MID-AMERICA TRANSPORTATION CENTER

Report # MATC-KSU: 164

Final Report

WBS:25-1121-0003-164

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Sustainable Asphalt Pavements Using Bio-Binders from Bio-Fuel Waste

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2014

A Coopertative Research Project sponsored by
U.S. Department of Tranportation-Research, Innovation and Technology Innovation Administration

MATC

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A Report on Research Sponsored by

Mid-America Transportation Center

University of Nebraska-Lincoln

Federal Highway Administration

November 2014

Technical Report Documentation Page

1. Report No. 25-1121-0003-164	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Sustainable Asphalt Pavements Using Bio-Binders from Bio-Fuel Waste		5. Report Date November 2014
		6. Performing Organization Code
7. Author(s) Kenneth J. Klabunde and Khadga Shrestha		8. Performing Organization Report No. 25-1121-0003-164
9. Performing Organization Name and Address Kansas State University Fairchild Hall, Room No. 2 Manhattan, KS 66506-1103.		10. Work Unit No. (TRAIS)
		11. Contract or Grant No.
12. Sponsoring Organization Name and Address Mid-America Transportation Center Region VII University Transportation Center University of Nebraska-Lincoln 2200 Vine Street, 262 Whittier Building P.O. Box 830851 Lincoln, Nebraska 68583-0851		13. Type of Report and Period Covered July 2012-September 2014
		14. Sponsoring Agency Code MATC TRB RiP Project 36358
15. Supplementary Notes		

16. Abstract

Asphaltic binders that are used for asphalt pavements have been traditionally obtained either from fossil fuels or from natural sources. However, due to growing interest in sustainability, a search has been initiated for a non-petroleum binder that could be used for asphalt pavements. The objective of this study is to develop a modified asphalt binder from bio-refinery by-products and wastes that can be used as a replacement for bituminous adhesives/binders derived from fossil fuels for asphalt pavements. The chemical structures of the residue from fossil fuel processing and bio-fuel processing proved to be somewhat different. The Bio-Oil contains more oxygen (therefore, oxygen bearing organic functional groups, such as alcohols and ketones [-OH and C=O]). The Bio-Oil is more functionalized and polar in nature. Chemical structure studies were carried out by spectroscopic methods (nuclear magnetic resonance (NMR)), infra-red, and thermal gravimetric analyses, as well as solubility in a series of solvents. Future work would involve (1) studying a wider variety of Bio-Oil derived samples, (2) employing further analytical techniques, and (3) determining how the Bio-Oils can be converted to chemical structures more similar to the petroleum derived oils.

17. Key Words		18. Distribution Statement	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page)	21. No. of Pages 14	22. Price

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Acknowledgements

The authors gratefully acknowledge the Mid-America Transportation Center (MATC) for the sponsorship of this study.

Abstract

Asphaltic binders that are used for asphalt pavements have been traditionally obtained either from fossil fuels or from natural sources. However, due to growing interest in sustainability, a search has been initiated for a non-petroleum binder that could be used for asphalt pavements. The objective of this study is to develop a modified asphalt binder from bio-refinery by-products and wastes that can be used as a replacement for bituminous adhesives/binders derived from fossil fuels for asphalt pavements. The chemical structures of the residue from fossil fuel processing and bio-fuel processing proved to be somewhat different. The Bio-Oil contains more oxygen (therefore, oxygen bearing organic functional groups, such as alcohols and ketones [OH and C=O]). The Bio-Oil is more functionalized and polar in nature. Chemical structure studies were carried out by spectroscopic methods (nuclear magnetic resonance, NMR), infra-red, and thermal gravimetric analyses, as well as solubility in a series of solvents. Future work would involve (1) studying a wider variety of Bio-Oil derived samples, (2) employing further analytical techniques, and (3) determining how the Bio-Oils can be converted to chemical structures more similar to the petroleum-derived oils.

Chapter 1 Introduction

1.1 Introduction

Asphaltic binders that are used for asphalt pavements are obtained mainly from fossil fuels and to a small extent from natural sources. Asphaltic binders are mostly asphalt cements that are dark brown to black in color and are mostly produced by the distillation of petroleum crude oils (Brown et al. 2009). Many refineries in the United States are located near water-supplied transport or get crude via pipelines from marine terminals. Thus crude oil supply and price in the world market dictate the availability and price of petroleum-based asphalt cement. Most heavy asphalt containing crudes oils are imported from Mexico, Venezuela, Canada and the Middle East. However, in the US Midwest, most asphalt used are produced from crudes originating in west Texas and Montana (Canadian). The recent spike in asphalt binder prices has forced rethinking of asphalt paving and enhanced the search for an alternative to petroleum-based asphalt. The price increase of petroleum-based asphalt has made competition from Portland cement concrete more intense. Again, due to growing interest in sustainability, a search has been initiated for a non-petroleum binder that could be used for asphalt pavements. The efforts by Colas, S.A. in France and Iowa State University (ISU) in the United States in this respect are notable (Colas 2012, Williams 2012). In 2004, Colas patented a vegetable-based asphalt binder. In October of 2010, a bicycle path in Des Moines, Iowa was paved with asphalt containing 3% bio-oils through a partnership between Iowa State University, the City of Des Moines, and Avello Bioenergy Inc. ISU research efforts to develop bio-binders have used bio-renewable sources such as triglyceride oils, proteins, starch, and other carbohydrates from different organic sources. A range of different vegetable oils have been investigated by ISU to determine their physical and chemical properties to study their applicability as bio-binders (Raouf and Williams 2010). It is to be noted that if the binder is developed from virgin raw materials, it will be expensive and may compete against the food or edible oil sector. Thus, an alternative approach is needed to develop such bio-binders.

1.2 Potential Use of Bio-Binders

Bio-binders can be used in three different ways to decrease the demand for fossil fuel-based bituminous binders: an alternative binder (100% replacement), a bitumen extender (25% to 75% bitumen replacement), or a bitumen modifier (<10% bitumen replacement). Irrespective of the approach taken, the resulting binder rheological properties should have relationships with the following asphalt pavement performance (Brown et al. 2009):

(A) Raveling: Raveling can be caused by

(1) excessively aged or brittle or wrong grade of asphalt cement binder, and (2) lack of adhesion of the binder to aggregates;

(B) Load-associated cracking: Asphalt cement (AC) consistency influences development of fatigue cracks. Binders containing polymeric modifiers show some benefits in mitigating fatigue cracks. On the other hand, aged binders demonstrate poor fatigue life in thin AC overlays;

(C) Low-temperature cracking: High asphalt cement stiffness at low temperatures is the predominant cause of this type of cracking;

(D) Rutting: The high temperature stiffness of the asphalt cement is very important to minimize rutting; and

(E) Stripping or Moisture-induced damage: Binders with high viscosity are usually more resistant to moisture damage. However, care must be taken so that low-temperature cracking and reduced fatigue life of asphalt pavements may not happen due to the use of high-viscosity binder.

1.3 Objective of the Study

The objective of this study is to develop a modified asphalt binder from bio-refinery by-products and wastes that can be used as a replacement for bituminous adhesives/binders derived from fossil fuels for asphalt pavements.

1.4 Organization of the Report

The report is divided into three chapters. Chapter 1 is the introduction to the study. Chapter 2 describes the chemical tests and results. Finally, conclusions of this study and recommendations for further study are presented in chapter 3.

Chapter 2 Methodology

2.1 Task

The task was to study of chemical structure of bio-oils compared to Petroleum-derived oils, and oils compared with char and other samples.

2.2 Tests Done and Results

A total of 10 samples were compared using four scientific methods:

(A) Thermal Gravimetric Analysis (TGA) in the presence of air. This method shows if the sample can slowly oxidize to give off carbon dioxide.

(B) Solubility in various solvents shows if non-polar solvents or polar solvents will dissolve the sample.

(C) Infra-Red (IR) Spectroscopy, which shows what types of chemical bonds exist in the sample.

(D) Nuclear Magnetic Resonance (NMR) Spectra, which also shows chemical bonding differences.

Herein, only four pertinent samples were compared:

(1) PG 64-22 (a petroleum-derived asphalt binder)

(2) PG XX-34 (another petroleum-derived binder)

(3) Bio-oil Ave 110 (a bio-fuel-derived heavy oil from forest products)

(4) KSU Char (a sample derived from a bio-ethanol production process, black solid)

TGA Results

Petroleum-derived asphalts (PG 64-22 and PG XX-34) showed rapid oxidation and a weight loss of 93% at 350-500^{o} C, whereas Bio-Oil Ave 110 showed 150-600^{o} C and a 97% loss, and KSU Char showed slower reaction/oxidation over the range of 300-500^{o} C and a 85% loss of mass. The Bio-oil sample is more heat sensitive, while the KSU Char contains slightly more inorganic matter.

Solubility Results

The amount of PG XX-34 was calculated in different solvents—water, DMSO, THF, hexane, and toluene. One hundred fifty (150) ml of each solvent was taken during the experiment. The amount of PG XX was in the range of 300-500 ml.

Table 2.1 Solubility of PG XX-34

S.N.	Solvents	Soluble amount (wt %)
1	Water	5
2	DMSO	4
3	Hexane	89
4	THF	81
5	Toluene	97
6	Chloroform	96
7	Ethanol	Insoluble (Qualitatively)

The amount of PG 64-22 was also calculated in different solvents—water, DMSO, THF, Chloroform, hexane, and toluene. One hundred fifty (150) ml of each solvent was taken during the experiment. The amount of PG 64-22 was in the range of 300-500 ml.

Table 2.2 Solubility of PG 64-22 (petroleum-derived asphalt binder)

S.N.	Solvents	Soluble amount (wt %)
1	water	1.4
2	DMSO	1.2
3	Hexane	97.1
4	THF	97.4
5	Toluene	96.5
6	Chloroform	97
7	Ethanol	Insoluble (Qualitatively)

The amount of Bio-Oil soluble in different solvents was investigated. One hundred fifty (150 ml) of each solvent was taken during the experiment. The amount of Bio-Oil was in the range of 200-300 mg.

Table 2.3 Solubility of Bio-Oil Ave 110 (a bio-fuel-derived heavy oil as a possible replacement for petroleum-derived asphalt)

S.N.	Solvents	Soluble amount (wt %)
1	Water	41
2	DMSO	88
3	Hexane	11
4	THF	89
5	Toluene	17
6	Chloroform	79
7	Ethanol	96

Petroleum-derived (PG XX-34) was highly soluble in organic solvents (hexane 89%, toluene 97%, chloroform 96%), but insoluble in water and ethanol. Similar results were found for PG 64-22. However, Bio-oil was insoluble in hexane, partly soluble in chloroform, insoluble in water, but soluble in ethanol. Interestingly, the KSU Char sample was insoluble in all solvents.

Infra-Red Spectra (IR)

The IR spectra of petroleum-derived asphalt (PG 64-22) and the Bio-Oil are shown in figures later. The spectra are very different, and the petroleum-derived asphalt absorption bands for C-H bands (2800 cm^{-1}) C-C and C-H (near 1500 cm^{-1}). However, the Bio-Oil sample shows multiple bands for C-H, C-O C=O, as well as a strong, broad band for O-H (3400 cm^{-1}).

The spectrum of PG 64-22 and PG XX-34 are quite similar, while the KSU Char shows no IR bands except for trapped CO_2.

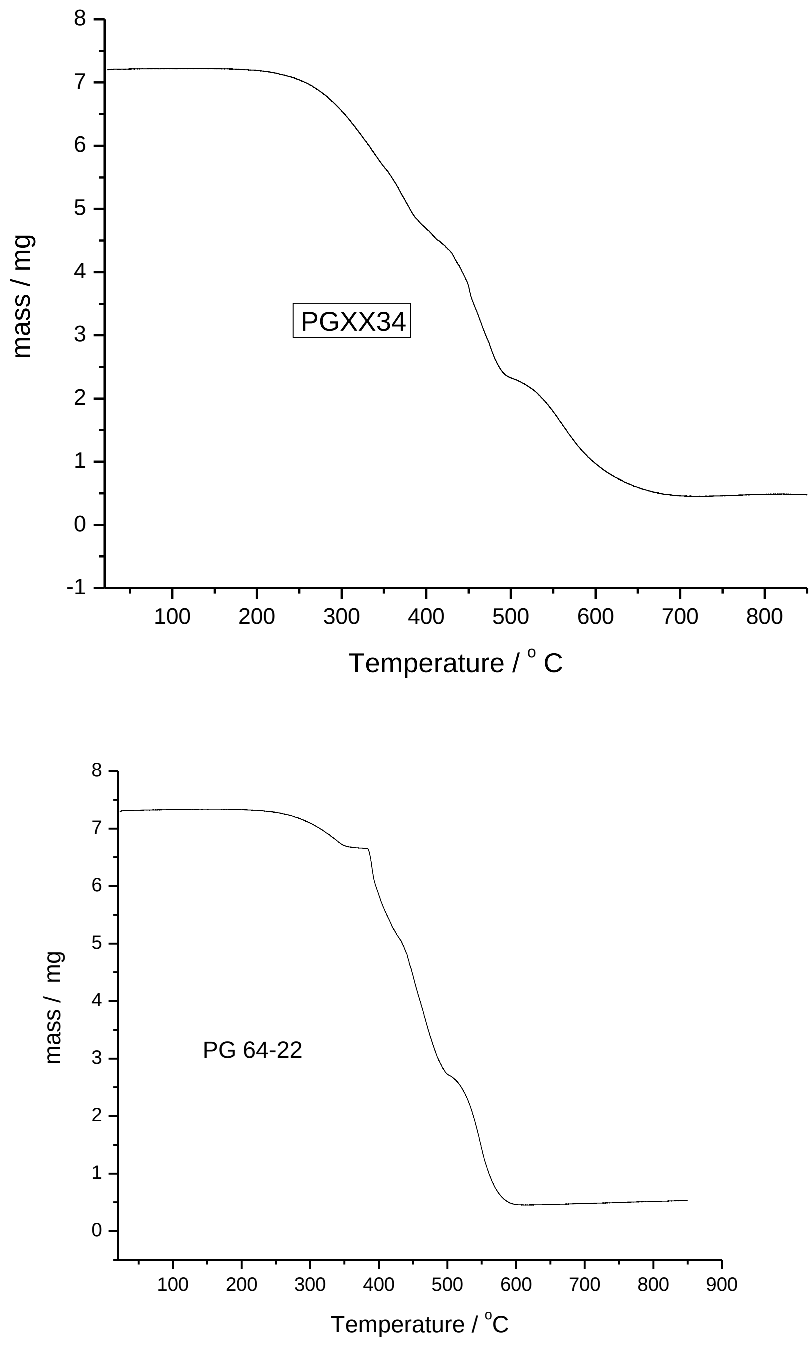

Figure 2.1 TGA spectra of petroleum-derived asphalt binders (PG XX-34 and PG 64-22)

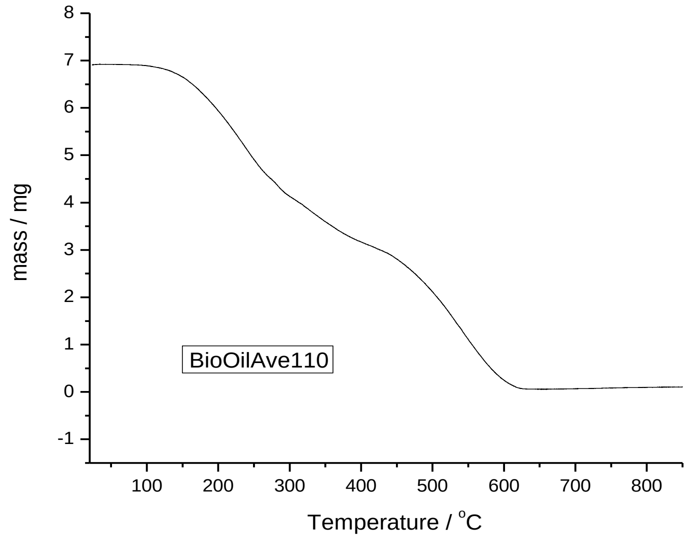

Figure 2.2 TGA spectrum of Bio-Oil-derived material

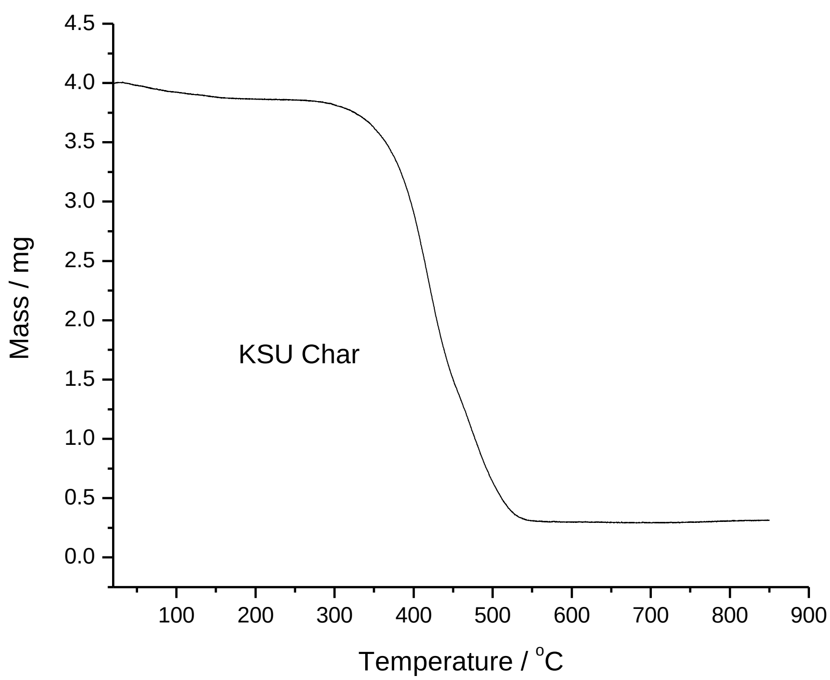

Figure 2.3 TGA spectrum of KSU Char

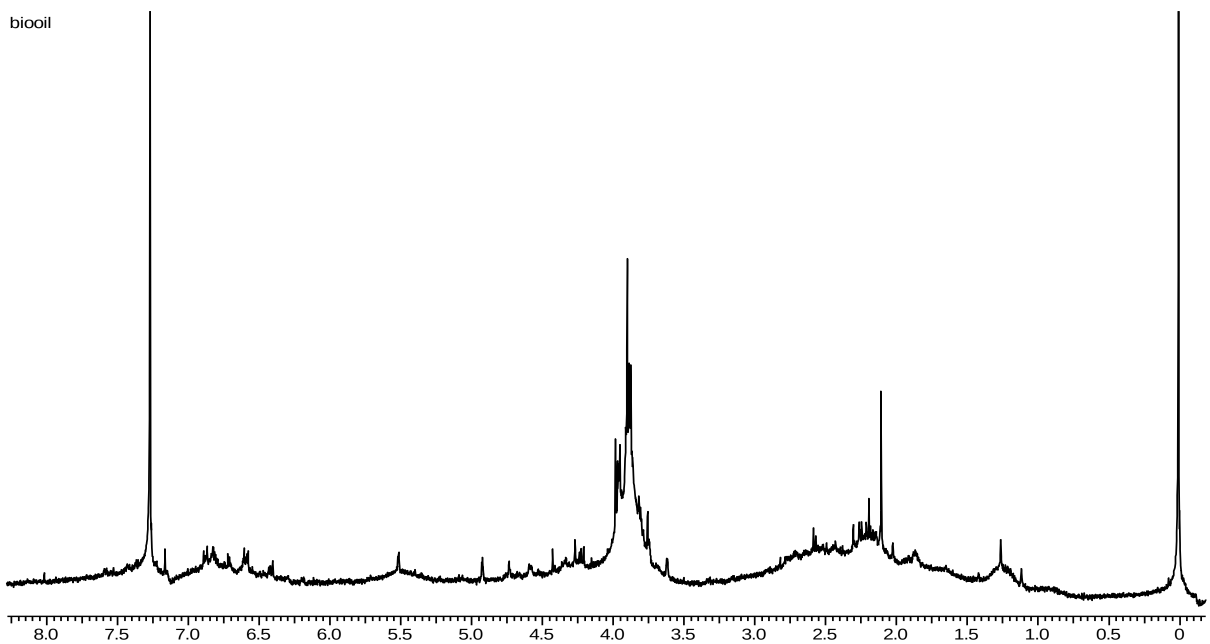

Figure 2.4 NMR spectrum of Bio-Oil Ave 110

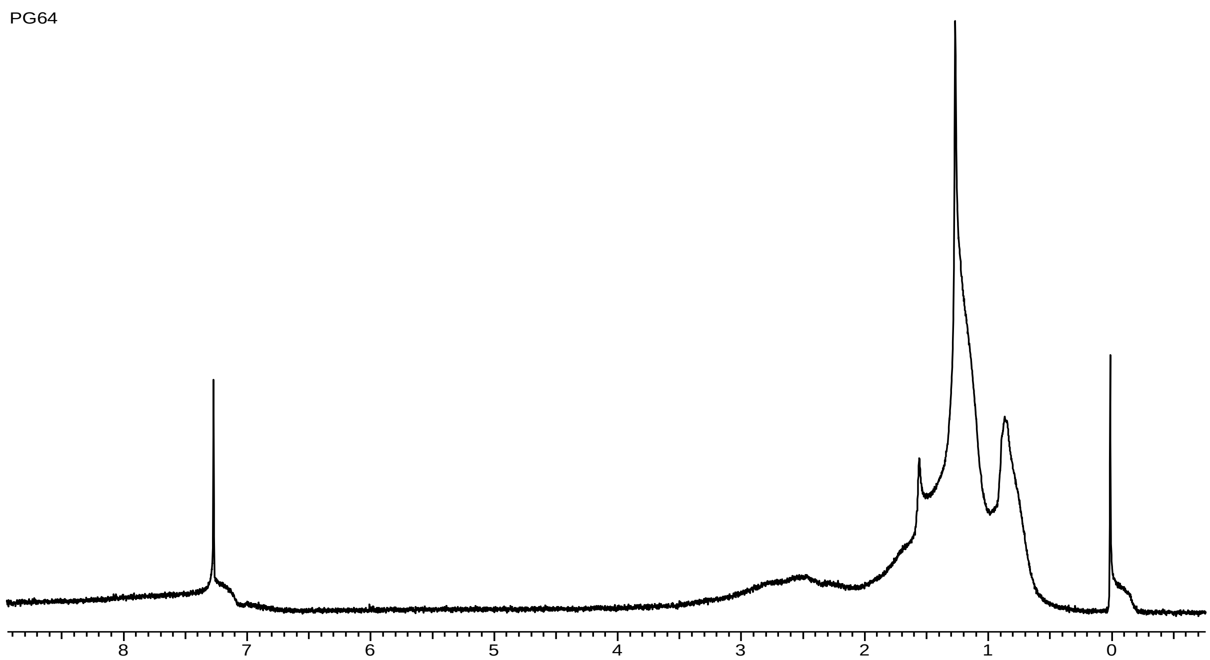

Figure 2.5 NMR spectrum of petroleum-derived asphalt binder PG 64-22

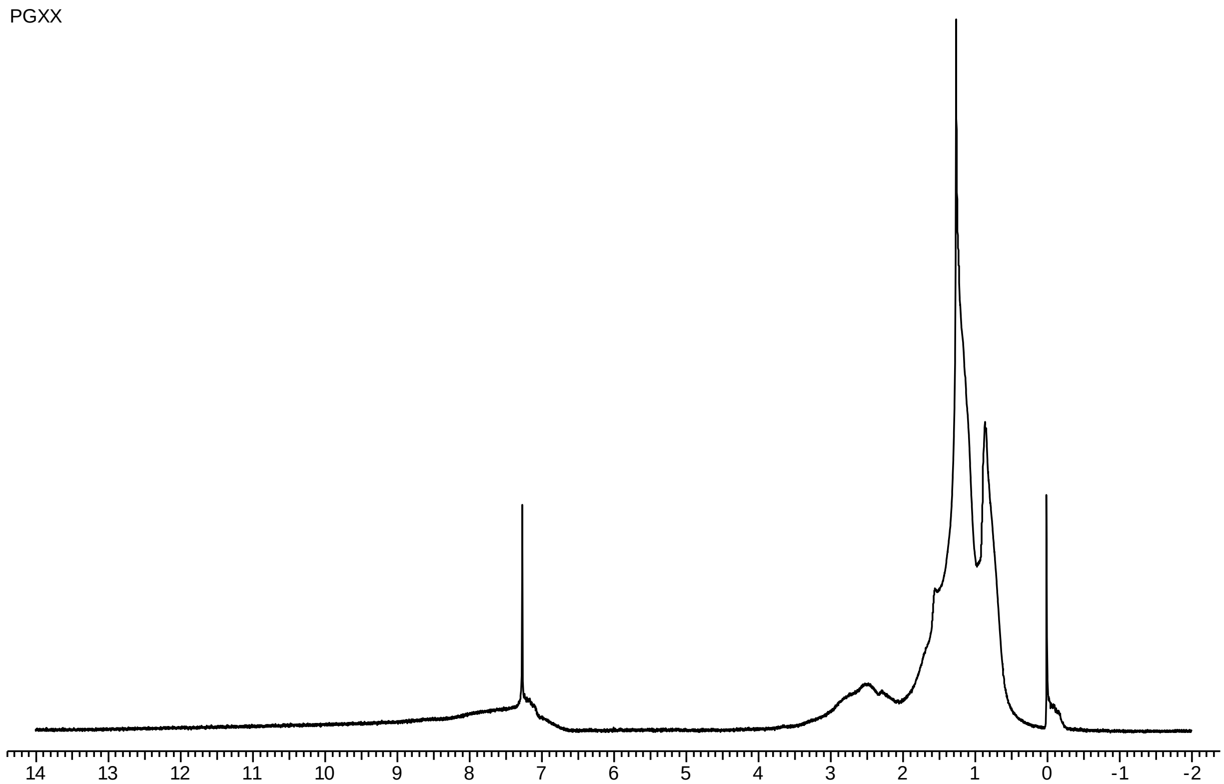

Figure 2.6 NMR spectrum of petroleum-derived asphalt binder PG XX-34

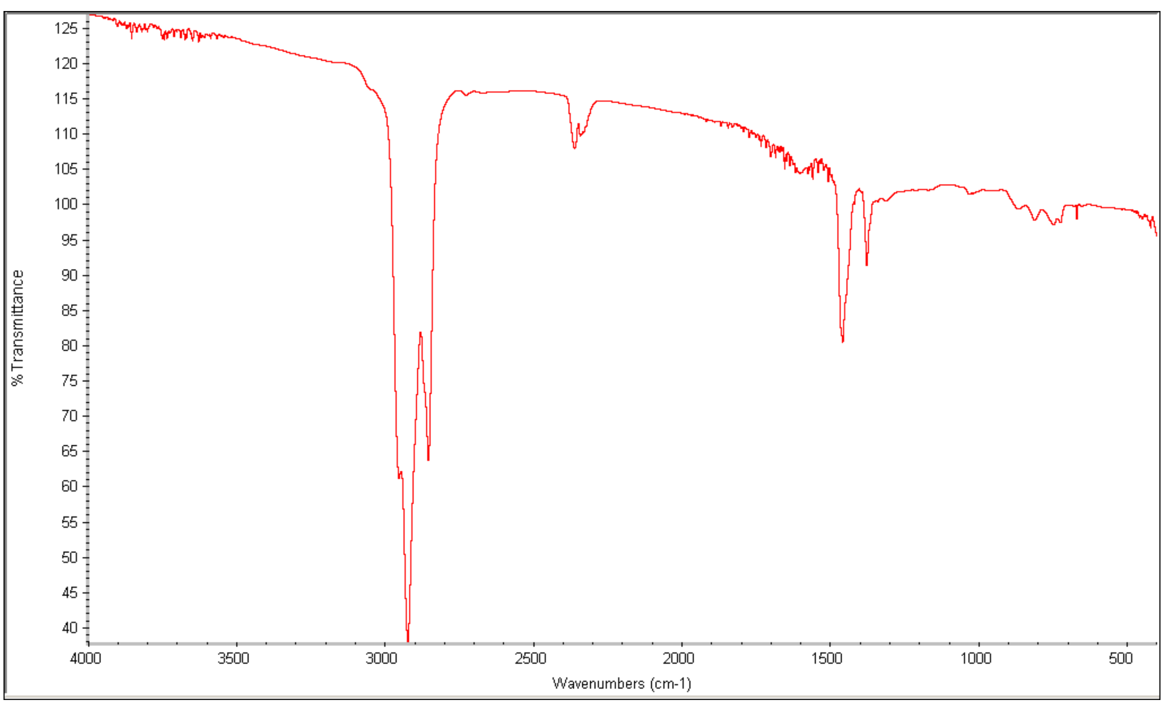

Figure 2.7 IR spectrum of PG XX-34

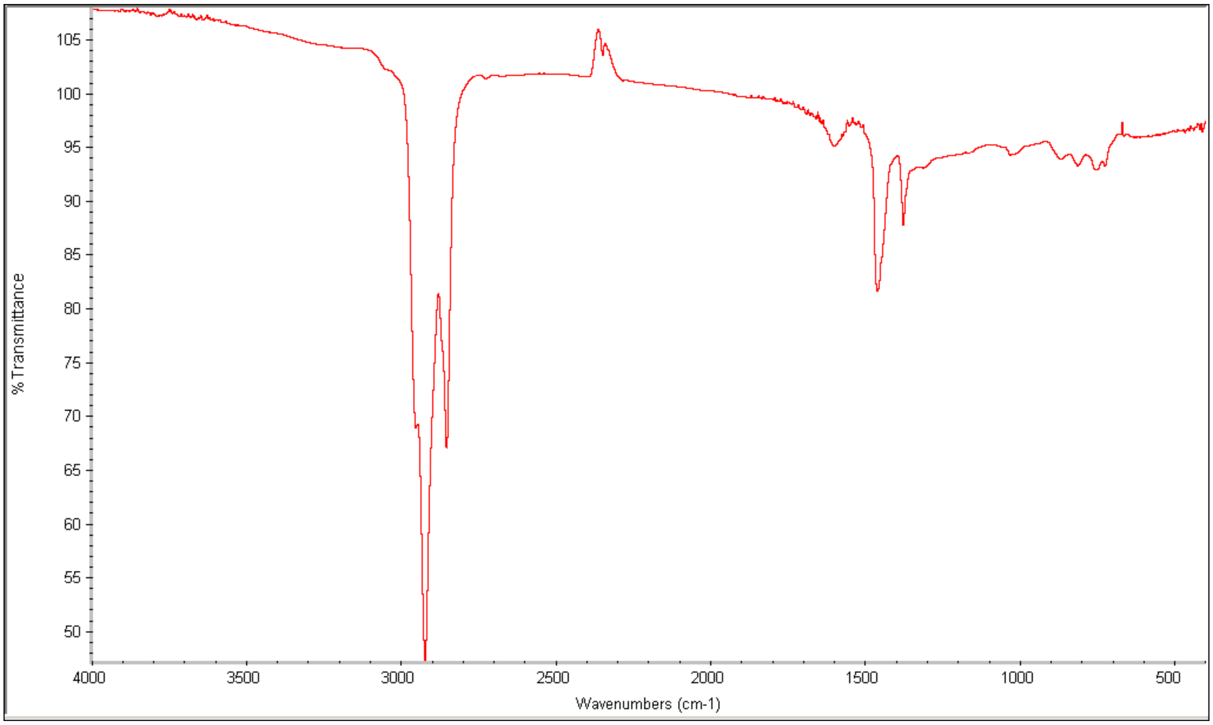

Figure 2.8 IR spectrum of PG 64-22

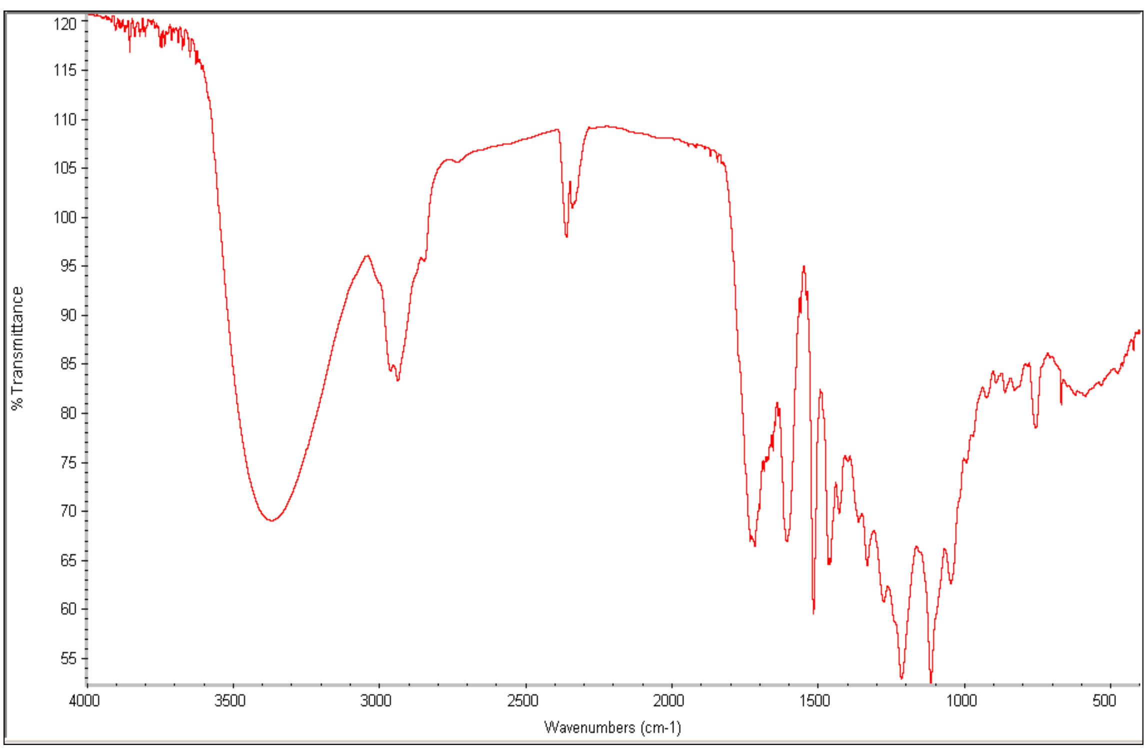

Figure 2.9 **IR spectrum of Bio-Oil Ave 110**

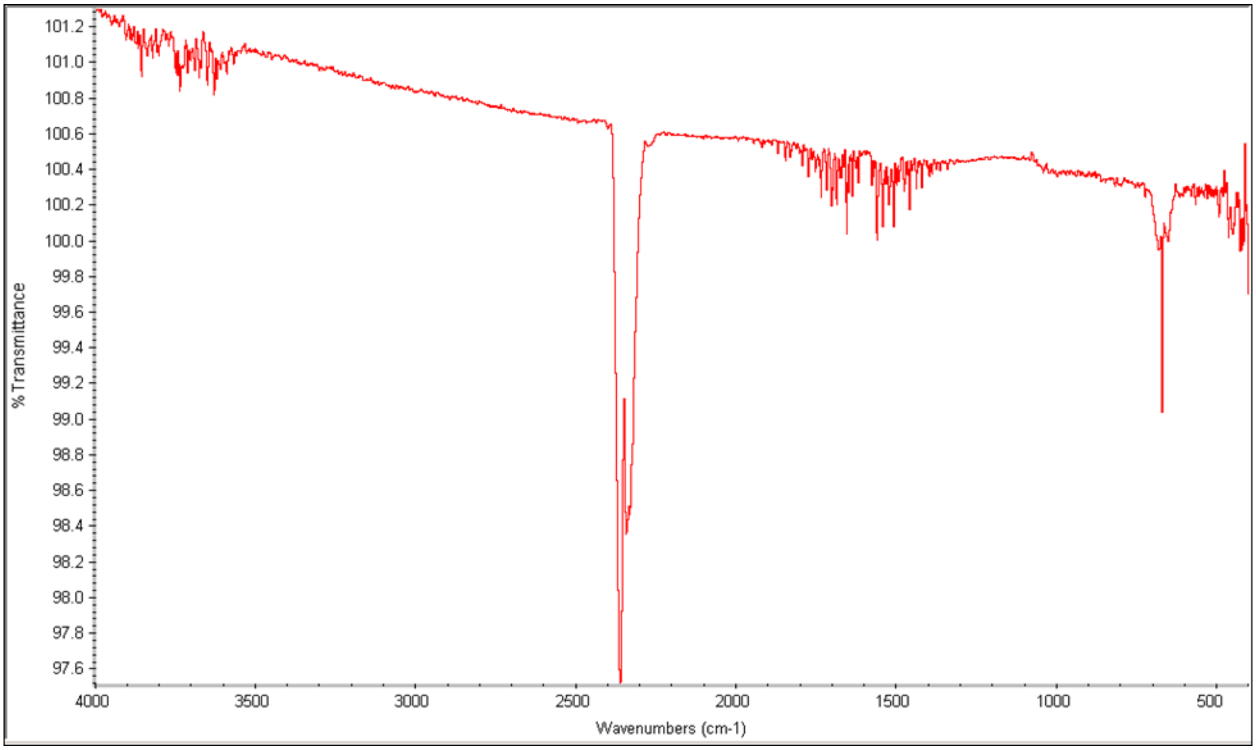

Figure 2.10 IR spectrum of KSU Char

Chapter 3 Conclusions and Recommendations

3.1 Conclusions

The objective of this study is to develop a modified asphalt binder from bio-refinery by-products and wastes that can be used as a replacement of bituminous adhesives/binders derived from fossil fuels for asphalt pavements. The objective was fulfilled through a study of the chemical structure of bio-oils compared to petroleum-derived oils, and oils compared with char and other samples using Thermal Gravimetric Analysis (TGA), solubility in various solvents, Infra-Red (IR) Spectroscopy, and Nuclear Magnetic Resonance (NMR) Spectra. It was concluded that the Bio-Oil contains more oxygen and is much more functionalized (more polar in nature).

3.2 Recommendations

The following recommendations are made from this study:

(1) Study a wider variety of Bio-Oil derived samples.

(2) Employ further analytical techniques such as NMR, UV-vis, particle size analysis, and more.

(3) Determine if the Bio-oils can be readily converted to chemical structures more similar to the petroleum-derived oils.

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