Study of Spectral Modifications in Acidified Ignitable Liquids by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

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Abstract

In this work, the spectral characteristics of two types of acidified gasoline and acidified diesel fuel are discussed. Neat and acidified ignitable liquids (ILs) infrared absorption spectra obtained by attenuated total reflection Fourier transform infrared spectroscopy were compared in order to identify the modifications produced by the reaction of the ILs with sulfuric acid. Several bands crucial for gasoline identification were modified, and new bands appeared over the reaction time. In the case of acidified diesel fuel, no significant modifications were observed. Additionally, the neat and acidified ILs spectra were used to perform a principal components analysis in order to confirm objectively the results. The complete discrimination among samples was successfully achieved, including the complete differentiation among gasoline types. Taking into account the results obtained in this work, it is possible to propose spectral fingerprints for the identification of non-burned acidified ILs in forensic investigations related with arson or the use of improvised incendiary devices (IIDs).

1. Introduction

Ignitable liquids (ILs) such as gasoline or diesel fuel can be used to commit arson, vandalism acts, or other criminal actions. Their detection and accurate identification can be of paramount importance in casework to provide intelligence to the investigation. Therefore, the characteristics of neat or non-burned ILs and ignitable liquid residues (ILRs) from fire debris have been deeply studied to date.[1–4] In order to ensure the highest accuracy in the results, the American Society for Testing and Materials (ASTM) collects accurate information and lists standardized analytical methodologies,[5] and the National Center for Forensic Science (NCFS) offers the Ignitable Liquids Reference Collection (ILRC) database.[6] Both institutions help forensic experts from all over the world. In addition, there is wide knowledge about the distortion effects of their chemical fingerprints, which can hinder the interpretation of the analytical results.[3] The microbial activity over samples, the presence of background pyrolysis products, or the weathering effect of the ILs are the most usual distortion effects.[7–11]

In a recent study carried out by our research group we described what might be considered a novel distortion effect of IL chemical fingerprints: the acidification of ILs.[12,13] The investigation showed how the action of a concentrated strong acid affects the ILs original chemical composition and their identification following the traditional identification criteria.[5] Mixtures of sulfuric acid and ILs are used to make dangerous improvised incendiary devices (IIDs) such as the chemical ignition Molotov cocktail (CIMC).[14,15] According to our results investigating ILs obtained from a Swiss gas station, when sulfuric acid was mixed with gasoline, some of its main distinctiveness compounds were altered. The abundance and relative abundance of the oxygenated and aromatic compounds changed over time, or these compounds even disappeared. In addition, new compounds were produced. In the case of sulfuric acid mixed with diesel fuel, the relative abundances of aromatic compounds were also altered. All these changes modified their distinctive chromatographic fingerprints, hindering the identification of ILs or ILRs using traditional identification criteria. In order to achieve the complete identification, some recommendations using chromatographic results for acidified gasoline and diesel fuel and their residues were proposed.[12,13]

The most commonly used analytical technique in forensic laboratories to analyze neat ILs or fire debris samples is gas chromatography with mass spectrometry (GC-MS).[2,3,5] In addition, during recent years interest in applying spectroscopic techniques such as Raman spectroscopy or Fourier transform infrared spectroscopy (FT-IR) to carry

out the analysis of these samples has increased. The portability of some of these instruments, no sample treatment, very fast scan time, or no sample destruction are some of their interesting advantages. To date, some works have been focused on the analysis of household materials (before and after burning using ILs or other ignition sources) by Raman spectroscopy and FT-IR with attenuated total reflection (ATR) sampling accessory.[16–18] In addition, the non-invasive analysis of pre-ignited IIDs (classic Molotov cocktails and CIMCs) by portable-Raman was recently reported by our research group.[19] In the case of analyzing classic Molotov cocktails, the complete identification of several neat ILs in glass bottles of different characteristics was achieved, and it was also possible to identify gasoline and sulfuric acid in CIMCs. However, in the CIMC case the derived compounds of the reactions between gasoline compounds and sulfuric acid showed intense fluorescence impeding their identification at certain times by Raman. As an alternative, FT-IR could be applied to analyze these mixtures. It is well known that FT-IR has been applied to identify neat gasoline or diesel fuel.[20] Nevertheless, some of the identifiable bands in the ILs IR absorption spectra are related to the presence of alkanes, aromatic (i.e., alkylbenzenes) or oxygenated compounds,[20] some of which are strongly affected when neat ILs are mixed with sulfuric acid, as was explained above. Therefore, it is necessary to assess the usefulness of this spectroscopic technique to analyze acidified ILs.

Medium region or mid-IR (4000 to 400 cm^{-1}) is the most commonly scanned range, which encompasses absorption by the majority of common organic functional groups in ILs. Attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR) has been applied to the characterization of gasoline or diesel fuel coupled to chemometric analysis, which can determine critical parameters for detecting and classifying ILs in quality control.[20–24] Principal components analysis (PCA) was applied to detect similarities among gasoline samples;[21] in addition, supervised pattern recognition methods such as discriminant analysis (LDA), partial least squares-discriminant analysis (PLS-DA), and support vector machines (SVM) were used to classify whether these samples containing additives or not.[21] Besides, a predictive procedure was developed by quadratic discriminant analysis (QDA), which was applied for the detection of passed/failed gasoline samples,[22] and partial least squares (PLS) was applied in another work to discriminate between different adulterated gasoline samples.[23] PLS was also applied as complementary tool to determine the main properties of diesel fuel.[24]

The aim of this work was to study the spectral characteristics of acidified gasoline and diesel fuel by ATR FT-IR. To that, IR absorption spectra of neat and acidified ILs

(gasoline 98 and 95 research octane number (RON), and diesel fuel obtained from a Spanish gas station) have been investigated to test how the concentrated sulfuric acid affects the ILs spectra over the reaction time. Finally, a PCA classification was explored with the neat and acidified spectra in order to achieve an objective interpretation of the results.

2. Material and Methods

Samples, Reagents, Materials, and Instruments

Gasoline 98 and 95 RON, and diesel fuel were acquired in a local petrol station (Alcalá de Henares, Madrid, Spain). All neat ILs were stored in closed containers at room temperature. Sulfuric acid (95–98%, m/v) was purchased from Labkem (Mataró, Barcelona, Spain). Glass vials with screw caps were purchased from Labbox (Mataró, Barcelona, Spain). A compact portable ALPHA FTIR spectrometer with ATR sampling accessory from Bruker Optics, Inc. (Billerica, MA, USA) was used to analyze the samples.

Sample Preparation and Analysis

Sulfuric acid and individual neat gasoline 98 RON, gasoline 95 RON, or diesel fuel were poured into 10 mL glass vials with screw caps. The acid/IL ratio was 1:3 and 2:3 (v/v), respectively. These vials were stored at room temperature, closed, and kept still during the experiments. Aliquots from the organic part were extracted and poured directly on the cleaned diamond crystal surface of the ATR sampling accessory. The instrument was cleaned between samples with a clean paper tissue and then with ethanol or isopropyl soaked tissues. Figure S1 (supplemental material) shows three vials containing the mixtures and the instrument used to analyze them. Analyses of each mixture were carried out every 24 h over 8 days (192 h). A total of three independent repetitions of each experiment were prepared. From each repetition three individual aliquots were analyzed each time. Additionally, in order to study the quick chemical changes at the initial part of the reaction gasoline–sulfuric acid, a new batch of mixtures was prepared and analyzed every 15 min during 8 h.

Data Acquisition

IR absorption spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}, and the signal aver- aged over 24 scans. Spectra at higher number of scans were not recorded due to the quick evaporation of the gasoline. Data were imported from Opus software (Bruker Optics, Inc., Billerica, MA, USA) into The Unscrambler X 10.2 soft- ware (CAMO, Norway) for pre-processing and statistical analysis.

Data Analysis

From each IL, a triplicate set of calibration spectra (each one containing three independent spectra), was considered to calculate a mean spectra set for all calibration samples in the time range of 0–192 h. This was done in order to get the spectral fingerprint of each IL, simplifying the plotting and its interpretation. Neat and acidified ILs spectra were pre-treated to allow their correct comparison. The spectral region selected for data treatment was 1300–400 cm—1 in order to focus on the spectral fingerprint region. Besides, baseline and offset corrections of the spectra were per- formed as automatic options given in the used software. The baseline offset subtracted the value of the lowest point in the spectrum from all the variables, thus the minimum value was set as 0 and the rest were positive values. The linear baseline correction transformed into a sloped base- line into a horizontal baseline. In this way, two variables defining the new baseline were pointed out and set as 0, and the rest of the variables were transformed according to this with linear interpolation/extrapolation. In addition, SNV normalization, and a nine-point window Savitzky- Golay smoothing were applied. These pre-processing methods and conditions were selected among others because they provided good spectra leading to the best models fit- ting and interpretability.

In the Unscrambler data matrix, the sample classes (rows groups) were the neat and acidified samples (IR spectra). They were grouped by their specific categorical variable: IL type named with their specific name and the time of mixing with sulfuric acid (e.g., neat gasoline 98 RON ''gas98_000,'' gasoline 98 RON after 48 h of mixing with sulfuric acid ''gas98_048,'' gasoline 95 RON after 192 h of mixing with sulfuric acid ''gas95_192,'' or diesel fuel after 24 h of mixing with sulfuric acid ''diesel_024''). The variables (columns) were every data point (wavenumbers) of the spectral region selected, and they were named with their specific wavenumbers (cm^{-1}). PCA models were generated for each sample class, including PCAs with and without the neat spectra. The data were auto- scaled, and cross-validation and non-linear iterative partial least

squares (NIPALS) algorithm were selected for the PCA analysis. Cross-validation was considered to preliminarily test the model performance instead of using an independent test based on a separate test set. In PCA, the data were organized in 3D scores plots using the three first principal components (PCs) according to the spectral similarities and differences among samples. From the PCs used, a value of explained variance is given. It quantifies the variation in the data and expresses the proportion of structure found in the data by the model.

3. Results and Discussion

ATR FT-IR Analysis of Neat and Acidified ILs

In order to identify the possible spectral changes in the IR spectra of neat gasoline and diesel fuel when they are mixed with sulfuric acid, neat ILs and acidified ILs were measured and their spectra were compared. Figure 1 shows the IR absorption spectra of the three neat ILs studied: gasoline 98 RON, gasoline 95 RON, and diesel fuel. Taking into account the bands assignment reported in the literature, both gasoline (Figure 1a, b) display bands corresponding to C–H stretching of alkanes, alkenes, and aromatic rings at around 3100–2800 cm^{-1}. Specifically, the intensity of the bands between 3100–3000 cm^{-1} is very low in gasoline spectra, which indicates the low concentration of alkenes. Besides, gasoline shows bands corresponding to stretching mode of aromatic rings at around 1600–1475 cm^{-1}, C–H bend of alkanes at around 1500–1300 cm^{-1}, and C–H out- of-plane bend of alkanes and aromatic rings at 1000–400 cm^{-1}.[21,25–29] C–H out-of-plane bends of aromatic rings represent important compounds in gasoline such as the aromatic mono- or di-substituted toluene and xylenes.[25] It is also interesting to mention the unequal-intensity doublet of bands might be related to tert-butyl groups (at approximately 1395–1360 cm—1).[28] A usual compound in European gasoline is the methyl tert-butyl ether (MTBE), which contains a tert- butyl group. Besides, the ether band of the MTBE and ethanol is seen in the range 1200–1075 cm^{-1}.[23] On the other hand, neat diesel fuel FT-IR spectrum (Figure 1c) shows bands of higher intensity in the region 3000–2800 cm^{-1} than in the gasoline samples. These bands, corresponding to C–H stretching of alkanes, present higher intensity because these compounds are more abundant in diesel fuel than in gasoline.[3] The bands in the range 1600–1475 cm^{-1} may correspond with the stretching mode of aromatic rings, although the proportion of aromatic compounds is considerably lower in diesel fuel[3] and the C–H bend bands of

alkanes at around 1500–1300 cm^{-1} can also be seen. However, differences are observed around 1400–1300 and 1200–1075 cm^{-1} when compared to neat gasoline because diesel fuel does not have oxygenated compounds such as MTBE,[30] and around 1000–400 cm^{-1} due to the lower proportion of aromatic compounds.

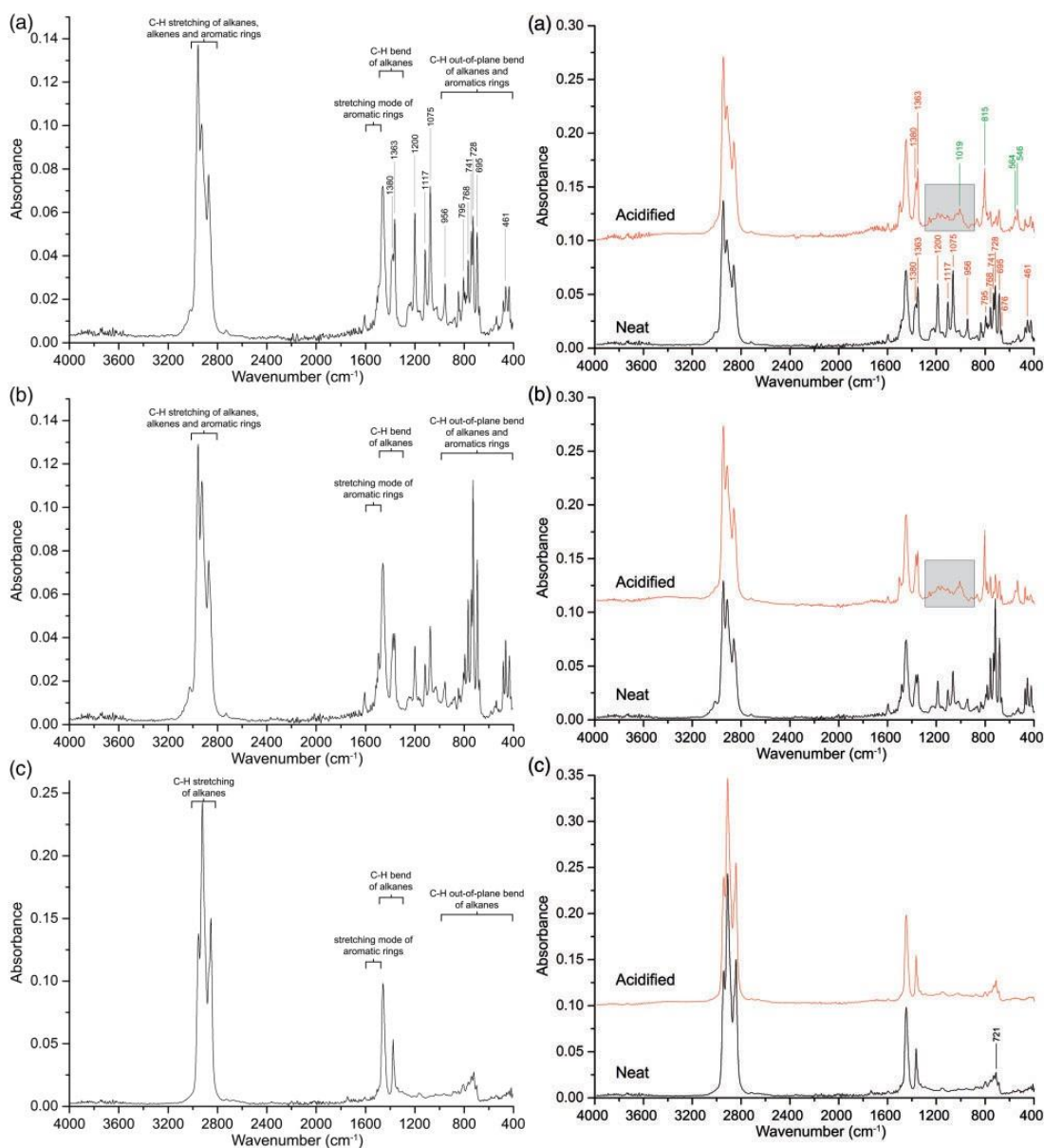**Figure 1.** (a) Neat gasoline 98 RON, (b) neat gasoline 95 RON, and (c) neat diesel fuel spectra of the mid-IR region (4000–400 cm^{-1}). Chemical compound groups, their corresponding vibrations, and number of bands are labeled on the figure.

Figure 2. Neat ILs (in black) versus acidified ILs (in red). (a) Gasoline 98 RON, (b) gasoline 95 RON, and (c) diesel fuel. Acidified ILs were measured 24 h after mixing with sulfuric acid. The gray square indicates the modified region related to the oxygenated compounds. Numbers in green are the new identified bands in acidified gasoline.

Figure 2 shows the IR spectra of the three ILs before and after mixing with sulfuric acid. As can be seen in Figure 2a, the acidified gasoline 98 RON spectrum (measured after 24 h mixing with sulfuric acid) showed relevant differences with regard to the neat gasoline 98 RON spectrum. Specifically, the region at 1200–900 cm^{-1} is modified extensively (inside the gray square in Figure 2a). The ether band of MTBE at 1200 and 1117 cm^{-1}, and ethanol at 1075 cm^{-1} end up almost disappearing. The acid attacks the MTBE producing methanol and tert-butyl alcohol (TBA). Then, the TBA turn into isobutene due to the sulfuric acid action, and isobutene derives in tert-butyl carbocations.[12] Bands related to TBA were not detected in the acidified gasoline FTIR spectrum, except for the doublet of bands related to tert-butyl groups which remain in the acidified spectrum (at approximately 1370 cm^{-1}). On the other hand, methanol probably also reacts with sulfuric acid producing methyl hydrogen sulfate and/or dimethyl sulfate.[31] Interestingly, after some time of mixing, new bands seem to appear at around 1019, 815, 564, and 546 cm^{-1}, and some changes can also be observed in the region of 500–400 cm^{-1} (Table 1 and Figure 2a). Some of those bands might be attributed to methanol by-products. The shoulder (at 822 cm^{-1}) of the wide band at approximately 815 cm^{-1} may be related to asymmetric S–O stretch.[32] Bands at 546 and 564 cm^{-1} may be related to SO2 bending,[28] and new bands at approximately 500–438 cm^{-1} and 430–400 cm^{-1} may correspond to SO2 wagging, and SO2 rocking and twisting modes.[28] In addition to those modifications, it is possible that ethanol also reacts with sulfuric acid to pro- duce ethyl hydrogen sulfate and diethyl sulfate. These com- pounds might also be related to the new bands described above. Several other spectral modifications are observed in the range 1000–400 cm^{-1}, which represent common neat gasoline aromatic compounds such as the mono-substituted toluene (bands around 728, 695, and 461 cm^{-1}) or di-substituted xylenes (bands around 795, 768, 741, and 676 cm^{-1}). Similarly, the band at 956 cm^{-1} also disappeared.

Table 1. Infrared bands assignment for acidified gasoline 98 RON and gasoline 95 RON, showing the functional groups, type of vibration, new bands appearing, and which type of change occurs in the common bands of neat gasoline after 24 h mixing with sulfuric acid.

Wavenumber (cm^{-1})	Assignment	Functional group or possible compound	Changes after 24 h mixing with sulfuric acid	Reference
3100-2800	C-H stretching of alkanes, alkenes and aromatic rings	-CH$_3$; -CH$_2$-; ¼C-H (aromatic)	No or scarce modification	25-29
1600-1475	Aromatic rings stretching mode	Ring -C¼C-	No or scarce modification	25,26,29
1500-1300	C-H bend	-CH$_3$ (alkane); C-CH$_3$	No modification	25-27
1395-1360	C-H$_3$ symmetric bend	*tert*-butyl group	No modification	28
1200	C-O(H) stretching	MTBE	Abundance decreasing	25
1117	C-O(H) stretching	MTBE	Abundance decreasing	25
1075	C-OH stretching	Ethanol	Abundance decreasing	25
1019	*	*	New band	*
1000-400	C-H out of plane bend of alkanes and aromatic rings	Aromatic ¼ C-H	Several modifications	21,25,26
956	*	*	Abundance decreasing	*
822	Asymmetric S-O stretch	Dimethyl sulfate or methyl hydrogen sulfate	New band	28
815	¼C-H out-of-plane bend of aromatic rings	Aromatic ¼ C-H	New band	26
795	p-di- C-H out-of-plane bend of aromatic rings	*para*-Xylene	Abundance decreasing	25
768	m-di C-H out-of-plan bend of aromatic rings	*meta*-Xylene	Abundance decreasing	25
741	o-di C-H out-of-plane of aromatic rings	*ortho*-Xylene	Abundance decreasing	25
728	Mono- C-H out-of-plane of aromatic rings	Toluene	Abundance decreasing	25
695	Mono- C-H out-of-plane of aromatic rings	Toluene	Abundance decreasing	25
564	-SO$_2$- bending	Dimethyl sulfate or methyl hydrogen sulfate	New band	28
546	-SO$_2$- bending	Dimethyl sulfate or methyl hydrogen sulfate	New band	28
461	C-C-C in plane bending	Toluene	Abundance decreasing	23

*No data.

Table 1 summarizes the gasoline IR bands modified after mixing gasoline with sulfuric acid. As tertbutyl carbocations are attached to the aromatic compounds due to the action of sulfuric acid, new compounds are produced (e.g., 4-tert-butyltoluene).[12] Because these reactions do not involve the destruction of the original aromatic compounds, the chemical structures and bonds should remain still. Figure 2a shows the bands at 1600–1475 cm^{-1}, representing more stretching of the aromatic rings, which were scarcely modified. However, bands at 845–500 cm^{-1}, representing C–H out-of-plane bends of the aromatic rings, are strongly modified. It is important to stress that the new heavier compounds generated have a big tert-butyl group attached to the aromatic ring. This new configuration could influence the electron clouds and the characteristics of those bonds. One possible explanation could be as follows: In toluene, for instance, the bond between the aromatic ring and the methyl group becomes stronger due to the presence of the tert-butyl group in either para- or meta- position, forming 4-tert-butyltoluene or 3-tert-butyltoluene. This could explain the change of the original bands in

the neat gasoline IR spectrum and the appearance of new bands (e.g., 815 cm^{-1}) shifting to the left of the acidified gasoline IR spectrum. Another explanation for this behavior could be the increase of di-substituted aromatic rings in the para- position, which is represented at 840–810 cm^{-1}.[26,27] In this way, the mono-substituted compounds (represented at 795–695 cm^{-1}) would decrease over time after mixing with sulfuric acid, while the di-substituted ones would increase over time leading to the appearance of the new peak at around 815 cm^{-1}. Besides, as it was expected, peaks related to alkanes (3100–2800 cm^{-1} and 1500–1300 cm^{-1}) remained in the spectrum because they are not modified by sulfuric acid.[12] These results agree with our previous findings, where gasoline from a Swiss gas station was studied.[12] Similarly, after 24 h of mixing gasoline 95 RON with sulfuric acid, similar changes were observed in the obtained spectrum (Figure 2b). This is because the composition of gasoline 95 RON is substantially equal to the composition of gasoline 98 RON, with the exception of the amount of oxygenated compounds.[3] The bands in Figure 2b were intentionally unlabeled in order to better compare the spectra. Both gasoline mixtures were analyzed every 24 h for 8 days. However, no major differences were visually observed during the 8 days when comparing the IR spectra. As most spectral changes were observed within 24 h of mixing, new mixtures of gasoline 98 RON with sulfuric acid were prepared in order to study in detail the quick chemical changes at the beginning of the reaction. In this case, they were analyzed every 15 min during the first 8 h.
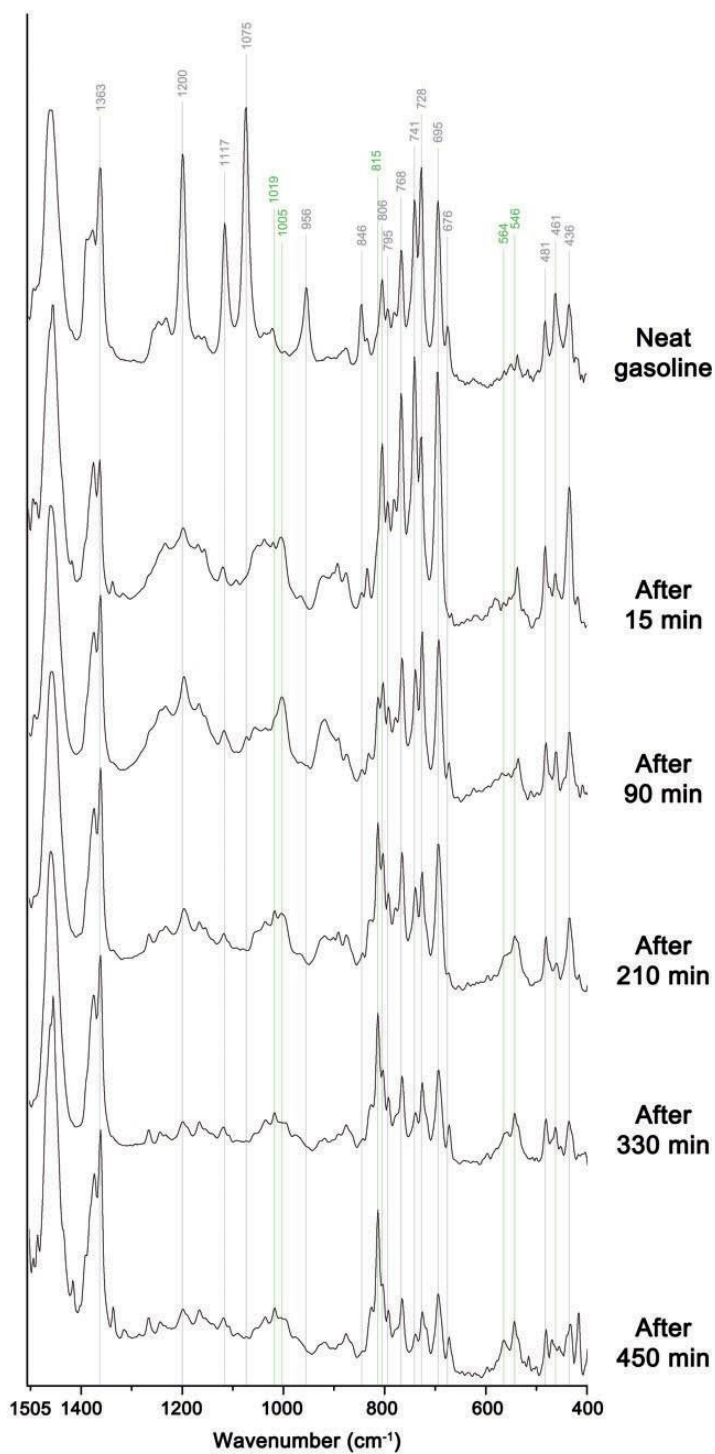
Figure 3. IR spectra of neat gasoline, and acidified gasoline 98 RON measured over time. Bands of neat gasoline and new bands of acidified gasoline are labeled in gray and green, respectively.

Figure 3 shows the spectral changes in the region 1500–400 cm^{-1} in acidified gasoline. For reasons of clarity, not every 15 min spectrum is drawn, only those showing particular tendencies (15, 90, 210, 330, and 450 min). The bands related to the ether band of the oxygenated com- pounds (at around 1200, 1117, and 1075 cm^{-1}) were

modified at the very beginning of the reaction, i.e., just after 15 min. Although small peaks remain after the first 15 min, they almost disappeared after 240 min (4 h) (spectrum not shown). Another band that disappeared instantly was situated at 956 cm^{-1}. Contrarily, a new peak at 1005 cm^{-1} appeared after 30 min (spectrum not shown), remaining in place for more than 90 min, and finally disappearing shortly after, while the small peak at 1019 cm^{-1} appeared after 180 min (3 h). Figure 3 also clearly shows how the bands at around 846–676 cm^{-1} are gradually modified over time during the first 480 min (8 h) of the reaction. However, the most interesting event in this region after the initial 60 min, is the continuous growth of the new peak at around 815 cm^{-1}. Another small band appeared after 15 min (at approximately 822 cm^{-1}) close to the new peak at 815 cm^{-1}. After several minutes, this small peak appeared as a shoulder of the wide band at 815 cm^{-1}. And finally, the modification of the bands at around 564–436 and 430–400 cm^{-1}, specifically the appearance of the bands at 564 and 546 cm^{-1} after some minutes and the modification of the band at 461 cm^{-1}.

In the case of the acidified diesel fuel, no major changes were observed in their IR spectra after 24 h of acid exposition (Figure 2c). Alkanes are the most abundant group of compounds in diesel fuel, which are not modified by sulfuric acid as was indicated previously. Although neat diesel fuel contains small proportion of aromatic compounds that can be detected by GC-MS, they were not detected clearly by ATR FT-IR spectroscopy. In this case, the reaction between aromatic compounds and sulfuric acid to produce polar aromatic sulfonates may be favored due to the absence of tert- butyl carbocations. However, there was not sign of their presence. These compounds are insoluble in non-polar solvents, hence their identification by analyzing the organic phase might be not possible. The organic fractions of these mixtures were analyzed every 24 h for 8 days. Their spectra were visually compared with each other, without observing major differences. These results also agreed with those previously found by GC-MS analyzing diesel fuel from a Swiss gas station.[12]

Chemometric Analysis of Acidified ILs

Although visual inspection of the IR spectra could be enough in most of the cases to discriminate acidified from neat gasoline, or neat gasoline from neat diesel fuel, it depends on the analyst's experience and interpretation capability. Therefore, an efficient and rather simple chemometric methodology, based on a PCA classification, is proposed to assure an objective sample discrimination.
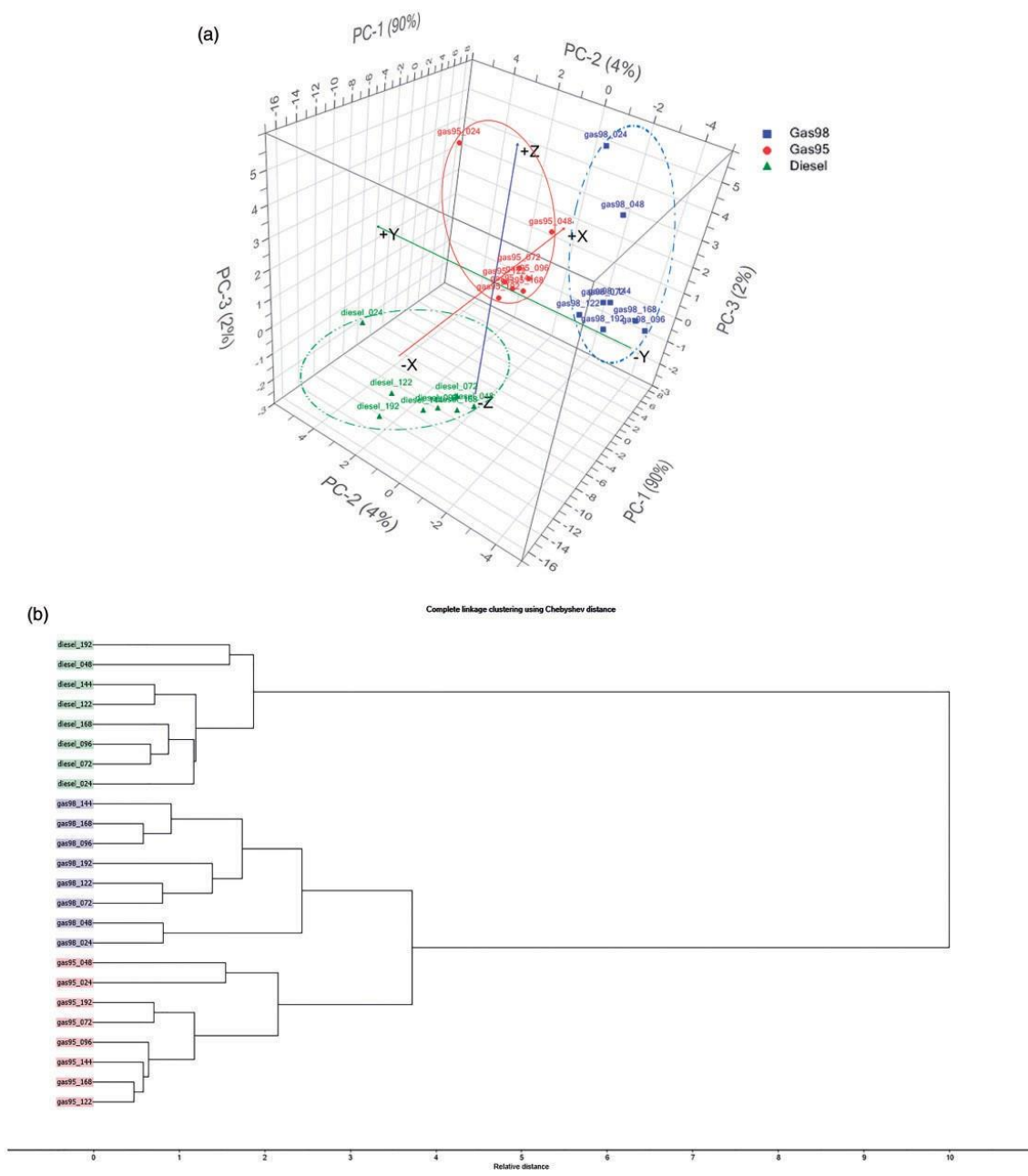
Figure 4. (a) 3D scores plot of PC factors 1, 2, and 3, showing all the studied acidified ILs IR spectra: gasoline 98 and 95 RON, and diesel fuel. Names and symbols of the samples are indicated in the figure; (b) linkage clustering analysis showing all the studied acidified ILs IR spectra: gasoline 98 (highlighted in blue), gasoline 95 (highlighted in red), and diesel fuel (highlighted in green).

This chemometric tool helped to graphically reveal more differences between the ILs, and the consequences of the exposition to sulfuric acid. First, a scores plot using the neat and acidified IL IR spectra was plotted (not shown) in order to point out the main disparities among the studied samples (calibrated samples in the range of 0–192 h). PC-

1, PC-2, and PC-3 showed a variability with a 94% confidence level among all samples. All acidified IL samples were clustered in two groups by type of IL: gasoline or diesel fuel. Besides, neat ILs appeared completely separate from the acidified ILs but also among them. The loadings plot (not shown) indicated the IR bands which most strongly influence the PCs. The difference between the two acidified gasoline and the other samples is mainly related to the new wide band in the acidified gasoline spectra at around 815 cm^{-1}, which did not appear in the neat ILs or acidified diesel fuel samples. Neat gasoline appeared separated from the acidified gasoline samples because of the presence of bands at around 1200–1075 cm^{-1}, which were modified by the treatment with sulfuric acid, confirming the results seen with the naked eye. Diesel fuel samples were clustered apart due to the influence of the band at around 721 cm^{-1} and small differences in the bands at around 800 cm^{-1}.

To look for more differences, only the acidified samples were selected to another PCA classification. In this case, neat samples were excluded since they had a strong influence over the other samples in the before explained PCA. Figure 4a shows a PCA scores plot for PC-1, PC-2, and PC-3. The samples were color-labeled according to the type of IL, and named according to the time of mixing with sulfuric acid (as mentioned above). In this case, these three PCs explained 96% of the variance in the dataset, which is a successful discrimination. As can be seen, it was possible to differentiate completely acidified diesel fuel and acidified gasoline on PC-1. It was expected because the diesel fuel composition is very different from gasoline, even when it is acidified. In addition to that, the two acidified gasolines appeared separated with no entanglements on PC-2 and PC-3. Although in PC-1 one sample (gas95_024) and in PC-2 another sample (gas98_024) showed relatively higher residual values, both samples were expected to behave differently. This is because during the time 0–48 h, they undergo a sharp change, which make them clearly distinct from the rest of their classes. Figure 4b shows that these samples were also clustered in the same way when performing a complete linkage clustering analysis. Similar results were observed by K-means clustering analysis (plot not shown).
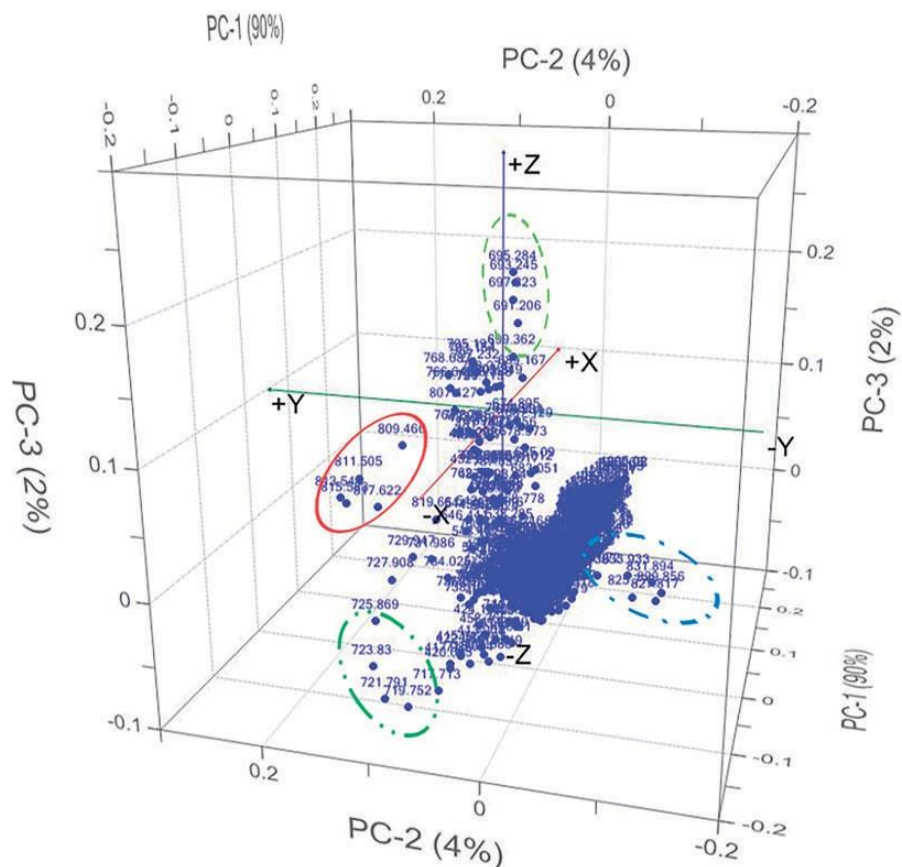
Figure 5. 3D loadings plot of PCA factors 1, 2, and 3, showing all the studied acidified ILs IR spectra: Gasoline 98 and 95 RON, and diesel fuel.

Figure 5 shows the loadings plot where the most relevant variables (IR absorbance bands) are plotted. The variables are labelled according to their IR band (wavenumber). The bands at around 721 cm^{-1} (inside the long dash dot-dot green line) are once again related with the bunch of acidified diesel fuel samples (see Figure 4a). Besides, the bands at around 817–809 cm^{-1} (inside the solid red line) and the bands 830–821 cm^{-1} (inside the dash-dot blue line) are related to the two types of acidified gasoline (see Figure 4a). Under the hypothesis mentioned before, this range of IR bands (from 840 cm^{-1} to 810 cm^{-1}) is related directly to the pro- duction of methanol and ethanol by-products in addition to new tert-butylated compounds. That is, the initial content of MTBE and ethanol, which is different in both gasolines (higher in gasoline 98 RON), and therefore the content of products derived of their hydrolysis (tert-butyl carbocations, and methanol and ethanol by-products) will be quantitatively different. As a consequence, the amount of aromatic compounds with the tert-butyl group attached forming the new tert-butylated compounds will be higher in gasoline 98 RON than gasoline 95 RON. This is shown in slight differences among the acidified gasoline

spectra, with a wide band appearing slightly to the left in acidified gasoline 98 RON (830–825 cm^{-1}) and slightly rightmost in acidified gasoline 95 RON (815–809 cm^{-1}). Besides, the acidified gasoline samples for 24 h and 48 h appeared slightly separate from their core groups (Figure 4a). The loadings plot (Figure 5) showed some bands at around 695 cm^{-1} (orange dashes) which influence these samples. As was revealed before, these bands are related with mono-substituted aromatic compounds such as toluene which is modified over the exposition time to the sulfuric acid. Thus, the modification of the original bands and the appearance of new bands would occur gradually and differently. Therefore, this suggests a sequential timing of the events during the ILs acidification (a specific order from 0 to 192 h) which may be logical with the chemical reaction. This similarly occurred with the acidified diesel fuel sample for 24 h (Figure 4a). However, these PCAs simply showed a tendency or group direction, and it is not possible to confirm the existence of a sequential timing of events.

4. Conclusions

The IR absorption spectra of neat gasoline 98 and 95 RON have shown several modifications after mixing gasoline with sulfuric acid. Bands representing oxygenated compounds (around 1200–1000 cm^{-1}) disappeared at the beginning of the reaction due to the sulfuric acid action over those compounds. Bands in the 1000–400 cm^{-1} range, where aromatic compounds are represented, were also modified over the reaction time. In addition, new bands appeared at around 1019, 820, 815, 564, and 546 cm^{-1}. Those bands can be related to new reaction products, the tert-butylated compounds, and methanol and ethanol by-products. Besides, bands related to alkanes remained unmodified. In the case of acidified diesel fuel the spectrum did not vary significantly from the neat diesel fuel spectrum due to the no alteration of alkanes by sulfuric acid.

In addition, applying an objective chemometric tool based on a PCA classification, the results observed with the naked eye were confirmed. The discrimination between acidified diesel fuel and acidified gasoline, and also among the two type of gasolines, was successfully achieved. The chemical reactions act slightly different in gasolines 98 and 95 RON, which has been mainly attributed to their different MTBE content.

All these observations enable to propose the acidified ILs IR spectra presented in this work as spectral fingerprints for identifying acidified ILs in casework (i.e., failed or seized CIMCs or when non-burned acidified ILs are recovered from the evidence). In addition, this information may be useful to further investigate the identification of acidified

ILs from fire debris by spectroscopic techniques. Further studies are also necessary to confirm the existence of a sequential timing of events during the acidification of ILs.

Acknowledgments

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