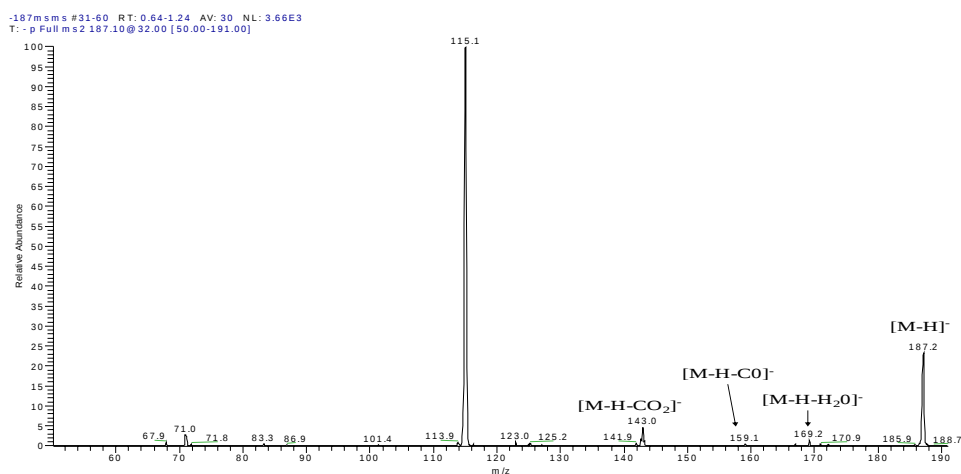


FIGURE 3-17: MS/MS of 187.2 m/z of naphthenic acid extract from crude oil with a mass range 50-190 m/z.

Figures 3-18 and 3-19 MS/MS of the parent peaks showing more fragmentation.

There was an intense peak signal at M-CO₂, M-CO, and M-H₂O mass loss. An intense peak found at 241.3 m/z for the parent peaks 335.3 m/z. There was an intense peak loss at 239 m/z, 241 m/z, and 252.9 m/z for the parent peak 347.2 m/z.

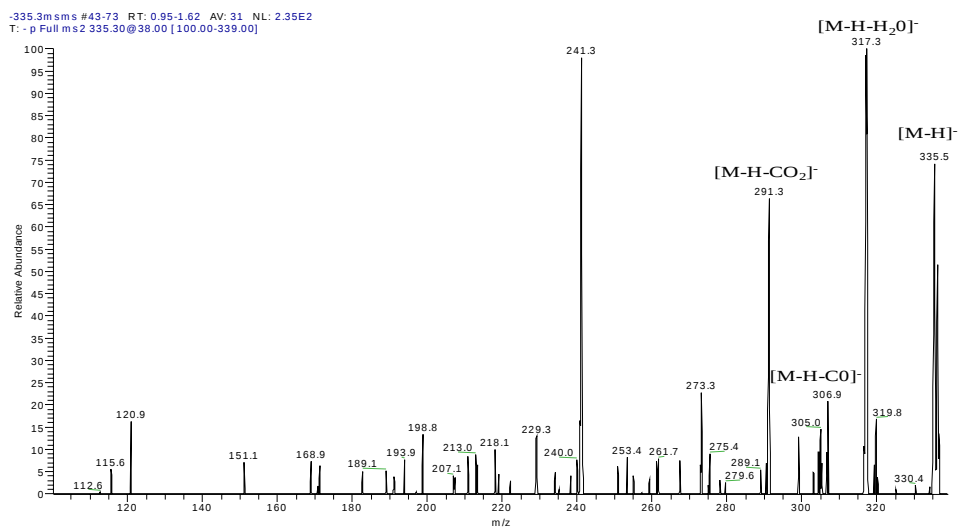


FIGURE 3-18: MS/MS of 335.3 m/z of naphthenic acid extract from crude oil within a mass range 100-340 m/z.

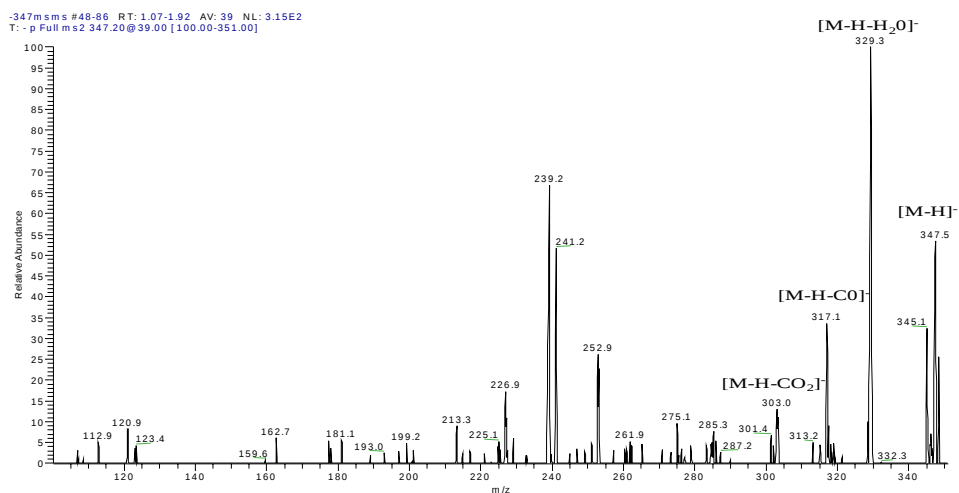


FIGURE 3-19: MS/MS of 347.2 m/z of naphthenic acid extract from crude oil within a mass range 100-350 m/z.

The MS/MS spectrum in Figure 3-20 illustrates the fragmentation pattern generated by a sulfur compound. There was sulfur associated with M-64 loss of SO_2 from the precursor ion.

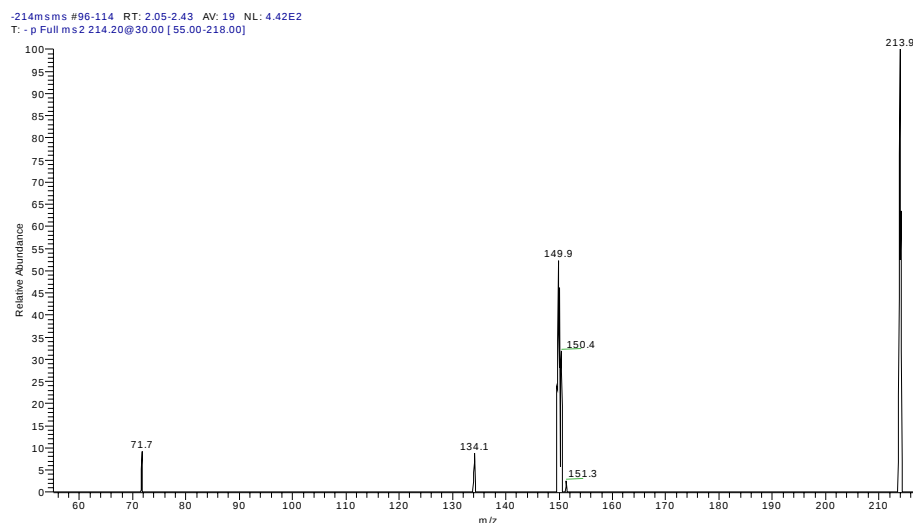


FIGURE 3-20: MS/MS of sulfur compound extracted from crude oil in acetonitrile in negative ion mode with a mass range 60 m/z to 220m/z.

The results indicate that the extraction procedure not only extracts naphthenic acids but also extracts other acid fractions present in crude oil, such as sulfonic acids. There was also a possibility that during the process of extraction of naphthenic acids, naphthenic acids might have been converted to their corresponding esters.

3.2.5 MS and MS/MS of naphthenic acids extracted from crude oil: samples run in 20% dichloromethane / 80% acetonitrile

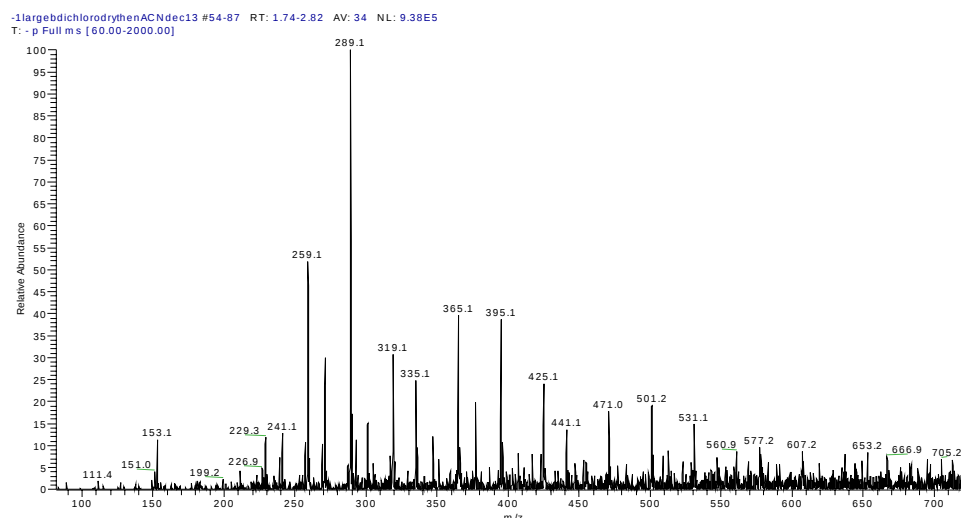


FIGURE 3-21: MS of naphthenic acids extracted from crude oil in 20% dichloromethane / 80% acetonitrile with 0.5% ammonia run in negative ion mode.

Figure 3-21, using a mass range of 200 m/z to 600 m/z, there shows that are more peaks found in 20% dichloromethane / 80% acetonitrile solvent system with 0.5% ammonia and also showed higher signal intensity.

TABLE-3: MS/MS results for naphthenic acids extracted from crude oil in 20% dichloromethane / 80% acetonitrile. The fragment ions are arranged in decreasing order of intensity.

Precursor	Fragment ions
229	227, 123, 211, 93, 199
241	239, 211, 233, 212, 135
259	241, 257, 153, 123
271	269, 253, 233, 235, 241
289	271, 153
301	253, 299, 283, 237, 265, 223, 151
319	301, 318, 302
335*	317, 241, 229, 305, 291, 199, 211, 123
347*	329, 239, 317, 253, 241, 121, 227, 213, 199, 289, 303
365	347, 271, 241, 229, 335, 259
377	359, 347, 269, 257
395	377, 271, 347, 365, 289, 289, 259, 153
425	407, 377, 395, 271, 301, 289
441*	423, 335, 347, 305, 411, 317, 229, 241
454	436, 407, 419, 360, 389, 301, 299, 348, 334, 289, 319, 240
471	453, 441, 435, 365, 347, 335, 377, 423
501	483, 471, 465, 365, 377, 395, 347, 259, 271, 289
530	513, 482, 501, 377, 395, 407, 289, 271, 425, 436, 465, 259, 301, 365

* A 44 Da mass loss is attributed to carbon dioxide from carboxylic acid.

Table -3 reports the MS/MS results for naphthenic acids extracted from crude oil. There was a mass loss of 18 (loss of water); other mass losses that appeared were at 30, 36, and 48. There were some extra peaks that were found in the MS when run with 20% / 80% dichloromethane/acetonitrile containing 0.5% ammonia when compared with an MS spectrum of an extract run with acetonitrile. The extra peaks were in the range of 420m/z - 600m/z, and found at 425, 441, 454, 471, 501, and 531. More fragmentation was observed with 20% / 80% dichloromethane / acetonitrile with 0.5% ammonia. Both solvent systems had common peaks, but showed different fragmentation patterns for a particular m/z. The mass loss of M-44 is observed with an extract run in acetonitrile but a 44 mass loss was not observed with 20%/80% dichloromethane / acetonitrile with 0.5% ammonia for the following peaks 241m/z, 271 m/z, 301 m/z, 377 m/z, and 395 m/z. It seems that 20% / 80% dichloromethane / acetonitrile with 0.5% ammonia as a solvent system do not favor the formation of fragments that can be ascribed to a carboxyl group.

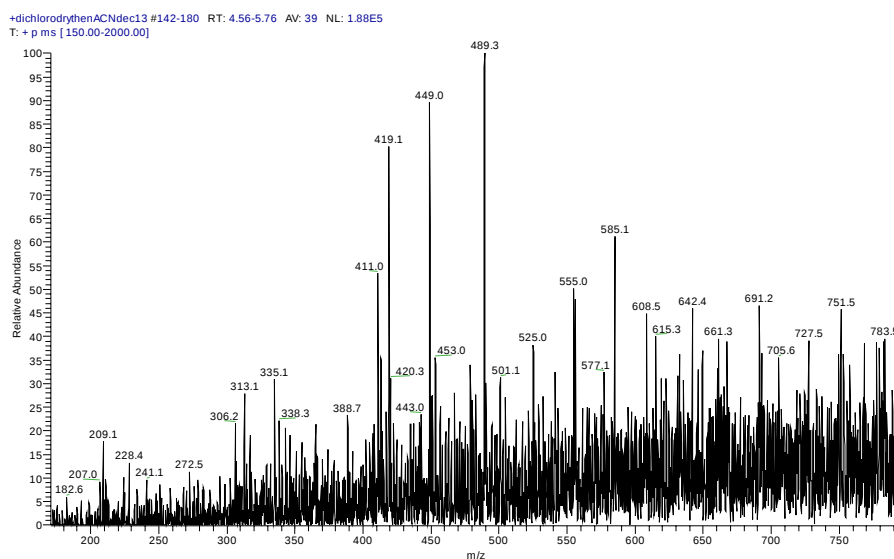


FIGURE 3-22: MS in positive ion mode of naphthenic acids extracted from crude oil in 20% dichloromethane / 80% acetonitrile with a mass range of 180 m/z to 800m/z.

Figure 3-22 shows some peaks in the range of 400 to 500 m/z that have high intensity in positive ion mode; they may be sulfur, nitrogen, and oxygen derivatives.⁴⁵ Our extraction procedure appears to extract other compounds in addition to naphthenic acids.

3.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

Merichem is a naphthenic acid mixture; it contains aliphatic and aromatic carboxylic acids. The NMR confirmed peaks that may be attributed to a carboxylic acid, and aliphatic, and aromatic hydrocarbon moieties.

3.3.1 NMR of Merichem

¹H NMR: Figure 3-23 shows peaks between 0.3-3 ppm. These may be attributed to hydrogens associated with methyl and methylene carbons. The peaks between 6.8-8 ppm may be attributed to hydrogens associated with an aromatic ring, while peaks between 11.5-12 ppm may be attributed to hydrogens associated with carboxylic acids. The deuterated chloroform solvent shows a peak at 7.26 ppm.

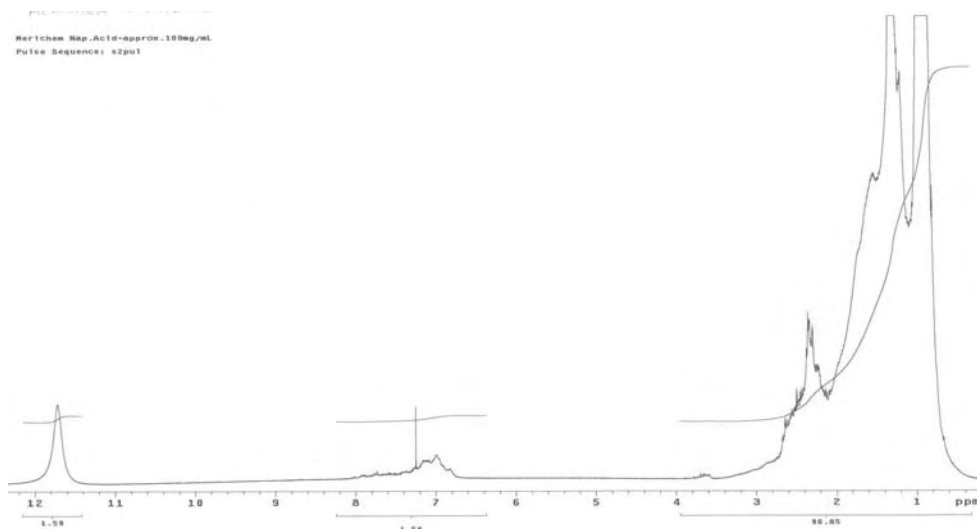


FIGURE 3-23: ^1H NMR of Merichem

C^{13} NMR: Figure 3-24 shows peaks between 10-60 ppm, which may be attributed to methyl and methylene carbons, whereas peaks between 120-130 ppm may be attributed to aromatic ring carbons. Peaks between 180-185 ppm may be attributed to a carboxylic acid carbon. The deuterated chloroform solvent shows a peak at 77 ppm.

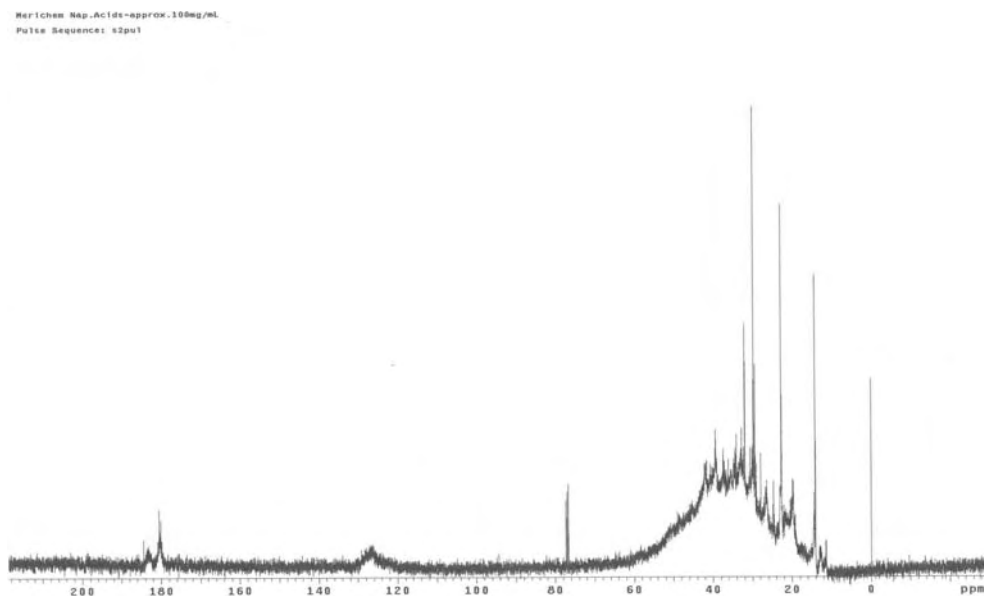


FIGURE 3-24: ^{13}C NMR of Merichem.

3.3.2 NMR of 5% Merichem in Tufflo after extraction

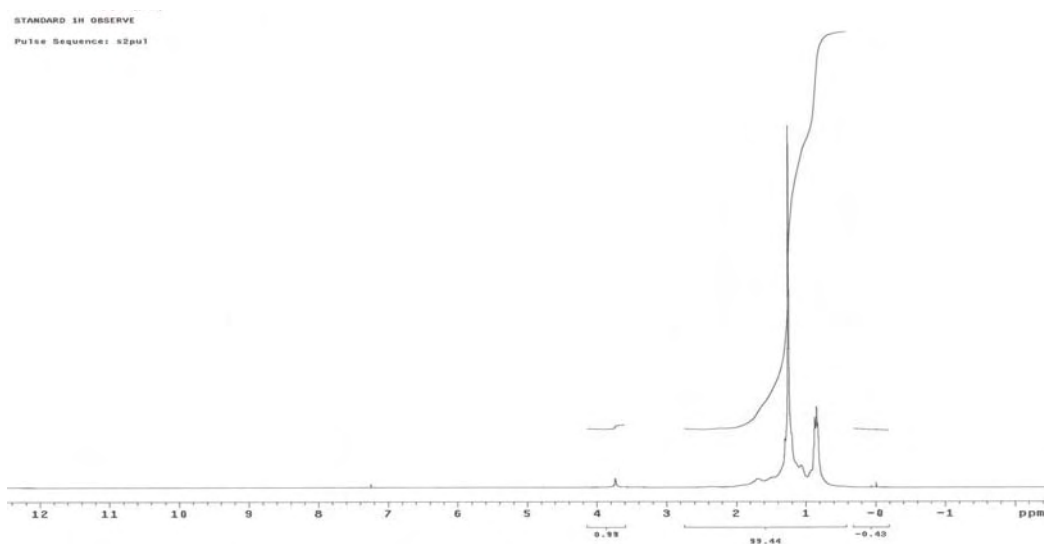


FIGURE 3-25: ^1H NMR of 5% Merichem in Tufflo after extraction.

The ^1H NMR of 5% Merichem in Tufflo, after extraction, did not show the expected carboxylic acid group present at 12 ppm. (See Figure 3-25) This may be due to

a very low concentration of naphthenic acid in the extract (5% Merichem in Tufflo) or the fact that the carboxylic acid group was modified in the process of extraction. We did not see the aromatic ring compounds that are known to be present, which lends further credence to the fact that lack of signal was probably due to a concentration effect. Peaks attributable to methyl and methylene hydrogen do appear in the range of 0.5-2 ppm, as well as a peak at 3.7 ppm due to ethylene glycol.

3.3.3 NMR of Tufflo supernatant after contact with ethylene glycol.

The ^1H NMR of Tufflo supernatant, after contact with ethylene glycol was shown in Figure 3-26, peaks attributable to methyl and methylene hydrogens in the range of 0.5-2 ppm, as well as a peak at 3.5 ppm due to ethylene glycol. The peak at 5.2 ppm may be due to ester functionality, and the peak at 7.26 ppm was attributed to deuterated chloroform.

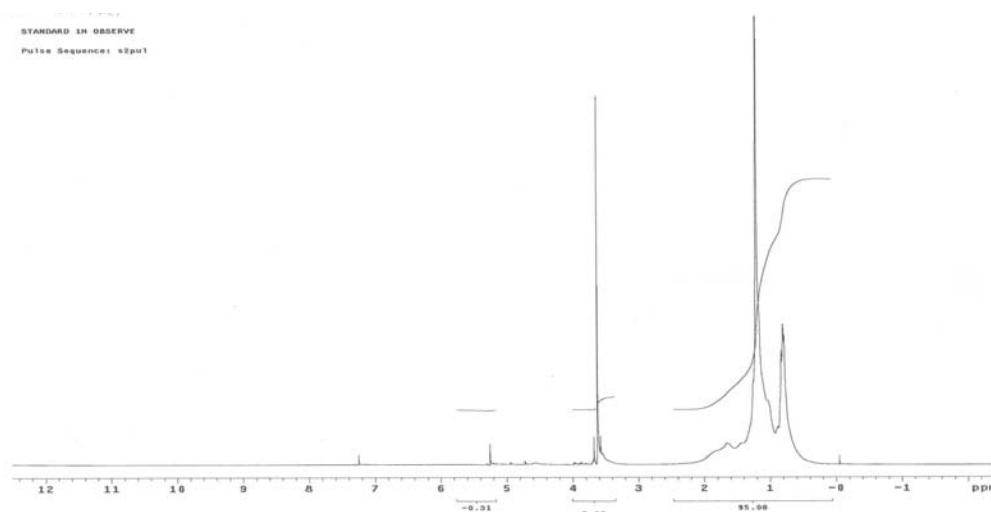


FIGURE 3-26: ^1H NMR of Tufflo supernatant after contact with ethylene glycol.

3.3.4 NMR of ethylene glycol layer after removal of ammonia

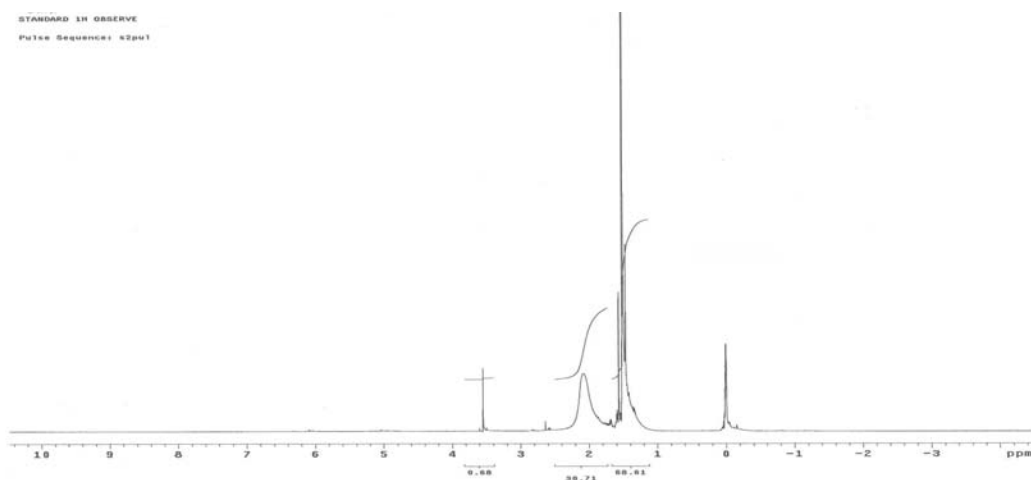


FIGURE 3-27: ^1H NMR of ethylene glycol layer after extraction of Merichem and boil off of ammonia.

Peaks shown in Figure 3-27, at 1.4-1.6 ppm are attributable to the hydrogen present in methyl group, and the peak at 3.5 ppm due to hydrogens in ethylene glycol. The deuterated acetone solvent shows a peak at 2.05 ppm.

3.3.5 NMR of naphthenic acids extracted from crude oil

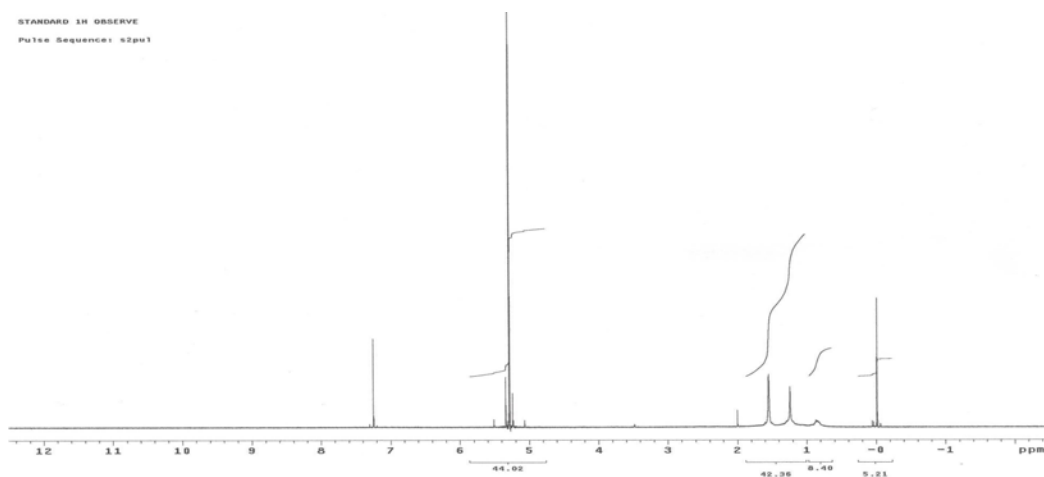


FIGURE 3-28: ^1H NMR of naphthenic acids extracted from crude oil.

Peaks in Figure 3-28, at 0.8, 1.2, and 1.6 ppm correspond to hydrogen's in aliphatic methyl, methylene, and methine hydrocarbons. The peak found at 2 ppm may be due to hydrogens in an ester. The peak at 3.5 ppm was due to hydrogen's in ethylene glycol, and the peak at 5.2 ppm may be attributable to hydrogen's present in a phenolic ester. The deuterated chloroform solvent shows a peak at 7.26 ppm. The carboxylic acid functional group was not found at 11-12 ppm.

3.3.6 NMR of crude oil supernatant after contact with ethylene glycol

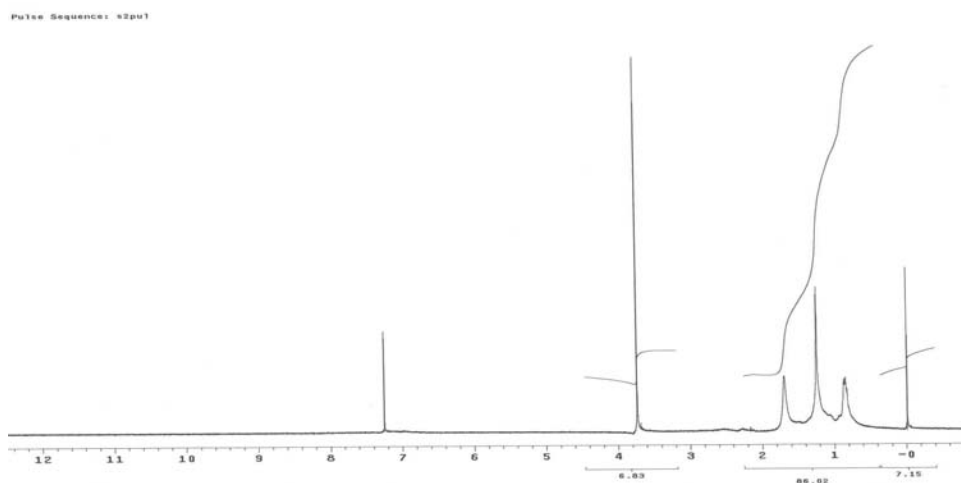


FIGURE 3-29: ^1H NMR of Crude oil fraction after extraction.

Figure 3-29 shows peaks at 0.8, 1.2, and 1.6 ppm corresponding to aliphatic methyl, methylene, and methine hydrocarbons. The peak at 3.7 ppm was due to ethylene glycol. The deuterated chloroform solvent shows a peak at 7.26 ppm.

3.3.7 NMR of ethylene glycol after contact with crude oil after removal of ammonia

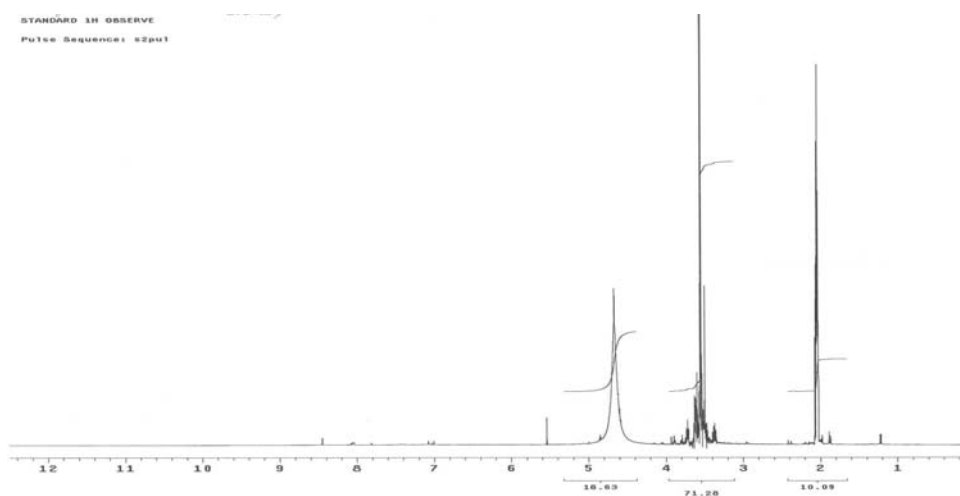


FIGURE 3-30: ^1H NMR of ethylene glycol after contact with crude oil after removal of ammonia.

The ^1H NMR spectrum was shown in figure 3-30. The peak appears at 2 ppm was due to deuterated acetone. The peak at 3.5 ppm was due to ethylene glycol; peaks found in between 4.5 to 8.5 ppm may be due to phenolic derivatives.

3.4 Infrared Spectroscopy (IR)

3.4.1 IR of polyethylene and petroleum ether

The background IR spectrum has peaks due to the polyethylene film and residual petroleum ether. Figure 3-31 was the background IR spectrum of polyethylene and petroleum ether. The IR spectrum, with sample, was interpreted by discounting the peaks shown by the polyethylene and petroleum ether background.

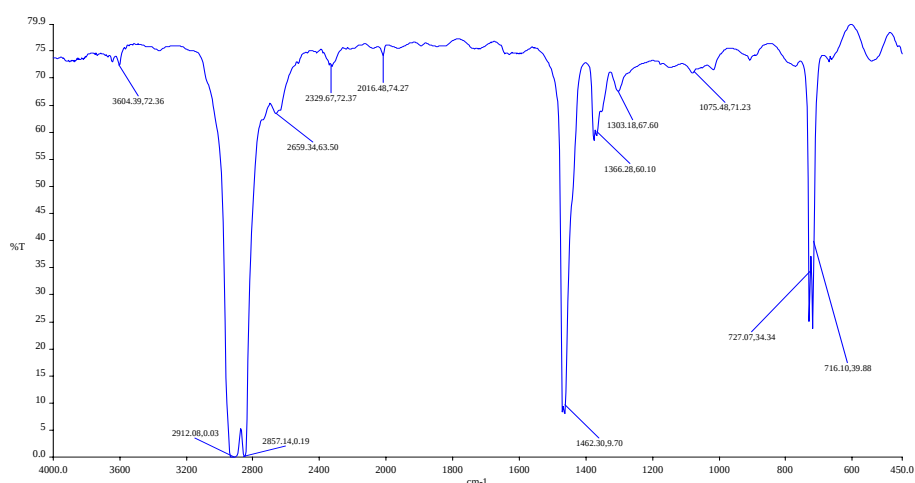


FIGURE 3-31: Background IR of polyethylene and petroleum ether.

3.4.2 IR of Merichem.

The IR spectrum of merichem in Figure 3-32 shows a broad OH stretch found at 3300-2500 cm⁻¹; the strong signal at 1703 cm⁻¹ was due to a carbonyl group. The strong signal at 1289 cm⁻¹ was due to a C-O stretch; the signal at 1377 cm⁻¹ was due to a C-O-H out of plane bend; and the signal at 935 cm⁻¹ was due to the O-H out of plane bend.

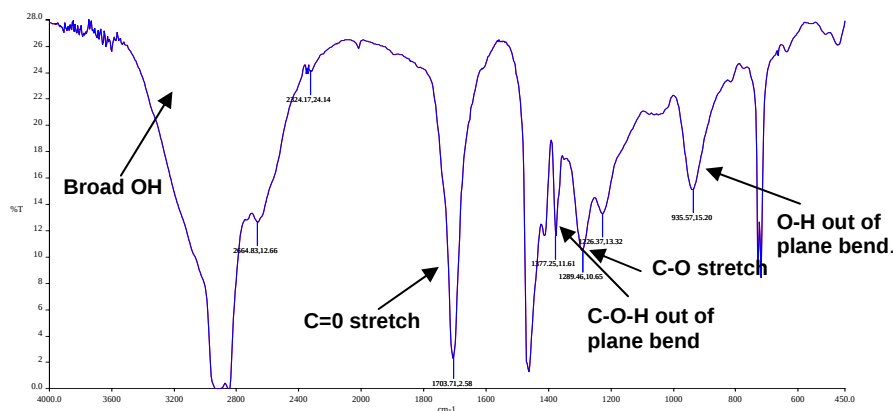


FIGURE 3-32: IR of Merichem dissolved in petroleum ether on a polyethylene film.

3.4.3 IR of 5% Merichem in Tufflo after extraction.

In Figure 3-33, the following peaks are identified: the strong signal of the C=O stretch at 1706 cm^{-1} , which may be due to a carboxylic acid or a derivative containing a C=O group, and a weak signal at 935 cm^{-1} due to an O-H out of plane bend. A broad OH stretch from $3300\text{--}2500\text{ cm}^{-1}$ was not found, possibly due to the low concentration of the extract. This issue needs further investigation.

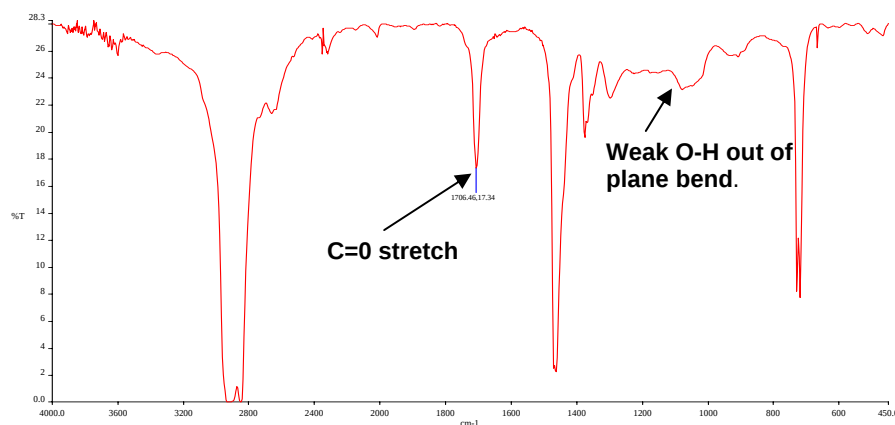


FIGURE 3-33: IR of 5% Merichem in Tufflo after extraction in petroleum ether on a polyethylene film.

3.4.4 IR of naphthenic acids extracted from crude oil

In figure 3-34, a weak signal may be due to the carbonyl group identified at 1728 cm^{-1} and 1637 cm^{-1} . Most of the peaks are not identified, which may be due to the low concentration of naphthenic acids after extraction from crude oil.

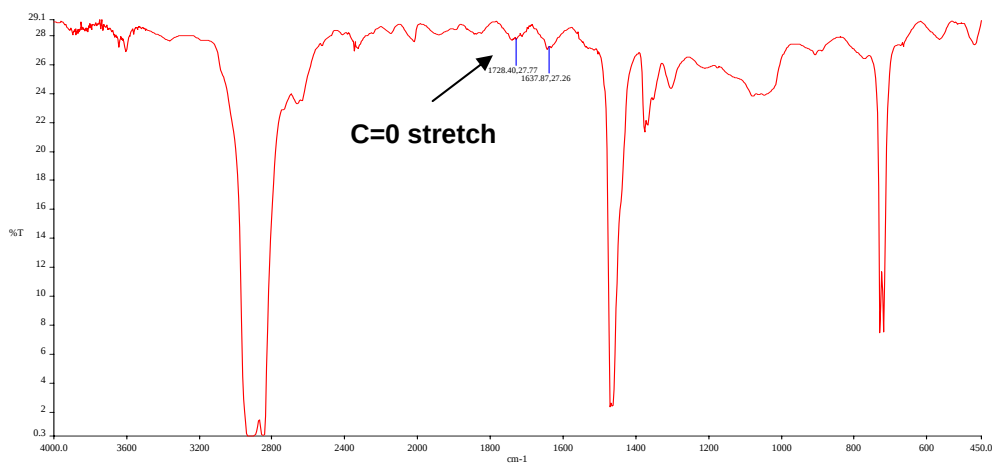


FIGURE 3-34: IR of Naphthenic acid extract from crude oil in petroleum ether on a polyethylene film.

CHAPTER 4

CONCLUSIONS

The extraction procedure shows a high yield, approximately 80%.

The MS of standard Merichem, before extraction, was compared with the MS of extracted Merichem. Most of the naphthenic acids were extracted but there were some naphthenic acids that were lost or not identified after the extraction procedure. Extraction of the petroleum crude oil and subsequent MS/MS experiments showed that not all of the extracted compounds were naphthenic acids.

NMR experiments showed no evidence of carboxylic acids and aromatic hydrocarbons; this might be due to the low concentrations of naphthenic acids present in the extract. There was also a possibility of naphthenic acids being modified to some other acid derivatives during the extraction process.

Polar and short chain naphthenic acids and other polar species might be more soluble in ethylene glycol than petroleum ether, so there was a possibility

that the more polar species could be lost during the extraction process. IR results show the presence of a carbonyl group in the extracts, but no –OH which would be associated with a carboxyl group. This might be due to the formation of an ester which would be the subject for future research.

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