



Transportation Consortium of South-Central States

Solving Emerging Transportation Resiliency, Sustainability, and Economic Challenges through the Use of Innovative Materials and Construction Methods: From Research to Implementation

Catalyst Regeneration of RAP-Binder in Asphalt

Project No. 20BLSU19

Lead University: Louisiana State University

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| 16. Abstract <p>Reclaimed Asphalt Pavement (RAP) binders are difficult to reuse because they often contain associated/aggregated molecules with very high molecular weights. This is due to the polarity gained during oxidative aging, causing the aggregation to occur. These high molecular weight components are responsible for RAP binder's increased viscosity and certain deteriorated rheological properties. One strategy to reuse RAP binder is to mix it with virgin asphalt binder and use this partially recycled mixture in asphalt. The RAP binder is usually improved before mixing by the addition of rejuvenators, softening agents, softer binders, and antioxidants to the asphalt binder mix to rebalance their rheological properties.</p> <p>The purpose of this research was to study effective ways to incorporate RAP content in asphalt mixtures using a novel approach of introducing a catalyst that can modify the binder's chemical composition; particularly to alter the oxidized molecules and reduce the number/content of aggregated structures. The use of a catalyst such as a Lewis acid to break the associated molecules in the RAP-binder is a new promising approach. The Lewis acids catalysts are known to catalyze the conversion of coal to liquid product, but the mechanism of action is not well understood. This report describes the result of our investigation into the effects of a Lewis acid catalyst such as Iron (III) chloride and Zinc chloride on the chemical composition of RAP-binder. The ultimate result is that Iron (III) chloride lowers the size of high molecular weight material when 2% w/w is used with RAP at 165 degrees Celsius for 30 minutes.</p> | | | |
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|--|-----------------------------|-----------------------------|-----------------------------|---------------------|
| LENGTH | | | | |
| in | inches | 25.4 | millimeters | mm |
| ft | feet | 0.305 | meters | m |
| yd | yards | 0.914 | meters | m |
| mi | miles | 1.61 | kilometers | km |
| AREA | | | | |
| in ² | square inches | 645.2 | square millimeters | mm ² |
| ft ² | square feet | 0.093 | square meters | m ² |
| yd ² | square yard | 0.836 | square meters | m ² |
| ac | acres | 0.405 | hectares | ha |
| mi ² | square miles | 2.59 | square kilometers | km ² |
| VOLUME | | | | |
| fl oz | fluid ounces | 29.57 | milliliters | mL |
| gal | gallons | 3.785 | liters | L |
| ft ³ | cubic feet | 0.028 | cubic meters | m ³ |
| yd ³ | cubic yards | 0.765 | cubic meters | m ³ |
| NOTE: volumes greater than 1000 L shall be shown in m ³ | | | | |
| MASS | | | | |
| oz | ounces | 28.35 | grams | g |
| lb | pounds | 0.454 | kilograms | kg |
| T | short tons (2000 lb) | 0.907 | megagrams (or "metric ton") | Mg (or "t") |
| TEMPERATURE (exact degrees) | | | | |
| °F | Fahrenheit | 5 (F-32)/9 or (F-32)/1.8 | Celsius | °C |
| ILLUMINATION | | | | |
| fc | foot-candles | 10.76 | lux | lx |
| fl | foot-Lamberts | 3.426 | candela/m ² | cd/m ² |
| FORCE and PRESSURE or STRESS | | | | |
| lbf | poundforce | 4.45 | newtons | N |
| lbf/in ² | poundforce per square inch | 6.89 | kilopascals | kPa |
| APPROXIMATE CONVERSIONS FROM SI UNITS | | | | |
| Symbol | When You Know | Multiply By | To Find | Symbol |
| LENGTH | | | | |
| mm | millimeters | 0.039 | inches | in |
| m | meters | 3.28 | feet | ft |
| m | meters | 1.09 | yards | yd |
| km | kilometers | 0.621 | miles | mi |
| AREA | | | | |
| mm ² | square millimeters | 0.0016 | square inches | in ² |
| m ² | square meters | 10.764 | square feet | ft ² |
| m ² | square meters | 1.195 | square yards | yd ² |
| ha | hectares | 2.47 | acres | ac |
| km ² | square kilometers | 0.386 | square miles | mi ² |
| VOLUME | | | | |
| mL | milliliters | 0.034 | fluid ounces | fl oz |
| L | liters | 0.264 | gallons | gal |
| m ³ | cubic meters | 35.314 | cubic feet | ft ³ |
| m ³ | cubic meters | 1.307 | cubic yards | yd ³ |
| MASS | | | | |
| g | grams | 0.035 | ounces | oz |
| kg | kilograms | 2.202 | pounds | lb |
| Mg (or "t") | megagrams (or "metric ton") | 1.103 | short tons (2000 lb) | T |
| TEMPERATURE (exact degrees) | | | | |
| °C | Celsius | 1.8C+32 | Fahrenheit | °F |
| ILLUMINATION | | | | |
| lx | lux | 0.0929 | foot-candles | fc |
| cd/m ² | candela/m ² | 0.2919 | foot-Lamberts | fl |
| FORCE and PRESSURE or STRESS | | | | |
| N | newtons | 0.225 | poundforce | lbf |
| kPa | kilopascals | 0.145 | poundforce per square inch | lbf/in ² |

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ACRONYMS, ABBREVIATIONS, AND SYMBOLS

| | |
|-------------------|-------------------------------|
| AFM | Atomic force microscopy |
| FTIR | Fourier Transform infrared |
| GPC | Gel permeation chromatography |
| HMA | Hot mix asphalt |
| LMS | Large molecular size |
| MS | Mass spectroscopy |
| MWV | Molecular weight |
| NMR | Nuclear magnetic resonance |
| SEC | Size exclusion chromatography |
| RAS | Reclaimed asphalt shingles |
| RAP | Reclaimed asphalt pavement |
| STM | Scanning tunneling microscopy |
| THF | Tetrahydrofuran |
| VPO | Vapor phase osmometry |
| XRD | X-ray diffraction |
| FeCl ₃ | Iron Chloride |
| ZnCl ₂ | Zinc Chloride |

EXECUTIVE SUMMARY

During service or aging, several changes can happen to asphalt due to oxidation and other chemical transformations. Research studies show that aging of asphalt is due to the changes in the asphalt chemical composition. Reclaimed Asphalt Pavement (RAP) binders are difficult to reuse because they often contain associated/aggregated molecules with very high molecular weights. This is due to the polarity gained during oxidative aging, causing the aggregation to occur. These high molecular weight components are responsible for RAP binder's increased viscosity and certain deteriorated rheological properties. One strategy to reuse RAP binder is to mix it with virgin asphalt binder and use this partially recycled mixture in asphalt pavement. Typically softening agents and rejuvenators are added to virgin – RAP mixture to aid the increase the amount of RAP binder to the virgin asphalt. It was reported that softening agents reduce the viscosity of RAP-binder and rejuvenators typically restore the chemical and rheological properties of RAP-binder to ensure a long performance period. However, the interaction and compatibility of these additives have shown conflicting results. Further it is not clear whether all types of rejuvenators are appropriate with regard to performance and environment. In Region-6 states, however, many state agencies are becoming more concerned with the use of high percentages of RAP (> 25%) with virgin materials. This is a potential issue because the increasing percentage may adversely affect the performance of asphalt pavements, eventually resulting in higher pavement maintenance and rehabilitation costs. The purpose of this research was to study effective ways to incorporate RAP content in asphalt mixtures using a novel approach of introducing a catalyst that can modify the binder's chemical composition; particularly to alter the oxidized molecules and reduce the number/content of aggregated structures. The use of a catalyst such as a Lewis acid to break the associated molecules in the RAP-binder is a new promising approach. The Lewis acids catalysts are known to catalyze the conversion of coal to liquid product, but the mechanism of action is not well understood.

This project is aimed to evaluate the effectiveness of Lewis acids to increase the amount of RAP binder incorporated in asphalt pavement, which will promote sustainable development by reducing the cost of using virgin binder materials, save valuable natural resources, and contribute to environmental protection. This report describes the result of our investigation into the effects of a Lewis acid catalyst such as Iron (III) chloride and Zinc chloride on the chemical composition of RAP-binder. Gel permeation chromatography (GPC) was used to measure the changes in the molecular aggregation via measuring the amount of high molecular weight fraction before and after the catalyst treatment. Fourier transform infrared (FTIR) spectroscopy was used to monitor the changes in the oxidation, as measured by carbonyl index value. For initial studies we measured the carbonyl index of the RAP samples treated with 0.2, 0.5, 1, 2, and 10 (wt./wt.) % of FeCl₃. The RAP samples were treated with the iron chloride for 30 minutes at 165 degrees Celsius; and for FTIR analysis, the RAP binder sample was dissolved in carbon disulfide (CS₂) solvent and filtered through a 0.45 μm filter. The optimal carbonyl index decrease was found for 2% FeCl₃ which showed a 47.6% decrease in the carbonyl index. The GPC results of the iron chloride treated RAP showed that as the amount of iron chloride increases, the relative area of the high molecular weight (MW) fraction decreases. At the same time, the relative area of the maltene fraction increases, and the relative area of the asphaltene fractions approximately remain constant. The 2% FeCl₃ was added to RAP for 30 minutes. The 2 (wt./wt.) % FeCl₃ treated RAP samples showed the maximum decrease of 56% loss of the high MW fractions. This data, along with a decrease in carbonyl index value as shown by FTIR, showed that the iron chloride may chemically transform

the carbonyl group (the chemistry of this is still not understood clearly) which may decrease the hydrogen bonding and hence decrease the size of the aggregates formed during the aging of asphalt binder.

1. INTRODUCTION

Reclaimed asphalt pavement (RAP) is obtained when existing asphalt pavement materials are removed during resurfacing, rehabilitation or reconstruction operations. During the service life of asphalt on the road, oxidative aging occurs. Oxidation of asphalts occurs over the service years and is augmented by solar radiation (especially UV rays), water, and atmospheric oxygen. UV-rays create radicals which then easily react with oxygen to form oxygen containing functional groups on the asphalt components. These polar functional moieties interact with each other to form aggregated structures, increasing the asphaltenes content in the mixture and hence the viscosity. These mechanisms first happen on the surface layer, later penetrating to lower layers as cracking occurs. The oxidative process may cause the mixture to become hard, brittle and susceptible to disintegration and cracking failure which, in the long run, results in excessive pavement cracking. Steric hardening of the asphalt pavement is caused by molecular reorganization due to the fluctuations in the temperature.

In recent years, a higher percentage of RAP has been used in the construction of hot mix asphalt (HMA) pavements. But, conflicting results were reported about the percentage of RAP that can be included with virgin asphalt while maintaining good performance. Although there is an increase in the use of asphalt mixtures containing Reclaimed Asphalt Pavement (RAP), many states are still cautious in their regulations to avoid durability problems related to the recycling process. On the other hand, many state agencies are taking a more aggressive approach by considering increasing the allowable percentages of RAP in hot-mix asphalt (HMA) to take full advantage of this promising technology.

Recycling agents such as softening agents and rejuvenators are added to increase the amount of RAP binder that can be incorporated in virgin asphalt. The softening agents are added to reduce the viscosity of RAP-binder and rejuvenators are used to restore the chemical and rheological properties of RAP-binder to ensure a long performance period. However, the interaction and compatibility of these additives have shown conflicting results. Also it is not clear whether all types of rejuvenators are appropriate with regard to performance and environment. In this work we employed a different approach to use of a Lewis catalyst to reverse the chemical changes occurs to asphalt molecules during its service, particularly oxidation and molecular aggregation. The main objective of this project is to treat the RAP samples with Lewis acid catalysts and evaluate the chemical changes in the RAP samples. We select iron chloride and zinc chloride for this purpose. We treat the RAP samples with different amounts of the catalysts (0.2, 0.5, 1, 2 and 10 (wt./wt.) %) as well as different treatment times (0.5, 1, 2 and 4 h). We used Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC) to measure the changes in the oxidation, as measured by carbonyl index value and changes in the molecular aggregation respectively after the catalyst treatment. Using the FTIR and the GPC results, we want to find out the optimum treatment conditions.

2. OBJECTIVES

The objective of this research was to study effective ways to incorporate RAP and RAS (reclaimed asphalt shingles) content in asphalt mixtures using a novel approach of introducing a catalyst that can modify the binder's chemical composition; particularly to alter the oxidized molecules and reduce the number/content of aggregated structures. The use of a catalyst such as a Lewis acid to break the associated molecules in the RAP-binder is a new promising approach. The Lewis acids catalysts are known to catalyze the conversion of coal to liquid product, but the mechanism of action is not well understood. This project is aimed to evaluate the effectiveness of Lewis acids in increasing the RAP and RAS percentage incorporated in asphalt pavement, which will promote sustainable development by reducing the cost of using virgin binder materials, save valuable natural resources, and contribute to environmental protection. This report describes the result of our investigation into the effects of a Lewis acid catalyst such as Iron (III) chloride and Zinc chloride on the chemical composition of RAP-binder.

3. LITERATURE REVIEW

3.1. Asphalt Binder Aging

Asphalt is derived from two main sources. One as a byproduct of the fractional distillation of crude oil at 300-350°C or as a natural deposit. Its unique properties include excellent water proofing, adhesion and thermoplasticity. A thermoplastic material is a material that can be liquefied by heating and solidified by cooling. During road construction, asphalt is heated to a liquid and is mixed with gravel and other ingredients and is then poured on the road while it is hot. When it comes to ambient temperature, it becomes nicely set and solid, ready for vehicles to drive on. After being in good condition for several years, the properties of the asphalt deteriorate, and the road will start breaking down. This is due to the hardening of asphalt binder, a process referred to as asphalt aging which contains aged asphalt binder and aggregate (1). At this stage, the road needs to be repaired or replaced.

During service or aging, several changes can happen to asphalt due to oxidation and other chemical transformations (2). Research studies show that the aging of asphalt is due to changes in the asphalt chemical composition. To understand how asphalt undergoes aging, we need to understand the four types (or fractions) of molecules present in the asphalt: saturates, aromatics, resins and asphaltenes, which are shown in Figure 1 (2-3). Asphalt is a colloidal system consists of these four types of complex molecules. The unique properties of the asphalt are due to the presence of a balanced combination and interaction between these molecules. During oxidation, oxygen containing functionalities are added to the asphalt molecules, causing increased molecular interactions.

Studies carried out on asphalt fractionation (Corbett) (4), suggest that, in asphalt, asphaltenes act as thickeners, the saturates provide fluidity, and naphthene aromatics plasticize the polar aromatic and asphaltenes fractions. In terms of properties, polar aromatic fractions impart ductility to the asphalts, and the saturate and naphthene aromatics, in combination with asphaltenes, form the complex flow properties of asphalt. Each fraction or combination of fractions is responsible for certain physical properties and a proper balance in the amounts of the different components is essential to produce asphalt with predictable properties (2).

The changes in chemical and physical properties of recycled asphalt have been studied by Corbett et al (6). Comparison of the Corbett fractions (SARA) of pristine and recycled samples showed that there is no change in the concentration of saturates. This demonstrates that no major changes occurred to the saturates during the aging process, which might be due to its hydrocarbon nature and low reactivity. However, there is a decrease in the quantity of naphthene aromatics and polar aromatics and an increase in the amount of asphaltenes. Naphthene aromatics and polar aromatics are prone to oxidation and become functionalized with oxygen-containing functional groups, forming asphaltenes. Several investigators have studied the uptake of oxygen by asphalt and have confirmed that asphalt components react with oxygen (5-6). Peterson et al (2,7) have ranked the relative reactivity of atmospheric oxygen with the SARA fractions in the order of 1:7:32:40 for saturates, naphthene aromatics (aromatics), polar aromatics (resins), and asphaltenes respectively. Therefore, the aged asphalt or the binder obtained from RAP will generally have an increased viscosity, increased carbonyl content, increased asphaltene content, and decreased penetration and ductility. These changes result in the deterioration of the asphalt pavement properties.

Various characterization techniques have proved the formation of strong intermolecular associations among molecules during the aging of asphalt and these associations produce molecular agglomerates and embrittlement of the asphalt (2). Additionally, these agglomerates seem to increase significantly in size with an increase in the asphaltene concentration.

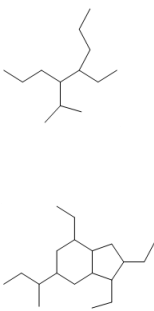
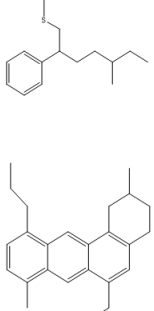
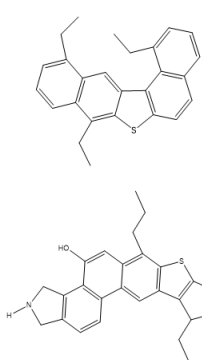
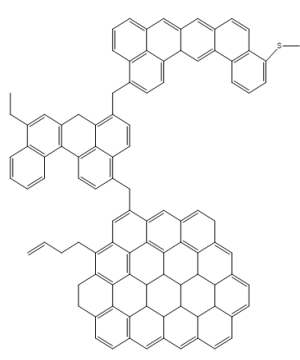
| Saturate | Aromatics | Resins | Asphaltenes |
|---|--|--|---|
|  |  |  |  |
| 5-15% Mostly Aliphatic, little aromaticity, Low hetero atom content | 30-40% Mostly aromatic (naphthalene type) and small amounts of aliphatic structures | 30-45% Aromatic compounds substituted with long alkyl chains | 5-20% Fused aromatic structures (4-20 rings) with alkyl chains and polar groups |

Figure 1. Representative structures of asphalt fractions SARA (saturates, aromatics, resins and asphaltenes).

Considerable research has been done to understand the size and molecular interactions of SARA fractions of asphalt and their influence on its physical properties. Griffin et al (8) reported the effect of different types of molecular interactions on the molecular weight and viscosity. They experimentally found the viscosity of molecular weight = 500 of each saturates, aromatics, and resin (fractions of the asphalt), as 10 Pa-s, 1,000 Pa-s and 1,000,000 Pa-s respectively at 25°C. This study shows that even if the true molecular weight of each fraction is the same, the molecular interactions have a great impact on the viscosity and other physical properties. In other words, the performance properties of asphalt are actually determined by the association properties of different molecules in the asphalt.

Dickie and Yen (9) studied the asphaltene fractions of seven different crude petroleum samples using various analytical methods including X-ray diffraction (XRD), mass spectroscopy (MS), Gel permeation chromatography (GPC), vapor phase osmometry (VPO), ultra-centrifugation and electron microscopy. Different methods yield molecular weight of asphaltenes that range from approximately 500 to 50,000 Daltons. Based on the X-ray diffraction results and other techniques, they proposed a model, later known as the Yen model, to explain the structure of asphaltene and the reason for the divergent molecular weight results. The Yen model proposed that the asphaltenes and resins (polar aromatics) exist as flat, condensed aromatic disks to which alkyl and naphthenic side chains are attached, forming a unit sheet. These unit sheets arrange in stacks through π -bonding between aromatic sheets, and hydrogen bonding between hetero atoms, to form particles or clusters. These particles can further associate to form micelles. They suggested that the size of the asphaltenes and resins are the same but they differ in the extent of condensation (9-12). They showed that the association of asphalt molecules in different levels: unit sheet, stacked sheet or particles comprised of several individual stacked unit sheets, and an association of several unit

cells into larger nuclei held together by intermolecular forces in to micelle like structures etc. The authors explained that the divergent molecular weight results from different molecular weight determination methods are because each measurement measures different structures (unit sheet, particle weight, micelle weight). The asphaltene fraction is the most complex fraction which undergoes changes in size and quantity during aging. Rostler et al. (13) reported that asphaltene, due to its limited solubility in the remaining components of the asphalt, is primarily responsible for the asphalt viscosity and colloidal behavior. Ultraviolet fluorescence (14), FTIR (15), X-ray Raman spectroscopy (16), NMR (17), AFM and STM (18) show that asphaltenes contain 4-20 aromatic rings with aliphatic side chains and that it can stack by molecular interactions.

Asphalt aging is complex phenomena resulting in the change in structure and composition of the chemical components. The oxidative process causes the mixture to become hard, brittle and susceptible to disintegration and cracking failure which (in the long run) results in excessive pavement deterioration.

3.2. Chemical Characterization Techniques

Several chemical methods are reported to help in understanding the changes in the molecular structure of asphalt binder before and after aging. The most widely used properties are molecular weight distribution and carbonyl content of asphalt. The most commonly used methods to study the molecular weight of asphalt and its components are mass spectrometry (MS), Vapor pressure Osmometry (VPO) and size exclusion chromatography (SEC)/gel permeation chromatography (GPC).

GPC is a simple technique which has been used more extensively to study the molecular weight distribution of asphalt and its fractions compared to other methods (19-20). A single binder and a virgin binder plot of molecular weight vs elution volume is rather similar for most of the asphalts, but upon aging of the asphalt, the GPC curve differs based on the extent of aging (19,21). Asphalts and its fractions can be easily analyzed by GPC, which has been extensively used to study the difference between asphalts, observe changes that occur to asphalt upon aging, and determine the low molecular weight contaminants. During aging associated molecular structures will be formed as result of intermolecular attraction. These structures can be easily observed in a GPC chromatogram, because the technique is based on the fractionation of molecules by size. An increase in the high molecular weight region, usually known as the large molecular size (LMS) region indicates the presence of high molecular weight components (or associated structures). If polymer is added as a modifier, it can be distinguished from the associated structure, as the polymer comes at a very high molecular weight region.

In Figure 2, the GPC chromatogram of the RAP-binder shows a very high increase in the large molecular size region (LMS) compared to the GPC of the virgin asphalt. This implies that the LMS content of the asphalt increased with aging, due to the association of molecules with polar functional groups. Since the presence of associated asphaltene molecules caused by aging is clearly reflected in the GPC molecular weight distribution curve (Chromatogram), GPC will be mainly used in this research to study the changes that occur to the RAP-binder on treatment with Lewis acid catalyst.

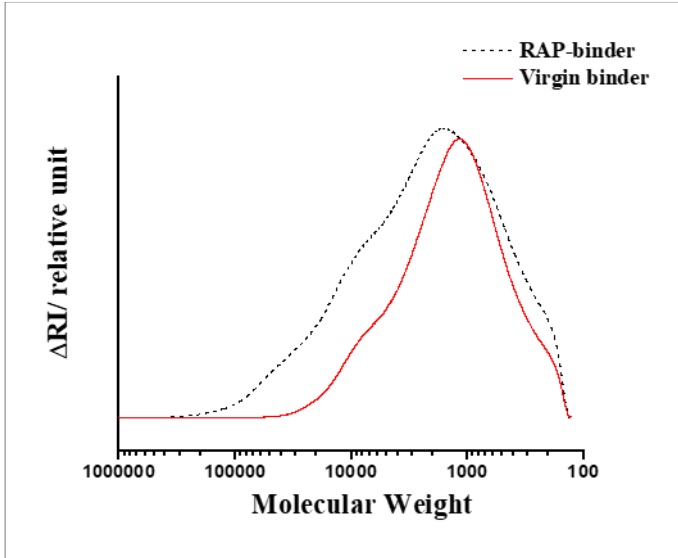


Figure 2. GPC chromatograms of a virgin binder and a RAP binder.

Reports on the aging mechanism of asphalt suggest that the major oxidation products formed during oxidative aging are ketones and sulfoxides. Another experimental method which can be effectively used to detect the extent of aging in asphalt is Fourier Transform Infrared Spectroscopy (FTIR) (22). FTIR allows for the identification of carbonyl (C=O) and sulphoxide (S=O) groups formed during oxidative aging. Many researchers (23-24) have used FTIR to analyze aging of polymer modified asphalt binders. They observed that during aging, the carbonyl peak (1695 cm^{-1}) increases compared to the saturated ethylene and methyl groups (reference peaks) centered at 1460 and 1375 cm^{-1} (Figure 3). The ratio of C=O and reference peak vibrations will provide a relative comparison of how much oxidation is happening. Increase in the value of this ratio indicates a higher level of oxidation. In a virgin asphalt binder this ratio is zero, due the absence of any carbonyl peak.

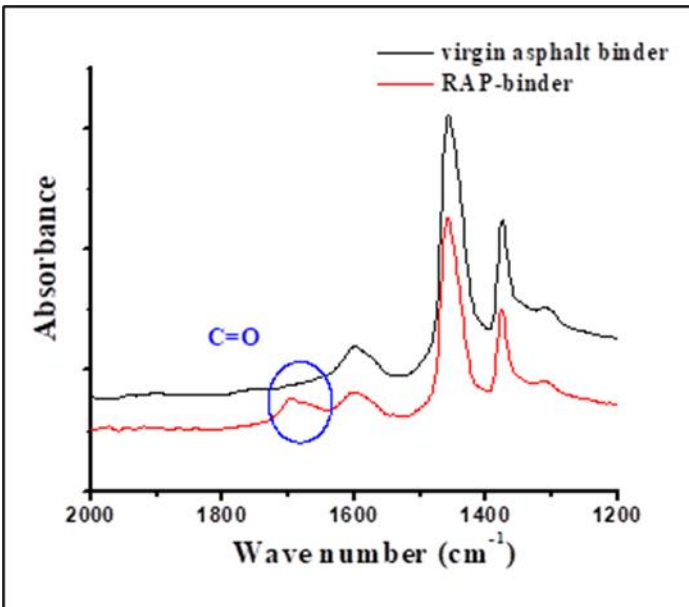


Figure 3. FTIR spectra of pristine and aged binder (wavenumber from $2000\text{--}1200\text{ cm}^{-1}$).

3.3. Reclaimed Asphalt Pavement (RAP)

Reclaimed asphalt pavement (RAP) is obtained when existing asphalt pavement materials are removed during resurfacing, rehabilitation or reconstruction operations (25). During the service life of asphalt on the road, oxidative aging occurs. As early as 1931, Hubbard and Reeve studied the effects of outdoor weathering on the physical and chemical properties of paving grade asphalt cements. Their one year study clearly showed that asphalt aging occurs through volatilization and oxidation (26). Since then, a significant amount of research has been devoted to understand the aging mechanism and its effects on the properties of asphalt binders (2,4,7,27). Oxidation of asphalts occurs over the service years and is augmented by solar radiation (especially UV rays), water, and atmospheric oxygen (2). UV-rays create radicals which then easily react with oxygen to form oxygen containing functional groups on the asphalt components. These polar functional moieties interact with each other to form aggregated structures, increasing the asphaltene content in the mixture and hence the viscosity. These mechanisms first happen on the surface layer, later penetrating to lower layers as cracking occurs. The oxidative process may cause the mixture to become hard, brittle and susceptible to disintegration and cracking failure which, in the long run, results in excessive pavement cracking. Steric hardening of the asphalt pavement is caused by molecular reorganization due to the fluctuations in the temperature.

In recent years, a higher percentage of RAP has been used in the construction of hot mix asphalt (HMA) pavements (25). The use of RAP in asphalt mixtures has been studied by many researchers. Kennedy et al characterized RAP binders combined with virgin binders using Superpave test specifications ENREF30 (22) leading to the development of a method to evaluate the relationship between the rheological properties of RAP and its potential field performance. Researchers have also studied the incorporation of RAP, but conflicting results were reported about the percentage of RAP that can be included with virgin asphalt while maintaining good performance (28,29). Recycling agents such as softening agents and rejuvenators are added to increase the amount of RAP binder that can be incorporated in virgin asphalt. The softening agents are added to reduce the viscosity of RAP-binder and rejuvenators are used to restore the chemical and rheological properties of RAP-binder to ensure a long performance period. Many types of rejuvenators are used such as super-soft asphalt binders (usually with low asphaltene content), bio-oils such as vegetable oils, waste-derived oils, and synthetic products. ASTM D4552 standard classifies rejuvenators into six different groups based on their viscosity at 60°C (30). However the interaction and compatibility of these additives have shown conflicting results (31). Also it is not clear whether all types of rejuvenators are appropriate with regard to performance and environment (32).

Sustainability can be achieved by using new technologies, processes, and products that directly enhances the product's environmental and economic sustainability through reduced consumption of energy and material. An important part of long-term sustainability is the transformation of a recycled material in to a resource for the new cycle. In this type of transformation, catalysts play an important role, because catalysis continuously uncovers new pathways of chemical transformations of both known and unknown resources (33). They are often able to drive a reaction which would otherwise not proceed, and result in additional advantages such as decreased energy input, reduced environmental impact, and overall cost- effectiveness. More than 90% of the current chemical products are produced by catalytic transformations (34) where the catalyst may be a small organic molecule, an enzyme, or a metal compound.

In this work we employed a different approach to use of a catalyst to reverse the chemical changes occurs to asphalt molecules during its service, particularly oxidation and molecular aggregation. Many organic transformations use Lewis acid catalysts because they provide high selectivity. Lewis acids have been successfully used in the liquefaction of coal (35,36). Lewis acid catalysts are also used in the air blowing of asphalt (37). Lewis acids contain an empty orbital which is capable of accepting electron pairs from Lewis bases such as oxygen, sulfur, nitrogen, and double bonds. When the aged asphalt is treated with a Lewis acid like FeCl_3 , it may react with polar groups like oxygen, nitrogen, and double bonds that are present in it and may aid in the dismantling of the self-assembly of the aggregates. The actual mechanism for this process remains to be clarified.

4. METHODOLOGY

4.1. Extraction of RAP-Binders from RAP Sources and their Characterization



Figure 4. RAP samples extracted from aggregates using InfraTest™ Asphalt Analyzer.

4.2. Chemical Characterization of RAP -Binders and Virgin Binders

4.2.1. Fourier Transform Infrared Spectrometer (FTIR)

FTIR analysis of the samples were done using a Bruker instrument located at the Chemistry Department of LSU (Figure 5). 1% solutions of asphalt samples were made in carbon disulfide solvent and filtered using a 0.45 μ filter. Few drops of the solution were placed on the ATR crystal plate and the solvent will be allowed to evaporate. The spectra will be collected after the complete evaporation of the solvent. Carbon disulfide has peaks around 1500 cm^{-1} and 2150 cm^{-1} which do not interfere with the characteristic peaks of asphalt. An OPUS 7.2 data collection program was used for the data analysis. The following settings will be used for data collection: 64 scans/sample, spectral resolution 4 cm^{-1} , wave number range 4000-500 cm^{-1} . Figure 6 shows the FTIR spectrum of the RAP asphalt binder and the assignment its peaks.



Figure 5. Bruker FTIR spectrophotometer.

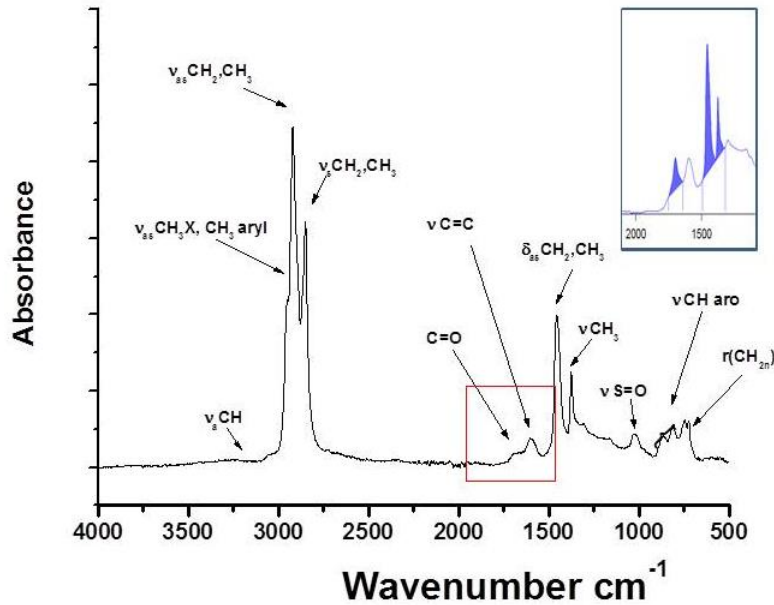


Figure 6. Typical FTIR spectrum of the RAP sample

Figure 7 shows the FTIR spectra of the virgin asphalt binder (PG 67-22) and that of the RAP binder. The FTIR of the RAP binder show a broad peak in the wave number between 1535 – 1720 cm^{-1} , characteristic of the carbonyl group, which is absent in the FTIR spectrum of the virgin asphalt binder (PG 67-22). These results are as expected in that the virgin asphalt contains mostly hydrocarbons structures such as aromatic, aliphatic and few functional components, hence it doesn't show the carbonyl group. The asphalt binder undergoes oxidation during its service time and hence the RAP binder showed the presence of carbonyl group. The relative amount of carbonyl groups present in the RAP binder sample was calculated based on its carbonyl index value.

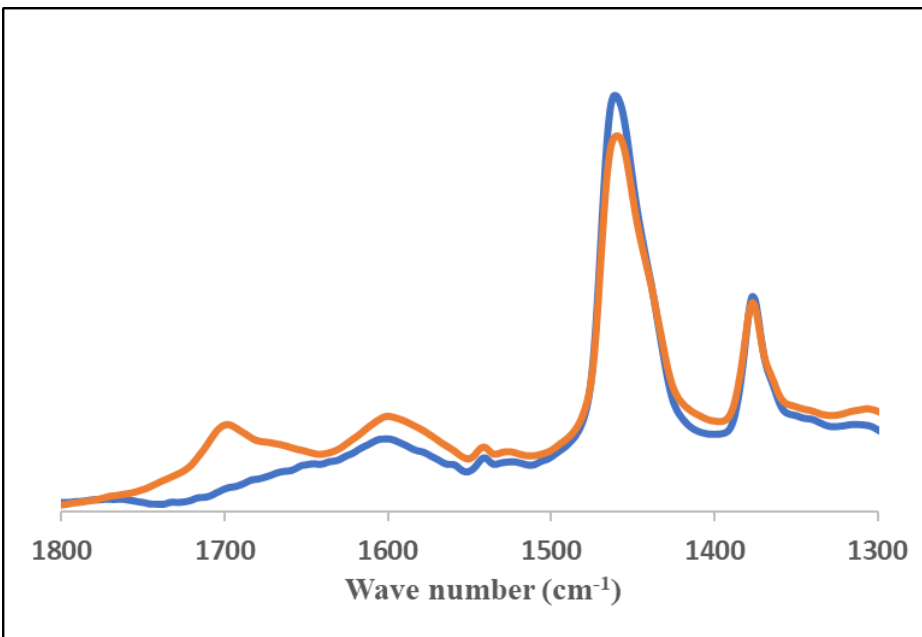


Figure 7: FTIR spectra of Virgin asphalt binder (Blue) and the RAP Binder (Red).

The carbonyl index value was calculated as the ratio of area under the carbonyl peak centered at 1695 cm^{-1} and the saturated ethylene and methyl groups peaks (reference peaks) centered at 1460 and 1375 cm^{-1} (Figure 8).

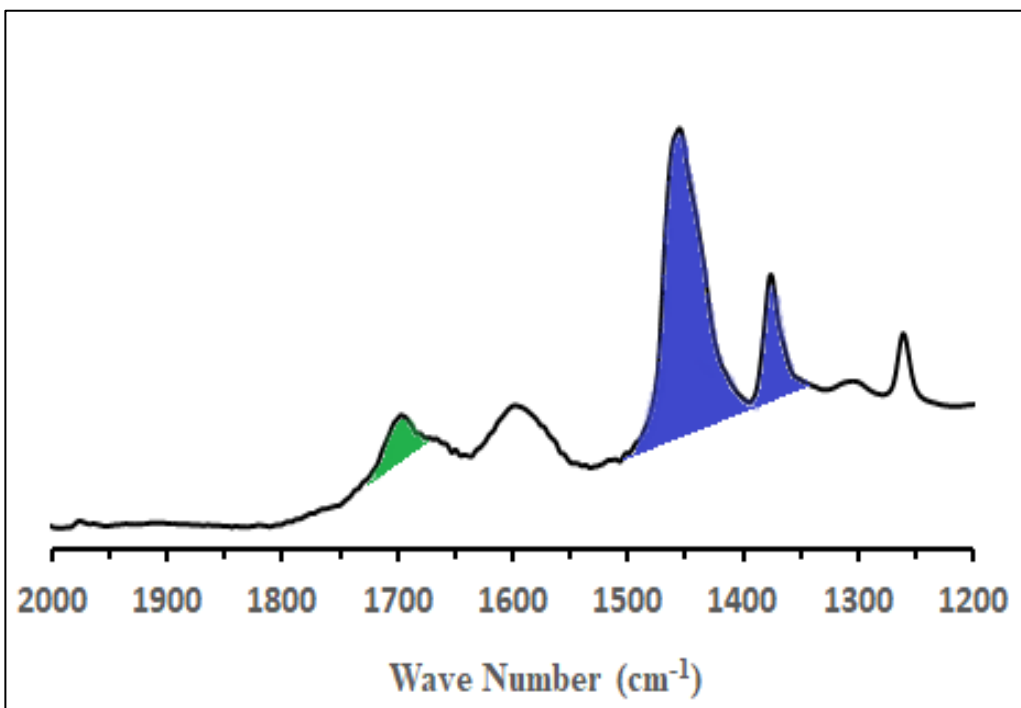


Figure 8. FTIR spectrum of the RAP binder sample along with the area of the peaks used for the carbonyl index value calculation.

$$\text{Carbonyl index} = \frac{\text{Area of the carbonyl centered around } 1700\text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 1490 \text{ and } 1320\text{ cm}^{-1}}$$

4.2.2. Gel Permeation chromatography (GPC)

GPC analysis will be performed using an EcoSEC high performance GPC system (HLC-8320GPC) of Tosoh Corporation (Figure 9), equipped with a differential refractive index detector (RI) and UV detector. The instrument for the analysis is located at DOTD Materials laboratory. Analysis will be done using tetrahydrofuran (THF) as the solvent at a flow rate of 0.35 mL/min . A set of four microstyragel columns of pore sizes 200 \AA , 75 \AA (2 columns) and 30 \AA from Tosoh Bioscience will be used for the analysis. The columns will be calibrated using polystyrene standard mixtures PStQuick B (MW= 5480000, 706000, 96400, 10200, 1000), PStQuick E (MW= 355000, 37900, 5970, 1000), and PstQuick F (MW= 190000, 18100, 2500, 500) from Tosoh Bioscience.



Figure 9. EcoSEC high performance GPC system (HLC-8320GPC).

Figure 10 shows the GPC results for the virgin asphalt binder (PG 67-22) and that of the RAP binder. The GPC chromatogram of the RAP binder shows broad shoulder at higher molecular weight (low retention time) region, showing the presence of high molecular aggregates present in the RAP binder compared to virgin asphalt binder.

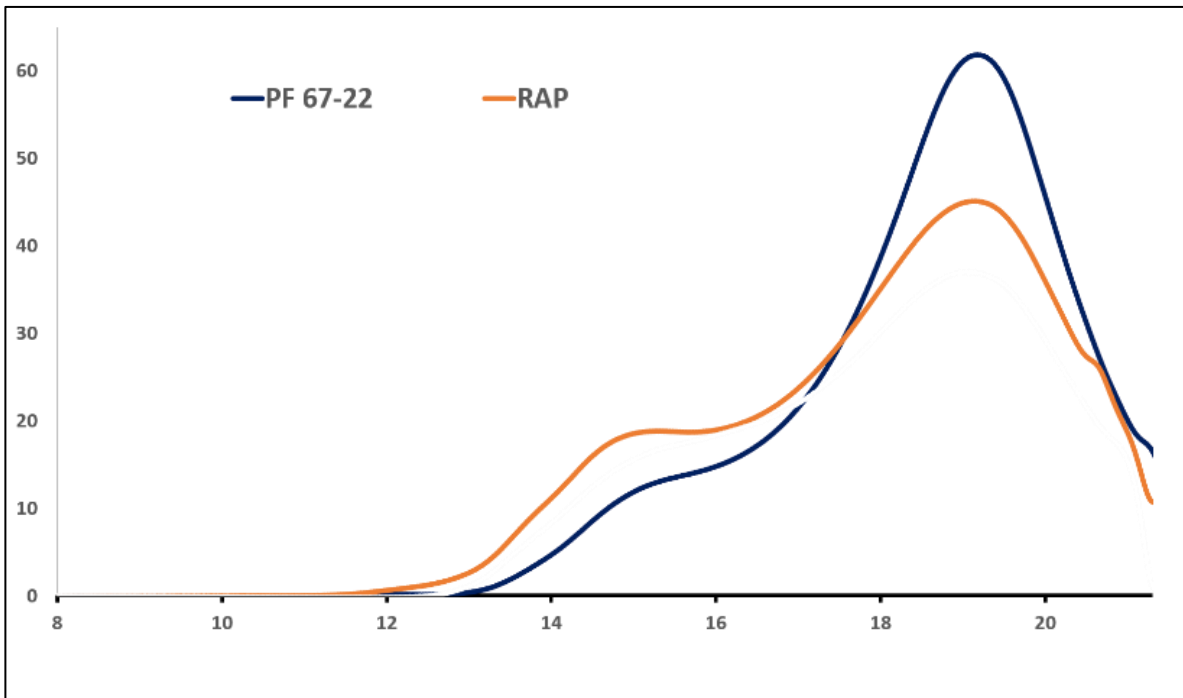


Figure 10. GPC chromatogram of the virgin asphalt binder (PG 67-22) and the RAP binder.

4.2.3. Nuclear Magnetic Resonance Spectrometer (NMR)

¹H NMR analysis was performed using the Bruker AVIII 400 MHz (Nanobay) (Figure 11). 10% solutions of asphalt samples will be made in deuterated trichloromethane (containing 0.03% trimethylsilane standard)



Figure 11. Bruker AVIII - 400 MHz (Nanobay) NMR spectrophotometer.

4.3. Reaction of RAP samples with Iron Chloride

The RAP sample, approximately 2 g, was taken in a 100 mL conical flask and kept it on a hot plate set at 165°C for 30 min. Then the appropriate amount of iron chloride was weighed and added to the heated RAP sample. This mixture was stirred using a glass rod to ensure the uniformity of the reaction. After the selected reaction/treatment time, the conical flask was removed from the hot plate, the sample was allowed to cool to the room temperature and then analyzed using FTIR or by GPC.

4.4. Reaction of Virgin Asphalt Samples with Iron Chloride

The virgin asphalt sample (PG 67-22), approximately 2 g, was taken in a 100 mL conical flask and kept it on a hot plate set at 165°C for 30 min. Then the appropriate amount of iron chloride was weighed and added to the heated virgin asphalt sample. This mixture was stirred using a glass rod to ensure the uniformity of the reaction. After the selected reaction/treatment time, the conical

flask was removed from the hot plate, the sample was allowed to cool to the room temperature and then analyzed using FTIR or by GPC.

4.5. Reaction of RAP Samples with Zinc Chloride

The RAP sample, approximately 2 g, was taken in a 100 mL conical flask and kept it on a hot plate set at 165°C for 30 min. Then the appropriate amount of zinc chloride was weighed and added to the heated RAP sample. This mixture was stirred using a glass rod to ensure the uniformity of the reaction. After the selected reaction/treatment time, the conical flask was removed from the hot plate, the sample was allowed to cool to the room temperature and then analyzed using FTIR or by GPC.

5. ANALYSIS AND FINDINGS

5.1. Reaction of Iron Chloride with RAP-Binder

The effectiveness of the catalysts was evaluated using the change in carbonyl index as measured by FTIR and in the change in the high molecular weight region as measured by GPC. The RAP samples were treated with the Lewis acid catalyst, FeCl₃ using the following procedure. First the RAP sample was taken in the beaker and heated to 165°C on a temperature controlled hot plate for 30 min. Then desired amount of FeCl₃ was added to the RAP sample and stirred for desired time at 165°C. Then the beaker was removed from the hot plate and allowed to cool. For FTIR analysis, the RAP binder sample was dissolved in carbon disulfide (CS₂) solvent and filtered through the 0.45 μm filter. For GPC analysis, the RAP binder sample was dissolved in tetrahydrofuran (THF) solvent and filtered through the 0.45 μm filter.

For initial studies we measured the carbonyl index of the RAP samples treated with 0.2, 0.5, 1, 2 and 10 (wt./wt.) % of FeCl₃ for 30 min. at 165°C and the results shown in Table-1. The carbonyl index of the treated RAP samples was expressed as the relative percentage with respect to the carbonyl index of the untreated RAP sample. The carbonyl index results showed that RAP samples treated with 2 (wt./wt.) % FeCl₃ showed maximum effect. Based on these results, we selected 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ treatment for different treatment time periods: 0.5, 1, 2 and 4 h. The 0.2 and 0.5 (wt./wt.) % FeCl₃ were selected to see if treatment with low amount of iron chloride, which is desired, with long treatment time can be effective. Table-2, showed the all the iron chloride treatment carried out with the RAP samples.

Table 1. Carbonyl index of the RAP samples treated with different amounts of Iron Chloride for 30 min at 165°C.

| Sample | Carbonyl Index |
|------------------------------|----------------|
| RAP | 100% |
| RAP + 0.2% FeCl ₃ | 94.9% |
| RAP + 0.5% FeCl ₃ | 92.5% |
| RAP + 1% FeCl ₃ | 60.7% |
| RAP + 2% FeCl ₃ | 47.6% |
| RAP + 10% FeCl ₃ | 63.6% |

Table 2. Iron chloride treatment carried out with the RAP samples.

| (wt./wt.) % FeCl ₃ | Treatment time (h) | | | |
|-------------------------------|--------------------|---|---|---|
| Control* | 0.5 | 1 | 2 | 4 |
| 0.2% FeCl ₃ | 0.5 | 1 | 2 | 4 |
| 0.5% FeCl ₃ | 0.5 | 1 | 2 | 4 |
| 2% FeCl ₃ | 0.5 | 1 | 2 | 4 |

* Control samples were prepared by heating the RAP samples at 165°C for 0.5, 1, 2 and 4 h. This was done to eliminate the effect of heating from the effective of the catalyst.

Figures 7-10 show the GPC results of control, 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ treated RAP samples for 0.5, 1, 2 and 4 h respectively. All these data showed that as the amount of iron chloride increases, the relative area of the high molecular weight (MW) fraction decreases, the relative area of the maltene fraction increases and the relative area of the asphaltene fractions approximately

remain constant. This data, along with decrease in carbonyl index value as shown by FTIR, showed that the iron chloride may chemically transform the carbonyl group (the chemistry of this is still not understood clearly) which may decrease the hydrogen bonding and hence decrease the size of the aggregates formed during the aging of asphalt binder.

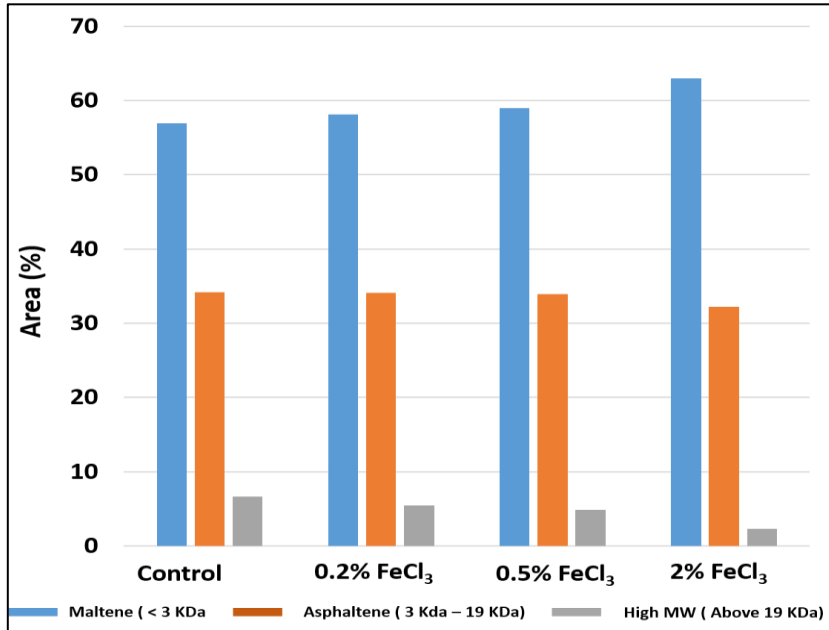


Figure 12. Different molecular weight fractions calculated from the GPC chromatogram for the control RAP sample along with the RAP samples treated with 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ for 30 min.

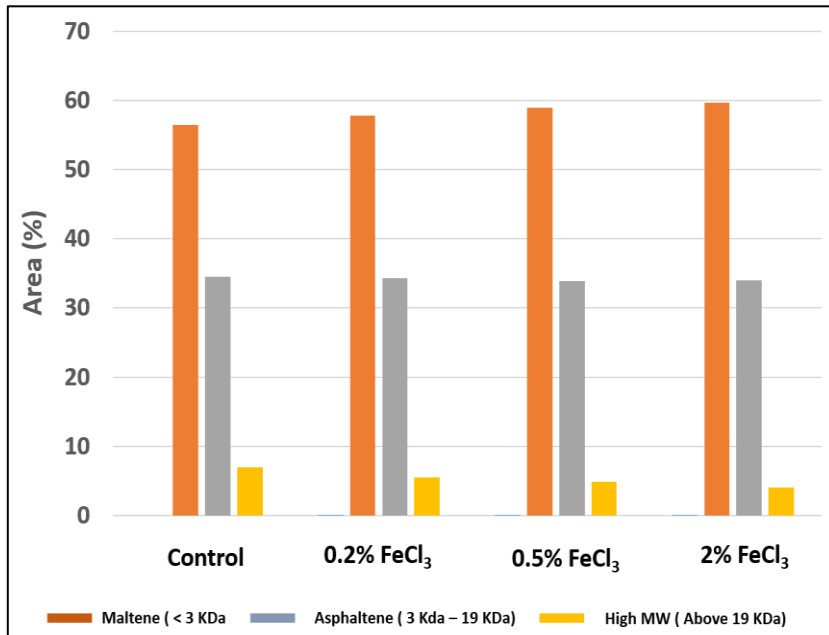


Figure 13. Different molecular weight fractions calculated from the GPC chromatogram for the control RAP sample along with the RAP samples treated with 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ for 1 h.

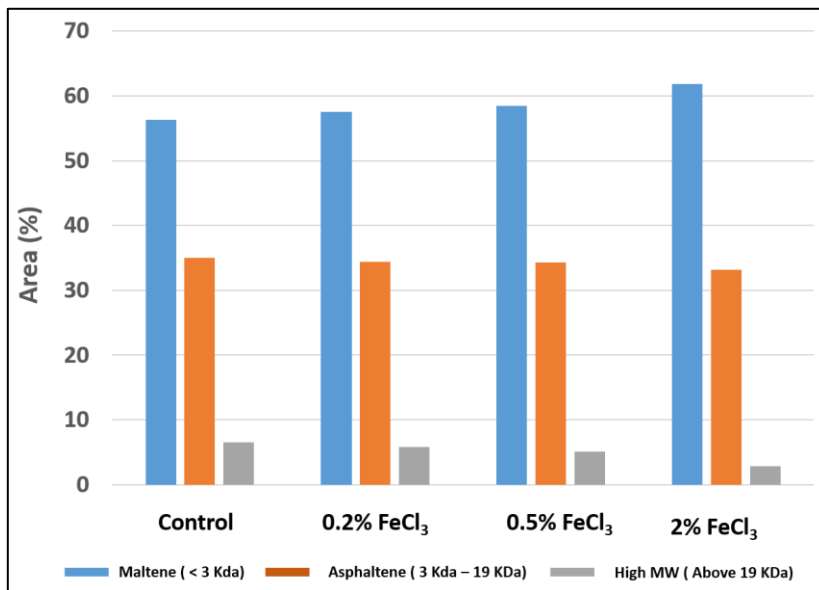


Figure 14. Different molecular weight fractions calculated from the GPC chromatogram for the control RAP sample along with RAP samples treated with 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ for 2 h.

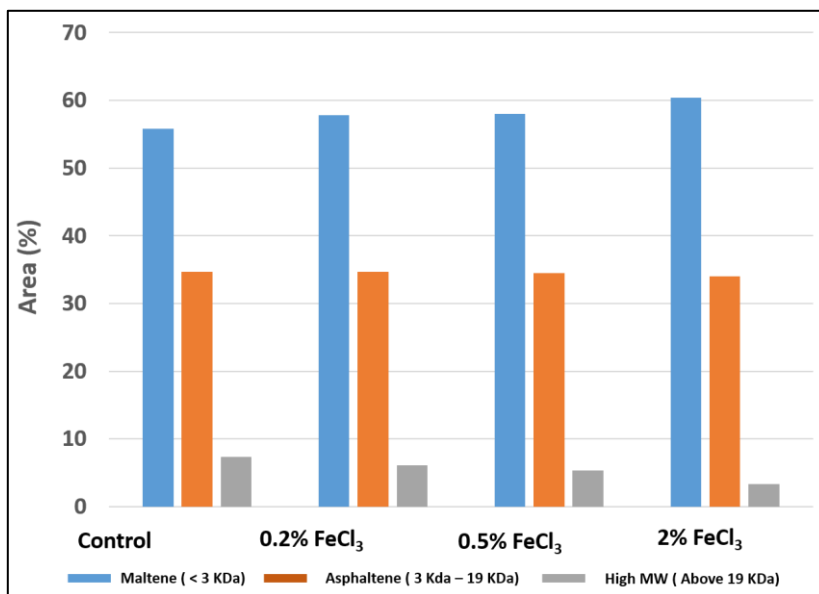


Figure 15. Different molecular weight fractions calculated from the GPC chromatogram for the control RAP sample along with the RAP samples treated with 0.2, 0.5 and 2 (wt./wt.) % FeCl₃ for 4 h.

Figure-10 also shows that as the amount of iron chloride increases the high molecular weight fraction decreases. In order to compare all the data, we selected the relative area of the high MW fraction of all the RAP treated sample (Table-3) to access the effectiveness of each treatment. The data in Table-3 showed that the amount of iron chloride has a large effect on the relative area of the high MW fractions. As the amount of iron chloride increases the relative area of the high MW fraction progressively decreases. The 2 (wt./wt.) % FeCl₃ treated RAP samples showed the maximum decrease in the high MW fractions. But the effect of treatment time is very minimal as seen from the relatively small standard deviation in the all the treatment time data for the each %

of FeCl₃. When we analyze the 2 (wt./wt.) % FeCl₃ treated RAP samples data (Figure -11), the 30 min treated RAP sample showed maximum decrease in the high MW fractions. Although the 2 h and 4 h data also showed good decrease in the high MW fractions and not much different from 30 min data, we selected the 165°C, 30 min treatment time with 2 (wt./wt.) % FeCl₃ treatment to be the optimum conditions for reclaiming and reuse of RAP samples along with virgin asphalt binder.

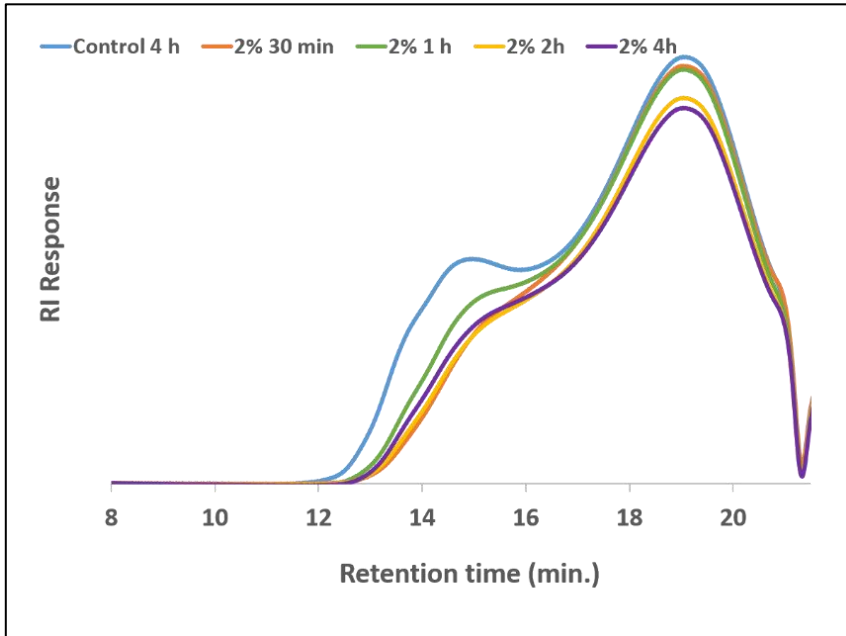


Figure 16. GPC chromatogram for the control RAP sample (blue) along with the RAP samples treated with 2 (wt./wt.) % FeCl₃ for 30 min., 1 h, 2h and 4 h.

Table 3. Changes in the area (%) of the high molecular weight (MW) fractions in different RAP treated samples compared to the corresponding control samples as determined by GPC. The average of each data column is also shown.

| Treatment time (h) | Amount of FeCl ₃ ((wt./wt.) %) | | |
|--------------------|---|-------------|-------------|
| | 0.2 % | 0.5 % | 2 % |
| 0.5 | -18 % | -26 % | -56% |
| 1 | -20 % | -30% | -52 % |
| 2 | -11 % | -22 % | -57% |
| 4 | -17% | -28% | -54% |
| Average | -16.5 ± 3.9 | -26.5 ± 3.4 | -54.8 ± 9.9 |

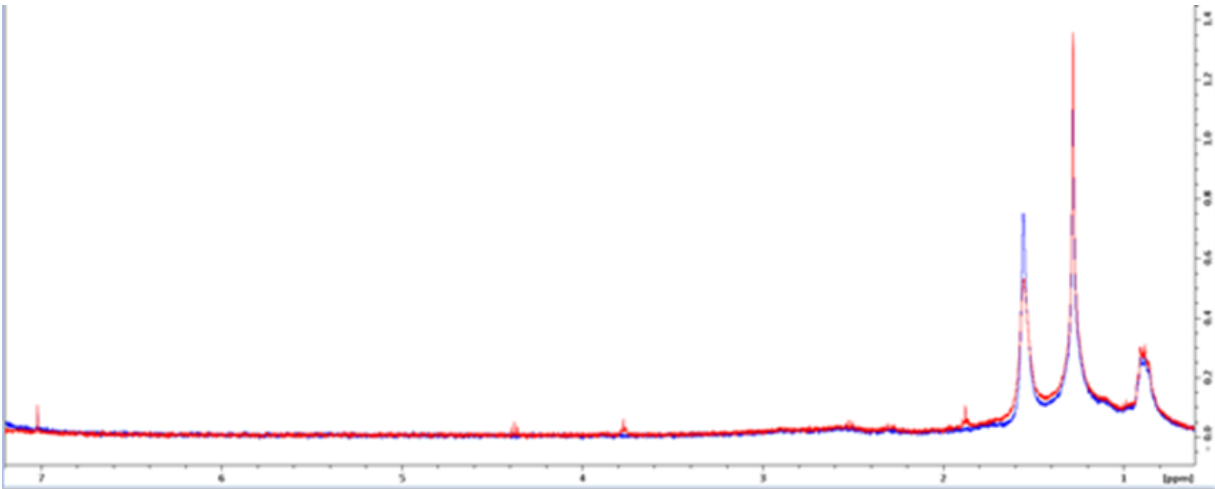


Figure 17. ^1H NMR of spectra of the RAP sample (blue) and the RAP sample treated with 2 (wt./wt.) % FeCl_3 for 30 min. at 165°C (red).

We also analyzed the RAP binder and the RAP binder treated with 2 (wt./wt.) % iron chloride at 165°C for 30 min by ^1H NMR (Figure 12). The ^1H NMR spectra of the iron chloride treated RAP sample was very close to the ^1H NMR spectra of the untreated RAP sample. The resolution for ^1H NMR spectral analysis is $\pm 5.0\%$, and within that range it appears that there is essentially no difference in the two spectra, especially in the aromatic range of 6.5-7.1 ppm which indicated changes in aromatic aggregation.

We also examined the effect of iron chloride on the virgin asphalt binder (PG 67-22); this was the only sample used for Task 4, which had polymer in the mixture, the most likely occurrence for RAP. The virgin asphalt binder was treated with 2 (wt./wt.) % iron chloride at 165°C for 30 min. After that the treated virgin asphalt for analyzed by FTIR. The results (Figure 13) showed that there were no measurable changes in the virgin asphalt after iron chloride treatment.

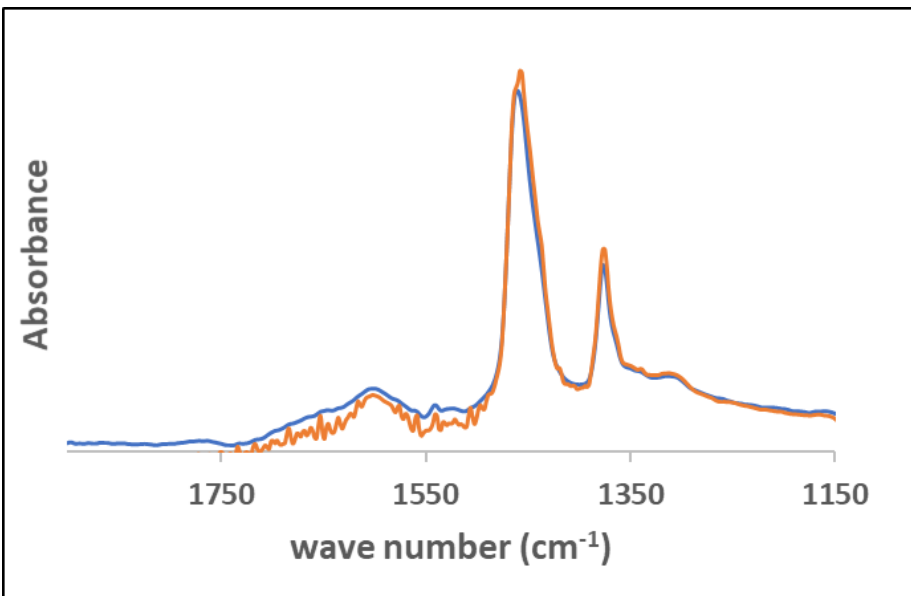


Figure 18. FTIR spectra of the virgin asphalt (blue) and the virgin asphalt after treatment with 2 (wt./wt.) % of iron chloride at 165°C for 30 min (red).

5.2. Reaction of Zinc Chloride with RAP-Binder

The RAP samples were treated with another Lewis acid catalyst, Zinc chloride $ZnCl_2$ using the procedure similar to one used for the iron chloride treatment. First the RAP sample was taken in the beaker and heated to $165^\circ C$ on a temperature controlled hot plate for 30 min. Then the desired amount of $ZnCl_2$ was added to the RAP sample and stirred for desired time at $165^\circ C$. Then the beaker was removed from the hot plate and allowed to cool. For FTIR analysis, the RAP binder sample was dissolved in carbon disulfide (CS_2) solvent and filtered through the $0.45 \mu m$ filter.

Table 4. Carbonyl index values for RAP sample along with RAP samples treated with 0.5 and 2 (wt./wt.) % of $ZnCl_2$ for 2 h at $165^\circ C$.

| Sample | Carbonyl Index value |
|---|----------------------|
| RAP sample | 0.1422 ± 0.008 |
| RAP sample treated with 0.5 (wt./wt.) % of $ZnCl_2$ | 0.1997 ± 0.003 |
| RAP sample treated with 2 (wt./wt.) % of $ZnCl_2$ | 0.1854 ± 0.028 |

The effectiveness of the treatment of RAP samples with $ZnCl_2$ was initially accessed by FTIR using change in carbonyl index value. The FTIR data showed that, the carbonyl index value increases upon zinc chloride treatment as shown in Table-4, which is the opposite of the desired outcome. Hence, zinc chloride treatment was not studied further.

We observed that there is batch-to-batch variation for the RAP samples both in the carbonyl index values as well as in the GPC chromatogram, as expected. Hence, it is important to carry out a set of experiments using same batch of the RAP samples.

6. CONCLUSIONS

This report describes the experiments and results of our investigation into the effects of a Lewis acid catalyst such as Iron (III) chloride and Zinc chloride on the chemical composition of RAP-binder. For initial studies we measured the carbonyl index of the RAP samples treated with 0.2, 0.5, 1, 2 and 10 (wt./wt.) % of FeCl_3 . The RAP samples were treated with the iron chloride for 30 minutes at 165 degrees Celsius; and for FTIR analysis, the RAP binder sample was dissolved in carbon disulfide (CS_2) solvent and filtered through a $0.45 \mu\text{m}$ filter. The optimal carbonyl index decrease was found for 2% FeCl_3 which showed a 47.6% decrease in the carbonyl index. The GPC results of the iron chloride treated RAP showed that as the amount of iron chloride increases, the relative area of the high molecular weight (MW) fraction decreases. At the same time, the relative area of the maltene fraction increases and the relative area of the asphaltene fractions approximately remain constant. The 2% FeCl_3 added to RAP for 30 minutes The 2 (wt./wt.) % FeCl_3 treated RAP samples showed the maximum decrease of 56% loss of the high MW fractions. This data, along with decrease in carbonyl index value as shown by FTIR, showed that the iron chloride may chemically transform the carbonyl group (the chemistry of this is still not understood clearly) which may decrease the hydrogen bonding and hence decrease the size of the aggregates formed during the aging of asphalt binder.

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