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Asphalt modification by utilizing bio-oil ESP and tall oil additive

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Asphalt modification by utilizing bio-oil ESP and tall oil additive

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Bio-oil is a dark-brown, mobile liquid derived from the thermo-chemical processing of biomass. Bio-oils generally contain water and lignin. Lignin is a highly-available, well-studied carbohydrate derivative known for its antioxidant properties. For asphalt pavements, oxidation can cause deterioration via long-term aging and eventually result in cracking. Therefore, bio-oil could potentially serve as an antioxidant additive in asphalt mixtures. The main objective of this research is to evaluate the effects of lignin-containing bio-oil for utilization in asphalt binders, and attempt to optimize the bio-oil modification formula by adding other additives. Using bio-oil as an antioxidant in asphalt production could prove to be an economical alternative to conventional methods while being conscious of the environment and increasing the longevity and performance of asphalt pavements.

Three bio-oils derived from corn stover, oak wood, and switch grass are tested and evaluated by blending with three conventional asphalt binders. The binders, in order of their susceptibility to oxidative aging, include two binders from the Federal Highway Administration's Materials Reference Library, AAM-1 and AAD-1, as well as a locally produced polymer modified asphalt binder. Bio-oil was added to the asphalt binders in three different percentages by weight, 3%, 6%, and 9%. Moreover, tall oil fatty acids, which is a viscous yellow odorous liquid as a by-product obtained from the southern kraft pulping process, was introduced to optimize the bio-oil modified binders. The Superpave testing and binder performance grading procedure from AASHTO M 320 was used to examine the antioxidant effects and determine the optimum fraction of bio-oil added to the binders. In addition, simple performance tests for an asphalt mixture were conducted to rank the performance properties of the different binders and

bio-oil combinations. The experimental asphalt samples for dynamic modulus testing were mixed by adding optimum percentages of bio-oil modified asphalt in the aggregate with a common gradation. Following by the dynamic modulus testing, the flow number tests were carried out with the same specimens as well. Besides ranking the performance, the statistical methods are applied and used to determine the statistically significant bio-oil treatment effects.

In general, the corn stover, oak wood, and switch grass derived bio-oil indicate that there is potential to increase the high temperature performance of asphalt binders. However, the increase in high temperature performance adversely affects the low temperature binder properties. The overall performance grade ranges vary depending on the combinations of three different binders and bio-oils. Tall oil does provide significant rehabilitation effects to the bio-oil modified binders at low temperatures. According to the data, some binders show antioxidant effects. Interestingly, the dynamic modulus test results do not necessarily coincide with the asphalt binder test results and suggest greater mix performance improvement than identified by the binders test results.

1 INTRODUCTION

1.1 Background

Bio-oil is a dark-brown, mobile liquid derived from the thermo-chemical processing of biomass. This liquid can be directly utilized as renewable fuel or taken as a source of valuable chemicals (Bridgwater 1999). The thermo-chemical process is known as pyrolysis, which can be divided into traditional and fast pyrolysis. Bio-oil mainly contains carbohydrate derivatives, water, and lignin, which is a highly-available, well-studied antioxidant. As a pavement ages, it becomes stiffener and more susceptible to failure. In this research work, tall oil, composed of rosins, fatty acids, sterols, high-molecular alcohols, and other alkyl chain materials was blended with different bio-oils as an asphalt additive to formulate modified asphalt binders. The potential use of bio-oil as an asphalt additive is an attractive way to increase the longevity and enhance the performance of asphalt pavements.

1.2 Objective

The purpose of the work was to investigate the feasibility of using bio-oil as an antioxidant additive to modify the AAD-1, the AAM-1 and a local polymer modified binder (LPMB) binders. To achieve this objective, evaluating the outcome of adding a small amount of electrostatic precipitant (ESP) bio-oil derived from corn stover, oak wood, and switch grass on the rheological properties of three conventional asphalt binders were done as the first research stage. After that detecting the mechanical effect of applying the bio-oil modified binder to hot mix asphalt (HMA) mixtures was carried out as well. Additionally, based on the evaluation results, tall oil was introduced to optimize the bio-oil modified binders, and it was the second stage. The Superpave binder test, asphalt simple performance test, and statistics tools were utilized to quantify the influence, make effect evaluations, and optimize the bio-oil/tall oil formulas.

1.3 Thesis organization

The explanations about how the bio-oil is generated by the fast pyrolysis processing, what the asphalt oxidation is, and how lignin acts as an antioxidant are presented in the literature review. Additionally, the summary of the past use of antioxidant research in asphalt materials is included in Chapter 2 as well. Chapter 3 explains the experimental methods, procedures and plan applied to analyze the lignin-containing bio-oil as an antioxidant additive as well as a performance enhancer in asphalt binders. The experimental data are summarized in Chapter 4. The statistical analyses of the binder performance testing data are presented in Chapter 5. Chapter 6 is dedicated to the asphalt mixture physical performance analysis. The final chapter summarizes the findings and demonstrates the conclusions of the experiment. Additionally, the recommendations for applying bio-oil/tall oil mixture to modify the asphalt binders and the future work that can be performed are made in the last chapter as well.

2 LITERATURE REVIEW

2.1 Fast pyrolysis of biomass for fuels and chemicals

Fast pyrolysis technology is used to produce bio-oil, a dark-brown, mobile liquid by heating the biomass such as corn stover, oak wood, and switch grass, rapidly to a high temperature in the absence of oxygen then followed by rapid quenching of the vapors to yield the bio-oil. Figure 1 illustrates the bio-oil mass pyrolysis pilot plant.

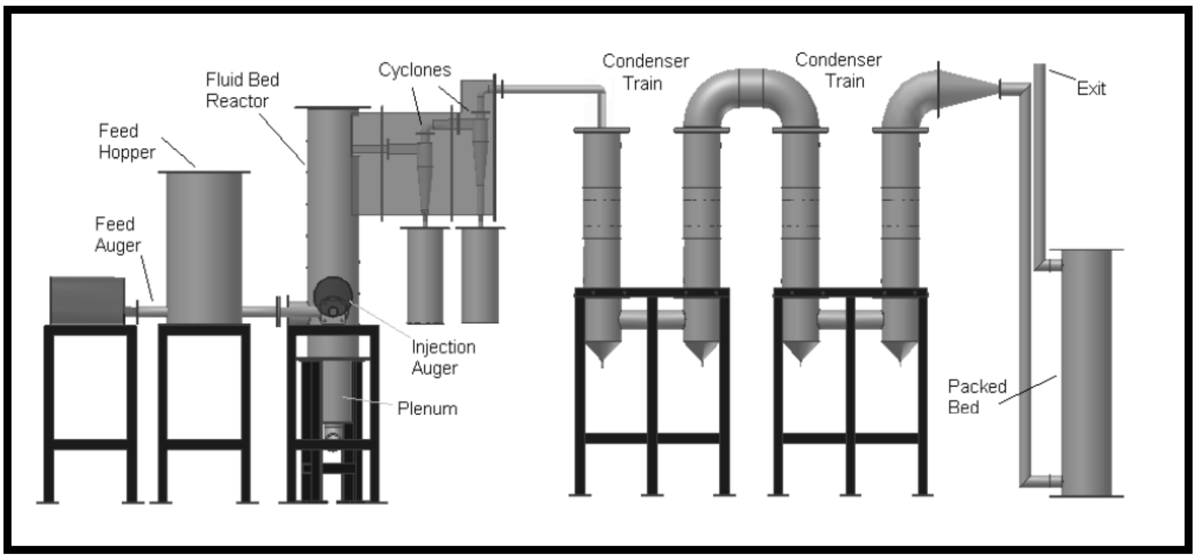


Figure 1. The Bio-oil mass pyrolysis pilot plant (Source: Iowa State University)

The essential features of the fast pyrolysis process can be summarized by (Bridgwater 1999):

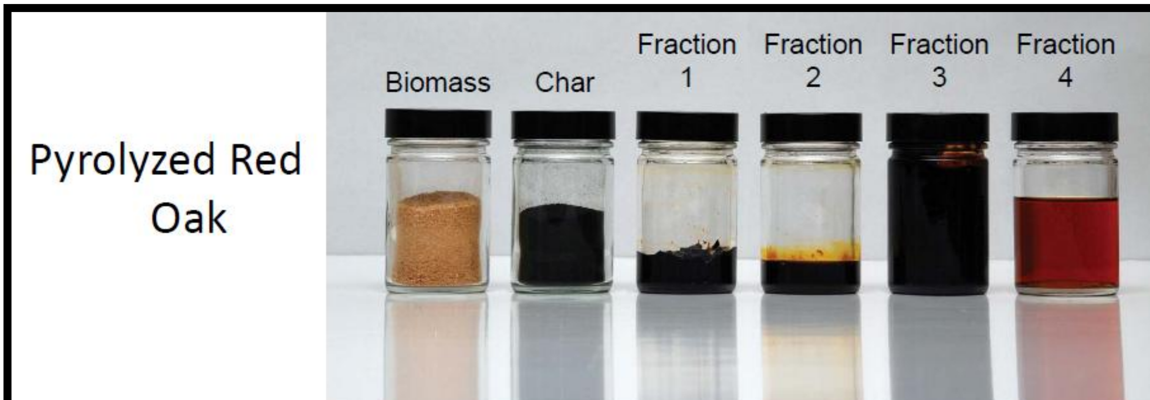
- Heating to approximately 500 °C at a high heat transfer rate,
- carefully controlled reaction temperature with short vapor residence times less than 2 seconds, and
- rapid cooling of the pyrolysis vapors to yield the bio-oil.

Compared with the biochemical platform which can only convert the carbohydrate into bio-fuel like ethanol, the fast pyrolysis process has advantages in using both carbohydrate and lignin. The disadvantages for pyrolysis platform are that the bio-oil is unstable and a corrosive liquid.

The yields from the fast pyrolysis are varied with the biomass feed stock and the reactor conditions (Diebold 1997). Generally, this process generates bio-oil, bio char, and some gas and moisture. The bio char can be used for carbon sequestration as a soil modifier by improving the soil's ability of conserving the fertilizer. The bio-oil (Figure 2) is a liquid fuel containing lignin that can be combusted by some engines or turbines for the electricity generation purpose (Bridgwater 1999). Since the bio-oil can have lignin contents of more than 35% by weight, using bio-oil as an antioxidant in asphalt production could prove to be an economical alternative to conventional methods while being conscious of the environment and increasing the longevity and performance of asphalt pavements.

Figure 2. Bio-oil Sample

Figure 3 illustrates the red oak biomass, bio char and bio-oils obtained from different condensers of the bio-oil pyrolysis pilot plant. Among the bio-oil from different condensers, the major chemicals vary. The electrostatic precipitant (ESP) bio-oil with higher lignin concentration than the other fractions was tested in this study.



	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Yield (wt-% of biomass)	8.2%	5.4%	29.0%	17.9%
Moisture	2.3%	3.2%	2.7%	44.9%
Insoluble fraction	59%	39%	36%	2%
Major chemicals	levoglucosan	phenolics	lignin oligomers	acids

Figure 3. Red oak bio-oil from different condensers

2.2 Asphalt oxidation

Asphalt or flexible pavement is built with several layers to form a layered system with better materials on the top where the intensity of stress is high and inferior materials are at the bottom where the stress intensity is low. The top layer, called the surface course, is made of hot mixture asphalt (HMA). All types of failure or distress can be classified by whether they are structural or functional failures and load associated or non-load associated distresses (Huang 2004). Surface course aging is considered as a non-load associated distress caused by climates/environmental effects (Witczak 1985). Many environmental factors can cause surface course aging damage, such as ozone, UV rays, oxygen, and thermal radiation (Witczak 1985). Oxidative aging causes the asphalt binder to become harder and more brittle (Ruan 2003), which can be derived from two parts, short-term aging and long-term aging.

Most of the short-term aging that occurs in asphalt begins with the blending of the aggregate with asphalt binders. The blending temperature in the asphalt plant primarily controls the oxidative aging rate of the asphalt (Gawel and Baginksa 2004). The short-term aging for the asphalt binder in the mixture continues until the end of the pavement construction. The methods such as warm mix asphalt and cold mix asphalt are the main solutions to reduce the short-term aging via heating and constructing the asphalt mixture at lower temperatures compared with hot mix asphalt.

During the service life, the long-term oxidative aging begins and it occurs at a much slower rate than the rate of aging during the mixing and construction. The brittleness of the asphalt mixture gradually increases due to physic-chemical changes in the binder. Exudation, evaporation, oxidation, and physical aging are all related to asphalt binder aging, while oxidation and physical hardening (steric hardening) are the most important direct consequences. Physical aging is a reversible process, which can produce changes in rheological, electrical and caloric properties, etc., without altering the chemical composition of the material. The oxidation of asphalt binder caused by chemical reactions makes some transformations between the asphalt components. Asphalt oxidation is the main cause of long-term deterioration and eventually results in cracking in asphalt pavements (Domeke 2000, Herrington 1994, Liu 1998). The asphalt can be separated into four generic fractions namely: asphaltenes, polar aromatics, naphthene aromatics, and saturates (Corbett 1969). Each fraction provides different properties. Asphaltenes mainly contributes to the viscosity (hardening effect), and the aromatics and saturates are correlated to the ductility (elastic effect) (Ruan *et al* 2003). Many researchers have compared the fractions of the aged asphalt with ones of the unaged asphalt. It was found that the oxidation of asphalt had an effect on their chemical properties and consequently on the rheological properties. While asphalt is aging, the viscosity increases due to the oxidative conversion of polar aromatics to asphaltenes (Chaquet 1991, Tallafiao 1993, Lin *et al* 1998). This transformation between the components during the oxidations can be described as follows: Aromatics → Resins → Asphaltenes (Corbett 1981, Tallafigo 1993, Petersen 1998). The polymerizations or condensations for the asphaltenes create larger molecules with long chained structures, and affect the hardening of the asphalt (Bagniska 2003). The oxidation causes a great increase in the asphaltenes and a larger amount of asphaltenes with high molecular weight as evident by correlations with the asphalt hardening. This asphalt hardening theory can be used to explain air-blown asphalt phenomena. The antioxidant additive is added to stop or delay the oxidative processes that convert aromatic fractions.

The common asphalt additives such as polymer, rubber, and plastic do not prevent oxidative aging of the binder. The polymer additives can react with the free radicals and then the degradation happens to the additives. The polymer and other rubbers cannot prevent the propagation of the free radical or peroxy radicals, because the polymer degradation can form new free radicals and the cycle repeats (Ouyang *et al* .2006).

The research has been done by adding the chemicals as antioxidant additives. No additive has been successful due to the environmental and economic concerns. Lead diamyldithiocarbamate (LDADC) does have an antioxidant effect, but it contains lead and is not environmentally friendly material. The zinc kailkyldiathiophashate (ZDDP) and zinc diabutyldithiocarbamate (ZDBC) have been tested and proven to have antioxidant effects in asphalt binder (Ouyang *et al* .2006), but their application can be limited by cost consideration.

The bio-oil generated from waste bio-mass at low cost is an environmentally friendly material containing the natural antioxidant lignin. The bio-oil shows potential to be successfully applied as an antioxidant additive in asphalt pavements.

2.3 Lignin as an antioxidant

Lignins can be described as amorphous three-dimensional network polymers comprised of phenylpropane unites that link together in different ways (Goring 1989). The phenylpropane unit is a benzene ring with a tail of three carbons. Figure 4 illustrates one of the possible structures of lignin.

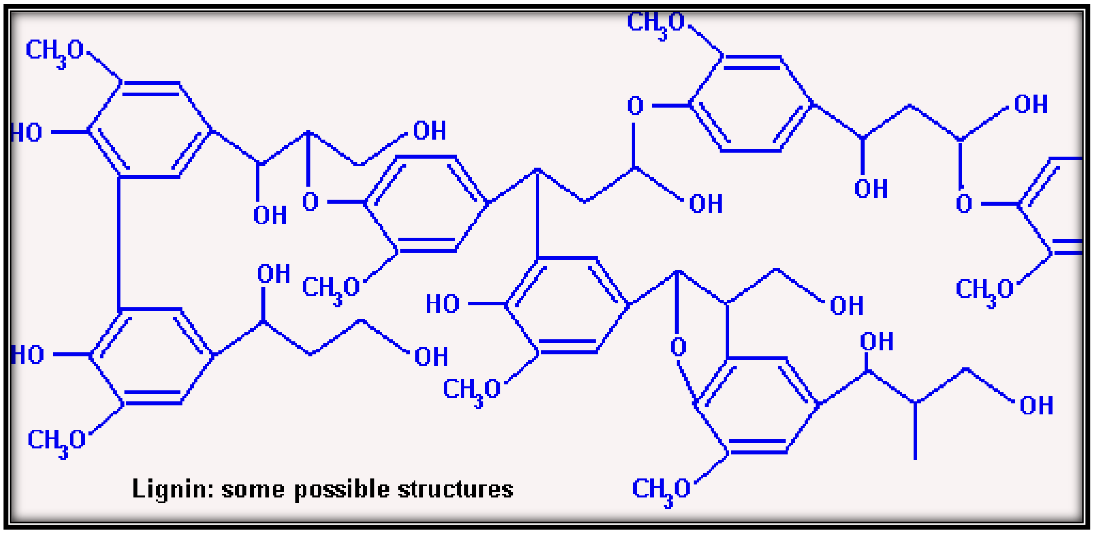


Figure 4. The structure of lignin

Lignins contain several functional chemical groups, such as phenolic, methoxyl, carbonyl and carboxyl. Most antioxidant effects of lignins are provided by the phenolic group capturing and reacting with the free radicals which contain oxygen. Free radicals are known to “attack” stable molecule structures of a substance by “stealing” an electron. Once the “attacked” molecule loses its electron, the substance’s chemical structure then is changed. When the chemical reaction occurs, new materials are formed and the asphalt starts aging with asphaltenes generated. Instead of letting the free radicals, which contain the oxygen ,oxidant the aromatics and convert aromatic molecules to asphaltenes, the lignin first reacts with those free radicals as a reducing agent. This radical scavenging property of lignin makes it recognized as an efficient antioxidant additive.

In the plant kingdom, lignin is present in large amounts in the cell wall of plants, especially in woody tissues. It is known that lignin can have different chemical composition and properties from trees, plants and agricultural crops. Even by operating different extraction methods, the physical and chemical properties are diverse (Dizhbite *et al* .2004).

The lignin used for this study was derived from three feed stocks including: corn stover, oak wood, and switch grass. Since the scavenging ability of lignin depends on the structural features of the lignin, the same amount of lignin with different structures may react with different amounts of free radicals (Dizhbite *et al* .2004). That is to say, the bio-oil with higher amounts of lignin does not have to display better antioxidant effects.

3 EXPERIMENTAL METHODS

3.1 Untreated materials

Three asphalt binders were chosen for this study: two binders from the Federal Highway Administration's (FHWA) Materials Reference Library (MRL), AAM-1 and AAD-1 as well as a locally produced polymer modified asphalt binder (LPMB). AAM-1 is a performance grade (PG) 64-16 West Texas Asphalt, which is less susceptible to oxidative aging. AAD-1 is PG 58-22 California coastal asphalt, which is more susceptible to oxidative aging compared with AAM-1 (Mortazavi and Moulthrop 1993). The LPMB is a styrene-butadiene-styrene (SBS) polymer modified PG 58-22 binder. The chemical compositions (by %) of the two MRL binders are shown in Table 1.

Table 1. Chemical contrast of AAD-1 and AAM-1 (Mortazavi and Moulthrop 1993)

Component Composition	AAD-1	AAM-1	Elemental Composition	AAD-1	AAM-1
Asphaltenes	23.9	9.4	Carbon	81.6	86.8
Polar aromatics	41.3	50.3	Hydrogen	10.8	11.2
Napthene aromatics	25.1	41.9	Oxygen	0.9	0.5
Saturates	8.6	1.9	Sulfur	6.9	1.2

Three experimental bio-oil fractions used for this study are derived from corn stover, oak wood, and switch biomass. All of the bio-oils were obtained from the same source, the Iowa State University's Center for Sustainable Environmental Technologies (CSET). CSET operates a pilot-scale biomass conversion system in the Biomass Energy Conversion Facility (BECON), located in Nevada, Iowa. Bio-oil samples were obtained from different condensers in the bio-oil pilot plant, but only the ESP bio-oils were tested in this study. This is due to the ESP bio-oil having higher lignin concentration and low water content as compared to other bio-oil derived fractions. Table 2 illustrates the characteristics of bio-oil from the different fractions.

Table 2. Characteristics of bio-oil from different condensers

Property	Cond. 1	Cond. 2	Cond. 3	Cond. 4	ESP
Fraction of total oil (wt%)	6	22	37	15	20
pH	-	3.5	2.7	2.5	3.3
Viscosity @40oC (cSt)	Solid	149	2.2	2.6	543
Lignin Content (wt%)	High	32	5.0	2.6	50
Water Content (wt%)	Low	9.3	46	46	3.3
C/H/O Molar Ratio	1/1.2/ 0.5	1/ 1.6/ 0.6	1/ 2.5 / 2	1/ 2.5 /1.5	1/1.5/ 0.5

Among the three ESP bio-oil fractions, the lignin content ranges varied too. Oak wood has the highest lignin fraction by weight. The second highest lignin containing sample is the corn stover bio-oil. The fractionated characteristics of the three ESP bio-oils are shown in Table 3.

Table 3. Characteristics of bio-oil

Property	Corn Stover	Oak Wood	Switch Grass
Lignin (wt%)	82.3	83.9	81.0
Moisture (wt%)	16.8	15.4	17.8
Solid (wt%)	0.6	0.6	1.1
Ash (wt%)	0.3	0.1	0.2

The tall oil fatty acids were used as a second additive in this research. Tall oil fatty acids are a viscous yellow odorous liquid produced as a by-product obtained from the southern kraft pulping process. The crude tall oil is a mixture composed of rosins, fatty acids, sterols, high-molecular alcohols, and other alkyl chain materials. The crude tall oil can then be distilled into tall oil rosin (having the rosin content of 10 - 35%). The further refining provides a tall oil fatty acid (the rosin content of 1 - 10%). Mainly, a tall oil fatty acid and its derivatives are used in the manufacturing of rubber, paper, soaps and detergents, printing inks, metalworking fluids, corrosion inhibitors and plasticizers.

In this research, the tall oil fatty acids (MWV L-5) provided by Mead Westvaco Corporation contain less than 5 percent rosin acid and more than 90 percent fatty acid. Tall oil fatty acids are often used as an emulsion additive in asphalt industry as well. To modify the asphalt binder with polymer, it is used as an emulsifier in the polymerization of synthetic rubber (SBR) polymerization for increasing fluidity. The purpose for applying the tall oil fatty acids additive companying with bio-oil is to modify the asphalt to achieve a he binder at negative low temperatures.

Limestone aggregate, concrete sand and bag house fines were selected to develop a mixture gradation for simple performance testing. The Table 4 gives the gradation of the materials. The normal maximum aggregate size (NMAS) was 12.5 mm.

Table 4. Gradation of the aggregate

Aggregate	Concrete Sand	Bag House Fines	25-mm Limestone	9.5-mm Limestone
% Used	26%	2%	25%	47%
U.S. Sieve, mm	% Passing	% Passing	% Passing	% Passing
25	100	100	100	100
19	100	100	88.7	100
12.5	100	100	56.8	100
9.5	100	100	38.7	97.8
4.75	97.7	100	10.5	31.3
2.36	86	100	2.2	10.66
1.18	67	100	1.1	6.5
0.6	29.6	100	1.1	4.7
0.3	6.6	100	1	2.9
0.15	0.6	100	1	1.6
0.08	0.1	100	1	0.4

3.2 Preparation of bio-oil or tall-oil treatment asphalt binder

A high speed shear mixer was used to prepare the ESP bio-oil modified asphalt, tall oil modified asphalt and bio-oil modified asphalt with tall oil. The binder mixing was conducted at 155^{o}C with a shearing speed of 5000 rotations per minute for one hour.

3.3 Superpave binder aging procedure

The rolling thin film oven (RTFO) was used to simulate the asphalt short-term aging as described in ASTM D2872. The long-term binder aging was addressed by the pressurized aging vessel (PAV) test (ASTM D 6521) by using the residue from the RTFO tests. The short-term aging is described as the aging during the HMA production and construction. The long-term aging represents approximately 12 years of in-service field aging.

3.4 Binder test methods

A dynamic shear rheometer (DSR) was used to test three replicate samples for each binder/bio-oil combination according to ASTM D 7175 (2005), which was used to characterize rheological properties of the binders at high and intermediate temperatures. The complex modulus (G*) and phase angle (δ) were determined with a DSR for the initial binder and residual binder after every asphalt aging treatment (RTFO, PAV). The complex modulus (G*) and phase angle (δ) later were used to find the high and intermediate critical temperatures and the PG ranges.

A bending beam rheometer (BBR) was applied to evaluate the treatment group's susceptibility to thermal cracking at low service temperatures (Roberts *et al*. 1996, The Asphalt Institute 2003). Two key properties, stiffness (S) and change in stiffness (m-value) were recorded according to ASTM 6648 (2001). The BBR test was used to determine the low critical temperatures.

All bio-oil and binder combinations, tall oil modified binder, and bio-oil modified binder with tall oil underwent the asphalt performance testing according to AASHTO M320 for grading an asphalt binder. The grading steps are shown in Figure 5.

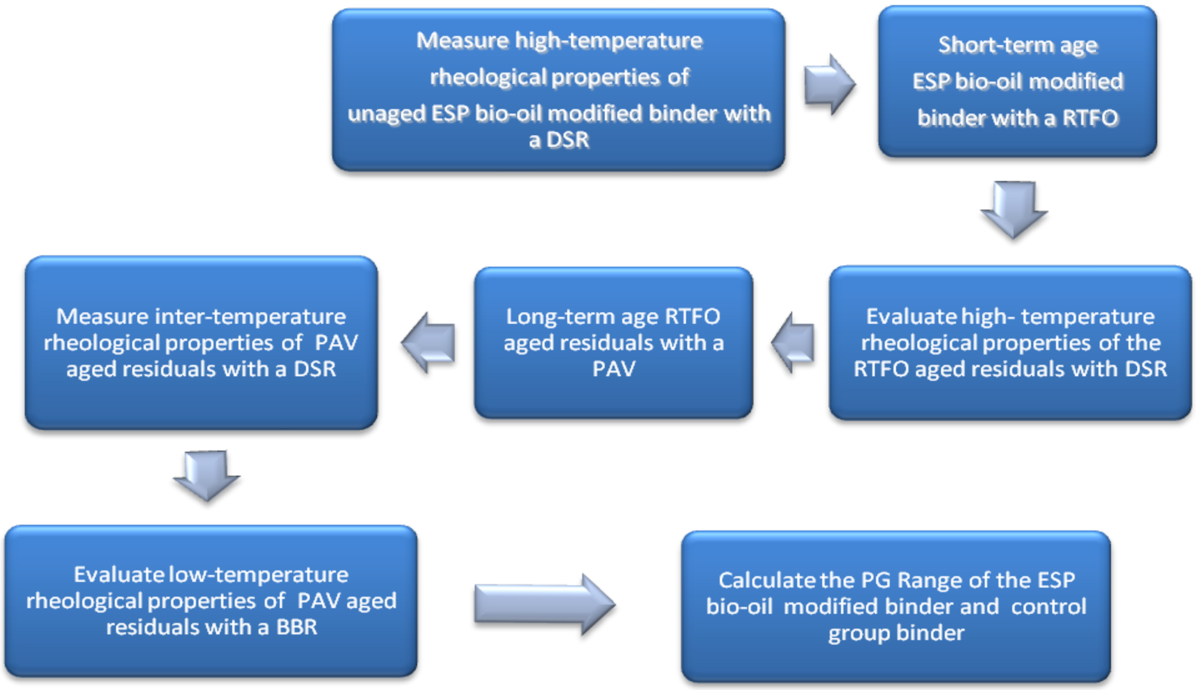


Figure 5. Experiment grading procedures.

3.5 Specimen procurement for Simple Performance Test (SPT)

The Superpave gyratory compacter was used to compact the specimens into the dimension of roughly 150 mm in height by 100 mm in diameter. All the samples were designed to include 7% ± 1% air voids at the same 5.6% optimum binder content using aggregates with the design gradation. The nominal maximum aggregate size of the mixture was all 12.5 mm. Since this research was meant to determine if there was any statistical difference between bio-oil modified binder mixtures with unmodified binder mixtures, having the same gradations for all samples will minimize the variability and influences on experiment outcomes brought by different aggregate sizes. In order to estimate the bio-oil modified binder's effect on mixtures' performances, five replicate samples were prepared to evaluate through the dynamic modulus and flow number tests.

3.6 Simple performance test method

Dynamic modulus testing of the asphalt mixtures (ASTM D3497-79) was used to detect the effect of applying the bio-oil modified binders to the HMA mixtures. The test was conducted at three temperatures (4^{o}C, 21^{o}C, and 37^{o}C) and at nine frequencies ranging from 0.01 Hz to 25 Hz. It took approximately 2.5 hours for each specimen to reach the required test temperature when it was placed in the conditioning chamber. The lowest frequency, 0.01 Hz, is analogous to slow moving traffic at an intersection, where as the highest frequency, 25 Hz, corresponds to the faster moving traffic on a freeway. However, the low frequencies also represent the high temperature conditions of the pavement where as with the higher frequencies represent the lower temperatures. Three linear variable differential transducers (LVDT) were utilized to measure strain of the samples. Dynamic modulus master curves were created from the data of five replicate test samples. The master curves illustrate the dynamic modulus versus the testing frequency at 21^{o}C.

The dynamic modulus testing is a nondestructive test since it is carried out under low strain (<120 μ strain) and for a small number of loading cycles. Each specimen first underwent dynamic modulus testing, and then the samples were used for the flow number test. The flow number test causes permanent deformation to the samples; therefore, they could not be reused.

The flow number testing temperature, 37 ^{o}C, is stipulated by an effective temperature in NCHRP Report 465, which is based on a typical location in the central United States. The stress level used for flow number was 600 kPa (87 psi), which simulates the stress level of the gyratory compactor with a Federal Highway Administration (FHWA) recommended contact stress of 30 kPa (4.4 psi). The vertical deformation was measured by a linear actuator. The data recorded the accumulated strain for every loading cycle.

4 EXPERIMENTAL RESULTS

The average high, intermediate, and low critical temperatures (T_c), as well as the performance grade range for the treatment combinations are listed in Tables 5, 6 and 7. The combinations that resulted in an increase in the PG range are shown in bold italics.

Table 5. Critical temperature grade for the bio-oil and tall oil evaluation

				Average Critical Temperatures (oC)				Grade Range, (°C)	
Asphalt ID	Bio-oil (%)	Tall-oil (%)	Bio-oil (type)	Average Unaged High T_c	Average RTFO Aged High T_c	Average PAV aged Int T_c	Average PAV Aged Low T_c	Unaged High Tc - Low Tc	RTFO Aged Tc - Low Tc
AAD-1	6	0.18	Corn Stover ESP	59.06	63.86	16.49	-24.19	83.25	88.05
	6	0.18	Oakwood ESP	59.64	66.21	19.63	-23.17	82.81	89.38
	6	0.18	Switchgrass ESP	57.93	64.78	18.38	-25.54	83.47	90.32
	3	0.09	Corn Stover ESP	62.16	66.23	18.45	-21.53	83.69	87.76
	3	0.09	Oakwood ESP	61.15	67.01	20.48	-19.39	80.54	86.40
	3	0.09	Switchgrass ESP	59.36	64.27	17.14	-24.54	83.90	88.81
	0	0	Initial binder	62.27	65.38	17.33	-25.18	87.46	90.56
AAM-1	6	0.18	Corn Stover ESP	65.84	67.68	19.77	-12.66	78.50	80.34
	6	0.18	Oakwood ESP	65.88	68.04	19.84	-12.86	78.74	80.90
	6	0.18	Switchgrass ESP	63.27	67.00	19.92	-11.40	74.67	78.41
	3	0.09	Corn Stover ESP	65.50	66.62	19.25	-12.87	78.38	79.49
	3	0.09	Oakwood ESP	65.38	68.15	19.79	-13.29	78.67	81.44
	3	0.09	Switchgrass ESP	64.35	66.54	19.40	-15.11	79.45	81.65
	0	0	Initial binder	67.77	66.68	20.26	-15.06	82.83	81.75
LPMB	**6**	**0.18**	**Corn Stover ESP**	**62.91**	**67.63**	**18.80**	**-21.13**	**84.05**	**88.77**
	6	**0.18**	**Oakwood ESP**	**65.08**	**69.82**	**19.82**	**-20.08**	**85.15**	**89.89**
	6	**0.18**	**Switchgrass ESP**	**62.43**	**68.72**	**19.10**	**-21.42**	**83.85**	**90.14**
	3	0.09	Corn Stover ESP	65.01	68.58	19.18	-19.44	84.45	88.02
	3	**0.09**	**Oakwood ESP**	**65.81**	**69.46**	**19.59**	**-20.48**	**86.29**	**89.94**
	3	**0.09**	**Switchgrass ESP**	**64.01**	**69.49**	**19.02**	**-21.29**	**85.30**	**90.78**
	0	0	Initial binder	65.97	66.74	20.09	-22.01	87.98	88.75

Table 6. Critical temperature grade

Asphalt ID	Bio-oil (%)	Bio-oil (type)	Average Critical Temperatures (oC): Average Unaged High T_c	Average Critical Temperatures (oC): Average RTFO Aged High T_c	Average Critical Temperatures (oC): Average PAV aged Int T_c	Average Critical Temperatures (oC): Average PAV Aged Low T_c	Grade Range (°C): Unaged High Tc - Low Tc	Grade Range (°C): RTFO Aged Tc - Low Tc
AAD-1	9	Corn Stover ESP	58.91	66.04	19.04	-21.77	80.68	87.81
	9	Oakwood ESP	60.23	72.49	22.63	-17	77.23	89.49
	9	Switchgrass ESP	55.78	64.12	18.44	-21.52	77.3	85.65
	6	Corn Stover ESP	60.26	65.8	18.9	-20.06	80.32	85.85
	6	Oakwood ESP	59.8	68.12	19.76	-18.6	78.4	86.72
	6	Switchgrass ESP	57.77	64.06	17.56	-21.84	79.6	85.9
	3	Corn Stover ESP	62.16	66.23	18.45	-21.53	83.69	87.76
	3	Oakwood ESP	61.15	67.01	20.48	-19.39	80.54	86.4
	3	Switchgrass ESP	59.36	64.27	17.14	-24.54	83.9	88.81
	0	Initial binder	62.27	65.38	17.33	-25.18	87.46	90.56
AAM-1	9	Corn Stover ESP	64.96	68.16	19.86	-11.97	76.94	80.13
	9	**Oakwood ESP**	**65.37**	**69.83**	**20.56**	**-13.04**	**78.4**	**82.87**
	9	**Switchgrass ESP**	**62.24**	**67.54**	**19.47**	**-13.98**	**76.22**	**81.52**
	6	Corn Stover ESP	65.26	67.69	19.69	-12.08	77.34	79.77
	6	**Oakwood ESP**	**65.92**	**69.2**	**20.46**	**-12.76**	**78.69**	**81.96**
	6	**Switchgrass ESP**	**63.15**	**66.91**	**19.61**	**-15.39**	**78.53**	**82.3**
	3	Corn Stover ESP	65.56	67.22	19.15	-12.6	78.16	79.82
	3	Oakwood ESP	66.96	67.44	20.25	-12.66	79.62	80.1
	3	Switchgrass ESP	64.27	66.57	19.32	-15.05	79.32	81.61
	0	Initial binder	67.77	66.68	20.26	-15.06	82.83	81.75
LPMB	9	Corn Stover ESP	62.73	68.91	20.31	-17.66	80.39	86.58
	9	Oakwood ESP	63.59	71.07	21.26	-16.66	80.25	87.73
	9	**Switchgrass ESP**	**61.87**	**68.19**	**19.7**	**-22.28**	**84.14**	**90.47**
	6	Corn Stover ESP	64.25	68.29	19.48	-18.04	82.28	86.33
	6	**Oakwood ESP**	**65.36**	**69.74**	**20.44**	**-19.24**	**84.6**	**88.98**
	6	**Switchgrass ESP**	**63.12**	**69.68**	**20.16**	**-20.71**	**83.83**	**90.39**
	3	Corn Stover ESP	65.58	68.97	19.19	-19.47	85.05	88.44
	3	**Oakwood ESP**	**65.46**	**69.52**	**19.26**	**-20.18**	**85.64**	**89.7**
	3	**Switchgrass ESP**	**65.33**	**68.7**	**18.34**	**-21.91**	**87.24**	**90.61**
	0	Initial binder	65.97	66.74	20.09	-22.01	87.98	88.75

Table 7. Critical temperature grade for tall oil evaluation

Asphalt ID	Tall-oil (%)	Average Critical Temperatures (oC) Average Unaged High T_c	Average RTFO Aged High T_c	Average PAV aged Int T_c	Average PAV Aged Low T_c	Grade Range, (^oC) Unaged High Tc - Low Tc	RTFO Aged Tc - Low Tc
	0.36	60.35	62.58	16.12	-23.53	83.88	86.11
	0.36	60.04	62.61	16.10	-24.61	84.65	87.22
	0.36	60.37	62.84	16.91	-23.20	83.57	86.04
AAD-1	0.18	60.34	63.55	17.07	-21.11	81.45	84.66
	0.18	60.43	63.26	17.10	-22.82	83.25	86.08
	0.18	60.24	63.19	17.00	-22.76	83.00	85.95
	0	62.27	65.38	17.33	-25.18	87.45	90.56
	0.36	65.68	65.61	17.88	-14.69	80.37	80.30
	0.36	65.01	65.67	18.95	-14.26	79.27	79.93
	0.36	65.54	65.59	18.93	-14.00	79.54	79.59
AAM-1	0.18	66.88	66.47	19.18	-14.55	81.43	81.02
	0.18	66.41	66.82	19.06	-13.15	79.56	79.97
	0.18	66.37	66.76	18.75	-14.52	80.89	81.28
	0	67.77	66.68	20.26	-15.06	82.83	81.74
	0.36	**66.54**	**68.08**	**17.91**	**-23.32**	**89.86**	**91.40**
	0.36	**67.01**	**68.19**	**17.74**	**-22.65**	**89.66**	**90.84**
	0.36	**66.85**	**68.26**	**18.09**	**-22.98**	**89.83**	**91.24**
LPMB	**0.18**	**66.93**	**68.80**	**18.10**	**-22.50**	**89.43**	**91.30**
	0.18	**66.73**	**68.78**	**18.31**	**-23.35**	**90.08**	**92.13**
	0.18	**66.94**	**68.85**	**17.95**	**-23.98**	**90.92**	**92.83**
	0	65.97	66.74	20.09	-22.01	87.98	88.75

5 STATISTICAL ANALYSIS

5.1 Introduction

According to the Superpave binder specification, the binder's physical properties are related directly to field performance and can be characterized by three critical temperatures: the high critical temperature, the intermediate critical temperature, and the low critical cracking temperature. The performance grade (PG) describing the asphalt application range depending upon the climate is determined by using the high critical temperature to the critical low temperature. In order to evaluate the influence of treatment on the rheological properties of the binders, the neat binders' high, intermediate, and low critical temperatures, as well as the performance grade are set as the benchmarks to be compared with the corresponding values obtained from the experiment treated binders. All the critical temperatures are the experimental responses and there are three treatment factors that the researchers are interested in: the bio-oil types, the fractions of the bio-oil and the tall oil. The factorial experiment design is applied in this project as it allows the researcher to investigate the effect of each factor individually, as well as the interaction of multiple factors together.

The analysis of variance (ANOVA) (Neter, Wasserman, and Kunter, 1990) method was used to evaluate the treatment effect by comparing the critical temperature means. The ANOVA technique measures the variations among the experimental data by computing the sums of squares (SS). The variation from one factor level to the next is counted as the factor sum of squares (SS (factor)). The variation within the samples is measured by the error sum of squares (SS(error)). Each of these SS has corresponding degrees of freedom (DF), in which is the SS is divided by to produce a mean square, MS. The ratio of MS (factor) to MS (error) produces an F-statistic that is used to test the hypothesis for the presence of statistically equal means. If the F-value is large enough (significant), the P-value should be small, then a conclusion can be made that the means are not all the same, which implies that the factor of interest does have a significant effect on the experimental response. If the ANOVA procedure concludes that the critical temperature means are not all the same, a follow-up analysis called a multiple comparisons test is conducted to determine which of the means are unequal. There are a variety of methods to test differences in group means (multiple comparisons). The Each Pair, student's t-test that computes individual pairwise comparisons using Student's t-test is least conservative and would result in a largely increased chance of committing a type I error, for this reason, in this research, it is not used in the large number of treatment groups means difference analysis. All Pairs, Tukey HSD test is used to evaluate the means difference due to its larger least squares difference (LSD) intervals compared to the student's t pairwise LSDs. The Tukey honest significant difference is more conservative and accurate with large amounts of comparisons. In this way, the best treatment can be identified.

Not only the statistical analysis methods were used to evaluate the experiment results, but also the Fit Models containing statistically significant factors were formed by applying JMP software. The Fit Model is set to create an asphalt addition formula function for revealing the relationship between asphalt additives with the asphalt binder and predicting other possible treatments' experimental outcomes. The effect tests in the Fit Model are applied to detect significant factors that affect the experimental response. The fit of the models was evaluated by the determination coefficient (R square). Additionally, the Fit models including all experimental data were used to predict the experimental values so that the response surface could be generated.

The concepts of prediction profiler and graphs of contour profiler from Response Surface Methodology (RSM) are applied to find the optimal response (the most desired experimental outcomes) within specified ranges of the factors (the manipulated experimental variables). In the asphalt industry, the desired experimental outcomes are trying to maximize high critical performance temperatures, minimize low critical performance temperatures, or widen the range of the performance grade for the asphalt binder. For the asphalt mixtures, the desired results are complex, depending on other considerations.

The JMP statistical software was used to conduct all the calculations, graphing and comparisons.

The performances represented by the dynamic modulus and flow number were evaluated by applying ANOVA. The 9% oak wood bio-oil treatment binders AAM-1, AAD-1 and LPMB are included in the separate analysis for the dynamic modulus and flow number tests. Those comparisons with the untreated asphalt binder are used to determine if the bio-oil derived from oak wood provides any significant benefit to the asphalt mixture mechanical properties.

5.2 Binder performance grades

5.2.1 Bio-oil modification effect evaluation

The bio-oils derived from corn stover, switch grass and oak wood were blended with binders AAM-1, AAD-1, and LPMB in three different percentages (by weight) to evaluate the bio-oil modification treatment effect.

5.2.1.1 Unaged high critical temperature for the AAD-1 binder

This two-way factorial experiment was designed to detect the difference in means of the unaged high critical temperatures for every treatment combination blends. Binder AAD-1 is the experimental unit. The unaged high critical temperatures are measured as the experimental responses. The two conditions are:

- **Factor A**- bio-oil type: Corn Stover, Switch Grass, and Oak Wood.
- **Factor B**- bio-oil fraction by weight: 0%, 3%, 6%, and 9%.

There are 12 treatment combinations. Asphalt AAD-1 was randomly assigned to those treatment combinations and blended with the bio-oil. Each blend was tested in triplicate to provide a good measure of random error. Figure 18 presents the experimental results. The addition of all types of bio-oil at all percentages decreases the unaged critical temperature. Generally, the more bio-oil added, the greater the decrease in critical temperature, except the bump up at the 9% Oak wood bio-oil treatment combination. In Figure 6, the lack of parallelism for the lines indicates possible interactions between the bio-oil type and the amount of the bio-oil. The modified AAD-1 binder behaves differently with different amount of bio-oil.

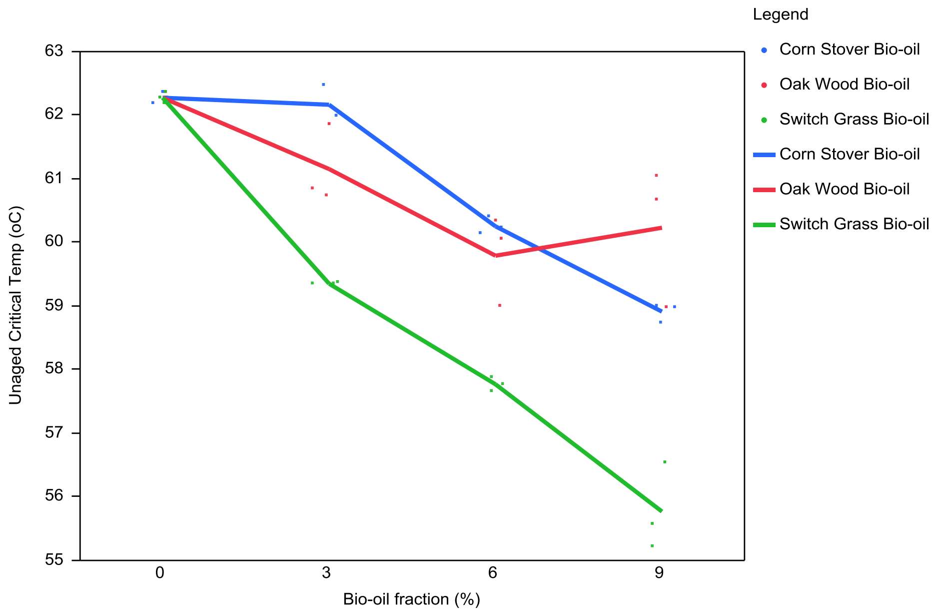


Figure 6. Unaged Critical Temp for AAD-1 vs. Bio-oil fraction (%) by Bio-oil types

The effect tests for the model that includes three structure factors: Factor A (Bio-oil types), Factor B (Bio-oil fraction) and Interaction (Bio-oil types*Bio-oil faction) are shown in Table 8. Type I error (α) of 0.05 was used for all statistical analysis and effect tests. An α of 0.05 states that there is a five percent chance of rejecting the null hypothesis when it is in fact true.

Table 8. Model ANOVA and effect tests for AAD-1 DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	137.02	12.46	55.09	<.0001	**Bio-oil type**	2	34.87	77.11	<.0001
Error	24	5.43	0.23			**Bio-oil fraction**	3	83.00	122.35	<.0001
C. Total	35	142.45				**Interaction**	6	19.16	14.12	<.0001

Four null hypotheses were tested including:

- There are no differences among the response means of 12 treatment combinations.
- The bio-oil type's effects are all zero.
- The bio-oil fraction effects are all zero.
- The interaction effects (bio-oil type*bio-oil fraction) are all zero.

The ANOVA table produces the F-statistics with a corresponding p-value, which are shown in Table 8. All of the null hypothesizes can be rejected, since every p-value is less than a (0.05). Therefore, there are statistically significant differences among some of the treatment sample means. The bio-oil type factor, the bio-oil fraction factor and even the interaction term are statistically significant in the mode. This is consistent with the plot in Figure 18 showing that the interaction between the bio-oil type and the bio-oil fraction. All of the factors and the interaction term have significant effect on the experiment response. This Fit Model with an R square equaling to 94% is useful in explaining the variation among the unaged critical temperatures.

Furthermore, the HSD (Tukey-Kramer) multiple comparisons procedure was used to determine which of the treatment means differ significantly. The comparison results are shown in the following Tables 9, 10 and 11.

Table 9 shows the traditional letter-coded report where means not sharing the same letter are significantly different. Among the bio-oil type levels, the unaged critical temperature for the AAD-1 binder modified by adding switch grass bio-oil is significantly lower than the modified binder by adding corn stover or oak wood bio-oil. And there is no difference between the treatment effect by adding corn stover bio-oil or oak wood bio-oil.

Table 9. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level			Mean
Corn Stover Bio-oil	A		60.90
Oak Wood Bio-oil	A		60.86
Switch Grass Bio-oil		B	58.79

Levels not connected by same letter are significantly different.

As shown in Table 10, all of the bio-oil fraction levels are marked by different letters, which implies that generally the bio-oil treatment does make a difference, since the 0% AAD-1 (neat binder) has a unique letter, and adding bio-oil in different dosages makes the unaged critical temperature changing significantly.

Table 10. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level					Mean
0	A				62.27
3%		B			60.89
6%			C		59.28
9%				D	58.30

Levels not connected by same letter are significantly

The Table 11 lists the ranked difference for every treatment combination from the highest critical temperature means to the lowest ones. Generally, the addition of all types of the bio-oil in the AAD-1 binder at all percentages affects the unaged critical high temperature. Although, adding the corn stover or oak wood bio-oil by 3 % may not decrease the critical temperature significantly compared with the neat AAD-1 binder, the more bio-oil added, the greater the decrease in the critical high temperature. The 9% switch grass treatment created the softest modified AAD-1 binder at unaged stage.

Table 11. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level						Mean
Neat AAD-1 Binder	A					62.27
Corn Stover Bio-oil,3	A					62.16
Oak Wood Bio-oil,3	A	B				61.15
Corn Stover Bio-oil,6		B	C			60.26
Oak Wood Bio-oil,9		B	C			60.23
Oak Wood Bio-oil,6		B	C			59.80
Switch Grass Bio-oil,3			C			59.36
Corn Stover Bio-oil,9			C	D		58.91
Switch Grass Bio-oil,6				D		57.77
Switch Grass Bio-oil,9					E	55.78

Levels not connected by same letter are significantly different.

5.2.1.2 Unaged high critical temperature for the AAM-1 binder

A similar experiment as the one testing the AAD-1 binder was conducted using the AAM-1 binder. The experimental data were analyzed using the same approach followed with the AAD-1 blends. Figure 7 illustrates the results. For all levels of bio-oil type as the amount of bio-oil increases, the mean unaged critical temperature decreases at different changing rates.

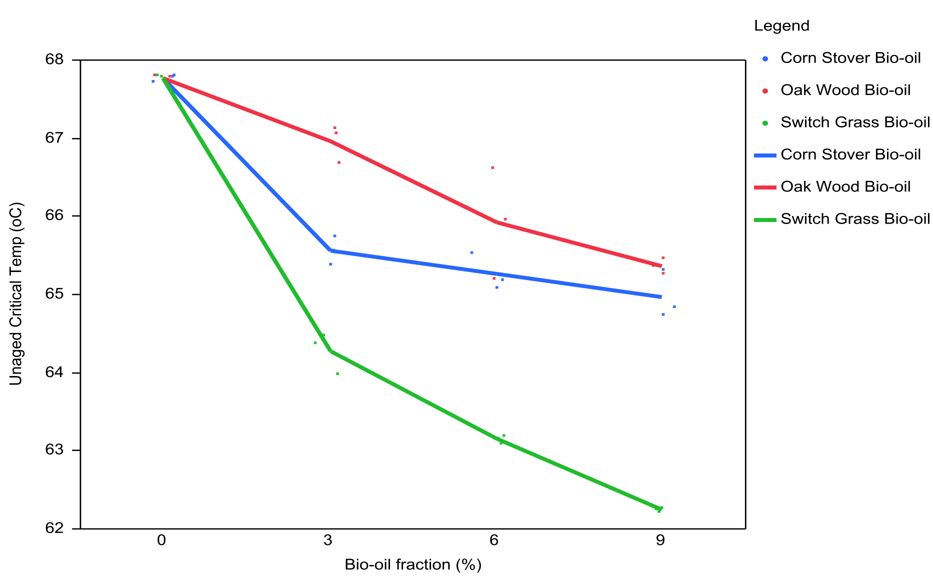


Figure 7. Unaged Critical Temp for AAM-1 vs. Bio-oil fraction (%) by Bio-oil types

The ANOVA and effect tests (Table 12) show that the model including the two factors and the interaction term is efficient to explain the variations, because the F ratios are big enough (significant) to let the p-values smaller than 0.05. The R square is equal to 98%. The conclusion towards the interaction term that is tested to be significant coincides with the unparallel lines shown in Figure 7.

Table 12. Model ANOVA and effect tests for AAM-1 DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	106.94	9.72	140.36	<.0001	**Bio-oil type**	2	29.31	211.55	<.0001
Error	24	1.66	0.07			**Bio-oil fraction**	3	66.19	318.54	<.0001
C. Total	35	108.60				**Interaction**	6	11.44	27.54	<.0001

Among the levels of the bio-oil types, three bio-oils are detected to affect the unaged critical temperatures and are significantly different. The discrepancies among the means of critical temperatures are attributed to treatments by adding different bio-oil, but not the experimental error. The switch grass bio-oil softens the AAM-1 binder more extensively than the other two types, which is shown in Table13.

Table 13. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				**Mean**
Oak Wood Bio-oil	A			66.50
Corn Stover Bio-oil		B		65.89
Switch Grass Bio-oil			C	64.36

Levels not connected by same letter are significantly different.

In order to evaluate the bio-oil fraction effect, the Tukey HSD testing was conducted. The results listed in Table 14 indicate the more bio-oil added, the greater the softening effect on AAM-1 binder.

Table 14. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level					Mean
0%	A				67.77
3%		B			65.60
6%			C		64.78
9%				D	64.19

Levels not connected by same letter are significantly different.

Tukey HSD testing letter-coded report (Table 15) ranks the softening effect for each treatment combination. All of bio-oil additives produce significantly softer unaged binder than the neat ones, due to the unique letter signed to the pure AAM-1 binder. Again, the 9% switch grass treatment created the softest modified AAM-1 binder at an unaged stage.

Table 15. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level								Mean
Neat AAM-1 Binder	A							67.77
Oak Wood Bio-oil,3		B						66.96
Oak Wood Bio-oil,6			C					65.92
Corn Stover Bio-oil,3			C	D				65.56
Oak Wood Bio-oil,9			C	D				65.37
Corn Stover Bio-oil,6			C	D				65.26
Corn Stover Bio-oil,9				D	E			64.96
Switch Grass Bio-oil,3					E			64.27
Switch Grass Bio-oil,6						F		63.15
Switch Grass Bio-oil,9							G	62.24

Levels not connected by same letter are significantly different.

5.2.1.3 Unaged high critical temperature for the LPMB binder

The LPMB binder is the local polymer modified binder. The same factorial experiment was carried out. In Figure 8, the data are presented. So as seen with AAD-1 and AAM-1, the more bio-oil added in spite of bio-oil types, the greater the softening effect and therefore the greater the decrease in critical temperature. Few variations in testing results among the bio-oil types at 3% bio-oil treatment were observed. Also the means of the 3% bio-oil treatment may not be different from the means of neat binder.

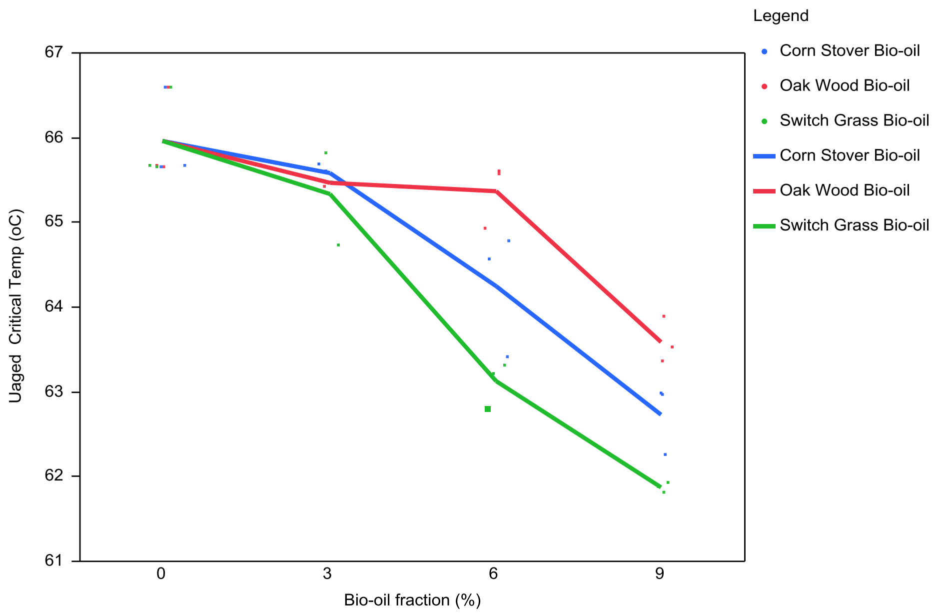


Figure 8. Unaged Critical Temp for LPMB vs. Bio-oil fraction (%) by Bio-oil types

The model ANOVA (Table 16) confirms the two factors with the interaction term model is useful. All four null hypotheses are the same as the tests in analyzing AAD-1 binder were tested and the corresponding F-ratios and p-values are presented in Table 16. The small p-value rejects all null hypotheses, indicating that there are some significant differences among the treatment combinations and all of the factors and the interaction term have significant effect on the experiment response. The Fit model has R square equaling 94%.

Table 16. Model ANOVA and effect tests for LPMB DSR data

Analysis of variance

Source	DF	Sum Squares	Mean Square	F Ratio	Prob > F
Model	11	68.25	6.20	34.32	<.0001
Error	24	4.34	0.18		
C. Total	35	72.59			

Effect tests

Source	DF	Sum Squares	F Ratio	Prob > F
Bio-oil type	2	6.28	17.38	<.0001
Bio-oil fraction	3	56.21	103.65	<.0001
Interaction	6	5.76	5.31	0.0013

As the Tukey HSD testing report shows in Table 17, all bio-oils behave differently when added to the LPMB binder. As outcomes of the tests on binders AAD-1 and AAM-1, the switch grass bio-oil modification makes the unaged binder significantly softer than any other treatment combinations.

Table 17. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				Mean
Oak Wood Bio-oil	A			65.09
Corn Stover Bio-oil		B		64.63
Switch Grass Bio-oil			C	64.07

Levels not connected by same letter are significantly different.

The same letter "A" sign to 0% and 3% bio-oil fraction levels in Table 18 implies that no significant effect can be detected when the 3% bio-oil are added into LPMB binder. The other fraction levels reduce the unaged critical temperature significantly when comparing with the neat binder.

Table 18. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
0	A			65.97
3%	A			65.46
6%		B		64.24
9%			C	62.73

Levels not connected by same letter are significantly different.

As shown in Table 19, not all treatment combinations possess a lower unaged high critical temperature. All of the 3% bio-oil treatments have the same letter as the neat LPMB binder. No treatments can be confirmed to produce a significant lower critical temperature for unaged binder as analyzed by the Tukey HSD tests, if all combinations are taken in consideration at the same time. Paired t-tests could be applied to make the comparison between two treatment means to find the difference.

Table 19. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level						Mean
Neat LPMB Binder	A					65.97
Corn Stover Bio-oil,3	A					65.58
Oak Wood Bio-oil,3	A	B				65.46
Oak Wood Bio-oil,6	A	B				65.36
Switch Grass Bio-oil,3	A	B				65.33
Corn Stover Bio-oil,6		B	C			64.25
Oak Wood Bio-oil,9			C	D		63.58
Switch Grass Bio-oil,6			C	D		63.12
Corn Stover Bio-oil,9				D	E	62.73
Switch Grass Bio-oil,9					E	61.87

Levels not connected by same letter are significantly different.

5.2.1.4 RTFO aged high critical temperature for the AAD-1 binder

The RTFO aged critical high temperatures for the AAD-1 binder combinations were analyzed similar to the unaged critical high temperatures. The experimental design was exactly the same as the unaged blends. A larger RTFO high critical temperature benefits the asphalt mixture to resist rutting. The RTFO critical high temperature indirectly represents a measure of the high temperature stiffness or rutting resistance of the asphalt binder (Bahia and Anderson 1995, The Asphalt Institute 2003). The oak wood and corn stover bio-oil increase the RTFO critical temperature considerably, which is not noticed for adding switch grass bio-oil in Figure 9. The effect of the treatment varies with the different bio-oils. The treatment effect evaluation by ANOVA model is shown in Table 20.

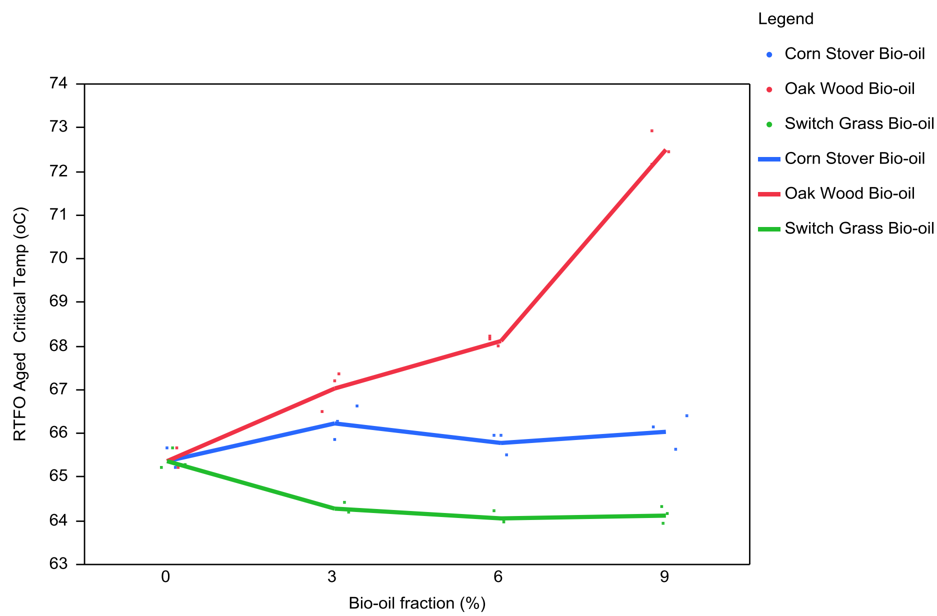


Figure 9. RTFO Critical Temp for AAD-1 vs. Bio-oil fraction (%) by Bio-oil types

All factors including the interaction term are significant. Every F-statistic listed in Table 20 is big enough to reject the null hypotheses. With an R square valve of 99%, this Fit model can be used to explain 99% of the variations. It is confirmed that the treatment effect is significant.

Table 20. Model ANOVA and effect tests for AAD-1 DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	175.96	16.00	195.24	<.0001	**Bio-oil type**	2	88.08	537.55	<.0001
Error	24	1.97	0.08			**Bio-oil fraction**	3	24.01	97.67	<.0001
C. Total	35	177.92				**Interaction**	6	63.87	129.92	<.0001

Tukey HSD test outcomes (Table 21) demonstrate that the different bio-oils behave significantly different when added into the AAD-1 binder. Generally, with the same amount of additive, utilizing oak wood bio-oil results the higher RTFO critical temperature than the other two, while the switch grass bio-oil modification processes the softest binder relatively.

Table 21. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				Mean
Oak Wood Bio-oil	A			68.25
Corn Stover Bio-oil		B		65.86
Switch Grass Bio-oil			C	64.46

Levels not connected by same letter are significantly different.

Table 22 shows that treating the AAD-1 binder by adding bio-oil in different amount makes some significant difference from the neat binder. No significant difference is observed between 3% and 6% dosages. But the 9% bio-oil treatment increases the RTFO critical temperature significantly, more than using other bio-oils. The linear relationship conclusion described as “the more bio-oil added, the greater the high temperature” cannot be addressed for AAD-1 binder in spite of the bio-oil types.

Table 22. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
9%	A			67.55
6%		B		65.99
3%		B		65.84
0			C	65.38

Levels not connected by same letter are significantly different.

Illustrated in Table 23, the switch grass bio-oil treatments are detected to have significant adverse effects on the RTFO critical temperatures. Tukey HSD testing discloses that the high percent level of oak wood bio-oil produces the larger high critical temperature than treatments adding corn stover bio-oil.

Table 23. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level							Mean
Oak Wood Bio-oil,9	A						72.49
Oak Wood Bio-oil,6		B					68.12
Oak Wood Bio-oil,3			C				67.01
Corn Stover Bio-oil,3			C	D			66.23
Corn Stover Bio-oil,9				D	E		66.04
Corn Stover Bio-oil,6				D	E		65.80
Neat AAD-1 Binder					E		65.38
Switch Grass Bio-oil,3						F	64.27
Switch Grass Bio-oil,9						F	64.12
Switch Grass Bio-oil,6						F	64.06

Levels not connected by same letter are significantly different.

5.2.1.5 RTFO aged high critical temperature for the AAM-1 binder

An obvious positive relationship between the RTFO aged high critical temperature and the bio-oil fraction for all bio-oil types is displayed in Figure 10. The general conclusion "the more bio-oil added, the greater the stiffening effect, and therefore the greater the increase in critical high temperature" is correct for the AAM-1 binder for most situations.

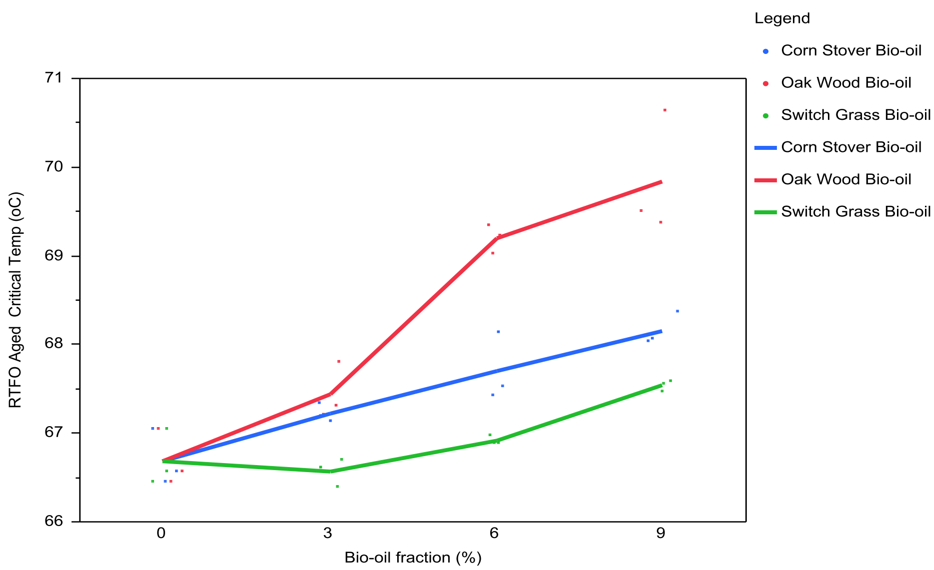


Figure 10. RTFO Critical Temp for AAM-1 vs. Bio-oil fraction (%) by Bio-oil types

The Fit model with two factors and interaction term was formed to analyze the bio-oil modification in binder AAM-1. Table 24 presents the ANOVA model and the effect test results. Significant differences were found with both factors and their interaction term, and the model with 94.1% R square is proved to be useful. Some treatment effects are significantly different.

Table 24. Model ANOVA and effect tests for AAM-1 DSR data

Analysis of variance						Effect tests				
Source	DF	Sum Squares	Mean Square	F Ratio	Prob > F	Source	DF	Sum Squares	F Ratio	Prob > F
Model	11	36.22	3.29	35.06	<.0001	Bio-oil type	2	11.37	60.52	<.0001
Error	24	2.25	0.09			Bio-oil fraction	3	18.44	65.44	<.0001
C. Total	35	38.48				Interaction	6	6.42	11.39	<.0001

The Tukey HSD testing discloses that the oak wood bio-oil modification could result a higher RTFO critical temperature than the other bio-oil if it is used with the AAM-1 binder. The corn stover bio-oil had a better testing outcome than the switch grass bio-oil.

Table 25. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				Mean
Oak Wood Bio-oil	A			68.29
Corn Stover Bio-oil		B		67.44
Switch Grass Bio-oil			C	66.93

Levels not connected by same letter are significantly different.

The same letter "C" connecting both level 3% and neat binder in Table 26 implies that these two levels are not significantly different. This Tukey HSD result plot is shown in Figure 10.

With the exception of the oak wood bio-oil treated at 9% or 6% dosage that exhibited a significant increase in the high critical temperature, the other treatment combinations do not really result in different critical temperatures compared to the neat AAM-1 binder in Table 27.

Table 26. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
9%	A			68.51
6%		B		67.94
3%			C	67.07
0			C	66.68

Levels not connected by same letter are significantly different.

Table 27. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level						Mean
Oak Wood Bio-oil,9	A					69.83
Oak Wood Bio-oil,6	A					69.20
Corn Stover Bio-oil,9		B				68.16
Corn Stover Bio-oil,6		B	C			67.69
Switch Grass Bio-oil,9		B	C	D		67.54
Oak Wood Bio-oil,3		B	C	D	E	67.44
Corn Stover Bio-oil,3			C	D	E	67.22
Switch Grass Bio-oil,6			C	D	E	66.91
Neat AAM-1 Binder				D	E	66.68
Switch Grass Bio-oil,3					E	66.57

Levels not connected by same letter are significantly different.

5.2.1.6 RTFO aged high critical temperature for the LPMB binder

The increments in RTFO critical temperatures are clearly illustrated in the Figure 11 for the LPMB binder combinations. The benefits via bio-oil modification are obvious for all bio-oil types at all percentages, but the trend and the changing rates are not easy to predicate. The difference between the bio-oil type levels may not be found, as well as the difference between the fraction levels.

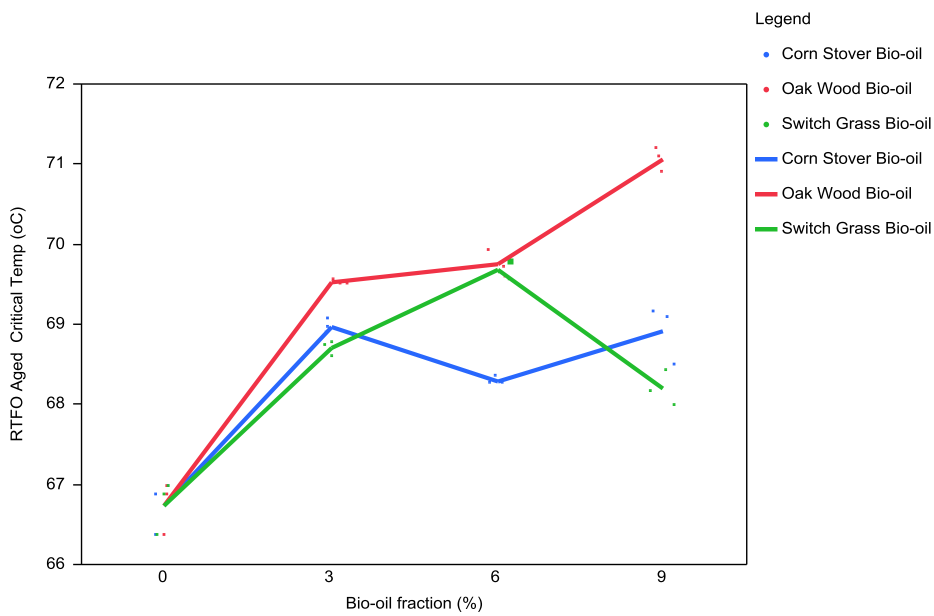


Figure 11. RTFO Critical Temp for LPMB vs. Bio-oil fraction (%) by Bio-oil types

The model is useful with a 98.1% R square. Some significant differences within the treatment means were indicated. Effect tests confirm all factors and the interaction term are significant with Table 28 illustrating the results.

Table 28. Model ANOVA and effect tests for LPMB DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	60.88	5.53	113.88	<.0001	**Bio-oil type**	2	7.87	80.99	<.0001
Error	24	1.17	0.05			**Bio-oil fraction**	3	42.37	290.64	<.0001
C. Total	35	62.04				**Interaction**	6	10.63	36.46	<.0001

For the bio-oil type factor, the corn stover and oak wood bio-oil levels are not significantly different in the means of RTFO critical temperatures shown in Table 29. However, both of the levels have a significant higher temperature means than switch grass level.

The positive effect is obvious but the trend and relationship between the bio-oil fractions and the experimental responses may not be palpable. Table 30 shows that all fraction levels are significantly different from the neat binder, which demonstrates that modified LPMB binder generally has a higher RTFO critical temperature by adding 3%, 6%, and 9%bio-oil. But significant differences cannot be detected among the bio-oil fractions.

Table 29. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level			Mean
Corn Stover Bio-oil	A		60.90
Oak Wood Bio-oil	A		60.86
Switch Grass Bio-oil		B	58.79

Levels not connected by same letter are significantly different.

Table 30. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
9%	A			69.39
6%	A	B		69.24
3%		B		69.07
0			C	66.74

Levels not connected by same letter are significantly different.

Table 31. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level								Mean
Oak Wood Bio-oil,9	A							71.07
Oak Wood Bio-oil,6		B						69.74
Switch Grass Bio-oil,6		B						69.68
Oak Wood Bio-oil,3		B	C					69.52
Corn Stover Bio-oil,3			C	D				68.97
Corn Stover Bio-oil,9			C	D	E			68.91
Switch Grass Bio-oil,3				D	E	F		68.70
Corn Stover Bio-oil,6					E	F		68.29
Switch Grass Bio-oil,9						F		68.19
Neat LPMB Binder							G	66.74

Levels not connected by same letter are significantly different.

The Tukey HSD multiple comparison testing (Table 31) reveals all treatments combinations result in significantly higher RTFO aged critical high temperatures. The application of bio-oil from all three sources at all tested percentages increases the rutting resistance of the binder Table 31.

5.2.1.7 BBR critical low temperature for the AAD-1 binder

As previously mentioned, a lower BBR critical temperature is beneficial in cold climates. Superpave specification uses the BBR critical low temperature to address the asphalt properties for preventing tthermal cracking. A smaller low critical temperature (negative number) is better.

The addition of corn stover, oak wood and switch grass bio-oil at all tested percentages to binder AAD-1 increases the critical low temperature. The trends for critical low temperature are changing similarly for each bio-oil type when increasing the dosage, except the corn stover bio-oil driving down the critical temperature when increasing the fraction to a higher percentage (9%).

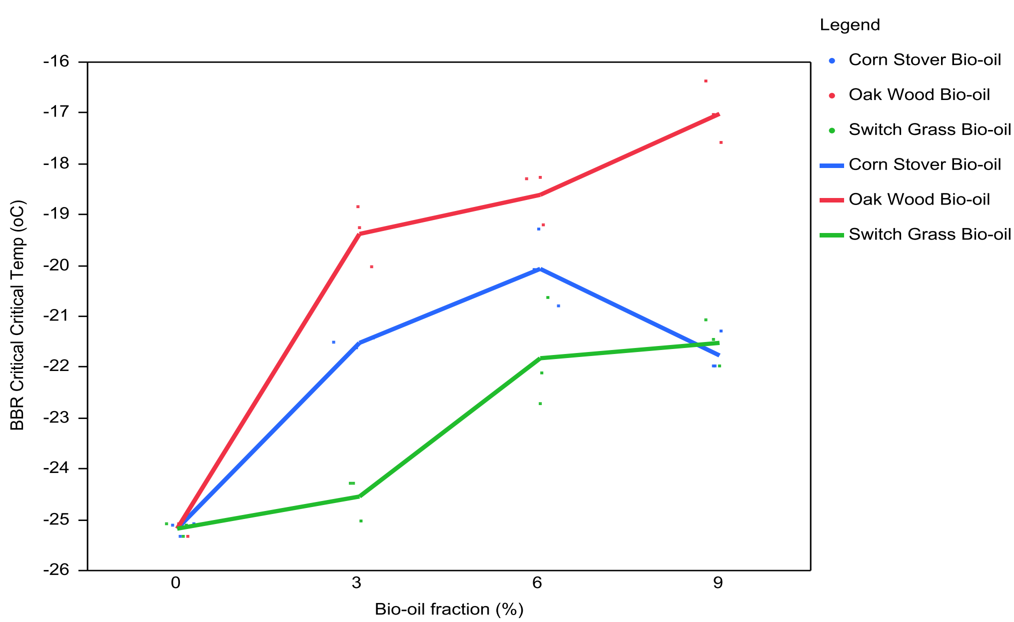


Figure 12. Low Critical Temp for AAD-1 vs. Bio-oil fraction (%) by Bio-oil types

The F-statistic and p-values shown in Table 32 reject the null hypotheses. The Fit-model with a 97% R square is efficient to explain 97% variations. All factors including the interaction term are significant.

Table 32. Model ANOVA and effect tests for AAD-1 DSR data

Analysis of variance						Effect tests				
Source	DF	Sum Squares	Mean Square	F Ratio	Prob > F	Source	DF	Sum Squares	F Ratio	Prob > F
Model	11	251.87	22.90	82.87	<.0001	Bio-oil type	2	64.28	116.33	<.0001
Error	24	6.63	0.28			Bio-oil fraction	3	152.77	184.30	<.0001
C. Total	35	258.50				Interaction	6	34.82	21.00	<.0001

Each bio-oil type level was tested to be significantly different from each other. The switch grass provides the lowest critical cracking temperature, followed by the oak wood bio-oil treatment. The corn stover modification leads to the highest critical cracking temperature.

Table 33. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				Mean
Oak Wood Bio-oil	A			-20.04
Corn Stover Bio-oil		B		-22.14
Switch Grass Bio-oil			C	-23.27

Levels not connected by same letter are significantly different.

The significant difference between the 9% and 6% dosage application cannot be detect (Table 34), which would be explain by the critical temperature dropping for corn stover treatment at 9% level, as shown in Figure 12.

Table 34. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
9%	A			-20.10
6%	A			-20.17
3%		B		-21.82
0			C	-25.18

Levels not connected by same letter are significantly different.

Table 35 illustrates the results of the Turkey HSD tests. All treatments except 3% switch grass, proved to significantly raise the critical low temperature, which decreases the asphalt low temperature cracking resistance. No significant difference can be detected between the neat AAD-1 binder and the 3% switch grass modified binder indicates that adding a small amount of switch grass bio-oil has limited adverse effects on the binder when subject to the low (negative) temperature environment.

Table 35. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level						Mean
Oak Wood Bio-oil,9	A					-17.00
Oak Wood Bio-oil,6		B				-18.60
Oak Wood Bio-oil,3		B				-19.39
Corn Stover Bio-oil,6		B	C			-20.07
Switch Grass Bio-oil,9			C	D		-21.52
Corn Stover Bio-oil,3			C	D		-21.53
Corn Stover Bio-oil,9				D		-21.77
Switch Grass Bio-oil,6				D		-21.84
Switch Grass Bio-oil,3					E	-24.54
Neat AAD-1 Binder					E	-25.18

Levels not connected by same letter are significantly different.

5.2.1.8 BBR critical low temperature for the AAM-1 binder

The AAM-1 binder behaves differently depending upon the type of bio-oil added. When the AAM-1 binder is blended with corn stover or oak wood bio-oil, the low critical temperature responsive bumps up to certain level and is relatively steady, even though the treatment dosage varies. On the contrary, the critical temperature of switch grass bio-oil modified binder changes slowly with the changing of the treatment dosage.

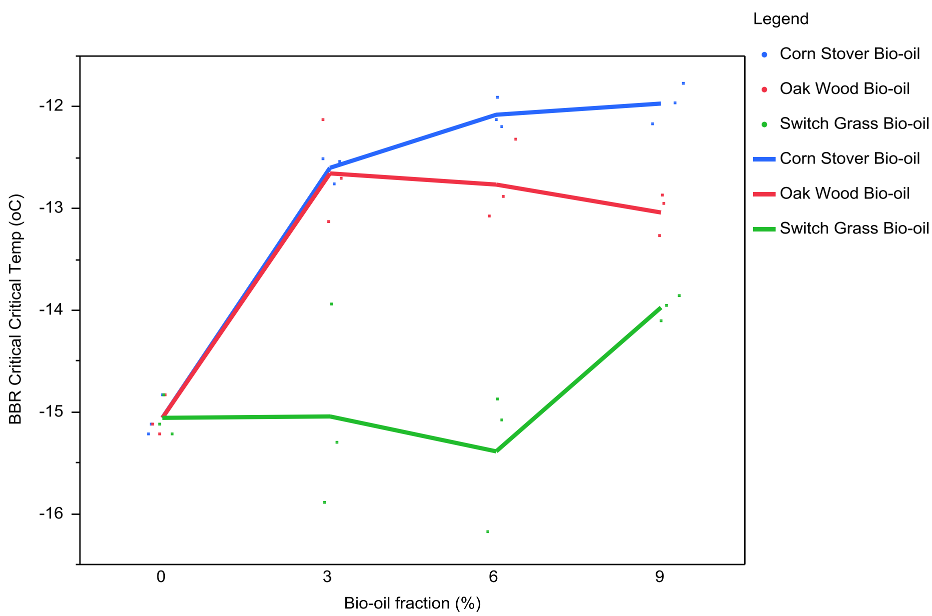


Figure 13. Low Critical Temp for AAM-1 vs. Bio-oil fraction (%) by Bio-oil types

An ANOVA and effect tests (Table 36) were done evaluating three, six, and nine percent of corn stover, oak wood, and switch grass bio-oil. Significant differences were found with both factors and their interaction term, and the model has a 93.1% R square value. Some treatment effects are significantly different.

Table 36. Model ANOVA and effect tests for AAM-1 DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	58.45	5.31	29.37	<.0001	**Bio-oil type**	2	24.69	68.24	<.0001
Error	24	4.34	0.18			**Bio-oil fraction**	3	22.47	41.40	<.0001
C. Total	35	62.79				**Interaction**	6	11.29	10.40	<.0001

Tukey HSD test (Table 37) reports the bio-oil type effect on binder AAM-1 as same as the outcome of the bio-oil type effect on AAD-1 binder. The switch grass modified binder has the potential to have better performance in low temperature environments than the other two bio-oils.

Increasing the bio-oil treatment dosage does not substantially raise the critical low temperature. As illustrated in Table 38, all of the bio-oil fraction levels are connected by same letter except the 0% percent level. There is no significant difference by adding bio-oil in different fractions, the significant effects of adding bio-oil to the AAM-1 binder at low critical cracking temperature is still true.

As shown in Table 39, the corn stover bio-oil treatment decreases the binder's low temperature application range the most, followed by the oak wood treatment, and the switch grass bio-oil modified binder has no significant difference in temperature means with the neat AAM-1 binder.

Table 37. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level				Mean
Corn Stover Bio-oil	A			-12.93
Oak Wood Bio-oil		B		-13.38
Switch Grass Bio-oil			C	-14.87

Levels not connected by same letter are significantly different.

Table 38. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level			Mean
9%	A		-13.00
6%	A		-13.41
3%	A		-13.44
0		B	-15.06

Levels not connected by same letter are significantly different.

Table 39. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level					Mean
Corn Stover Bio-oil,9	A				-11.97
Corn Stover Bio-oil,6	A				-12.08
Corn Stover Bio-oil,3	A				-12.60
Oak Wood Bio-oil,3	A				-12.66
Oak Wood Bio-oil,6	A	B			-12.76
Oak Wood Bio-oil,9	A	B			-13.04
Switch Grass Bio-oil,9		B	C		-13.98
Switch Grass Bio-oil,3			C	D	-15.05
Neat AAM-1 Binder			C	D	-15.06
Switch Grass Bio-oil,6				D	-15.39

Levels not connected by same letter are significantly different.

5.2.1.9 BBR critical low temperature for the LPMB binder

As mentioned above, the lower the critical BBR temperature, the better the cracking resistance. Figure 14 reveals the similarity of corn stover and oak wood effects on LPMB binder. The switch grass bio-oil modified binder behaves differently and is expected to maintain the low temperature cracking resistance of the LPHB binder. Because the low critical temperature decreases for the switch grass bio-oil treatment at the 9% dosage, the interaction term should be significant and the significant difference between the level of 6% and 9% fraction may not be detected.

The effect test reported in Table 40 shows the p-values are all small enough (<0.05) to reject the null hypothesis. Therefore, there is significant interaction between the bio-oil type and the bio-oil fraction, which is consistent with the plot shown in Figure 14. All factors prove to be significant.

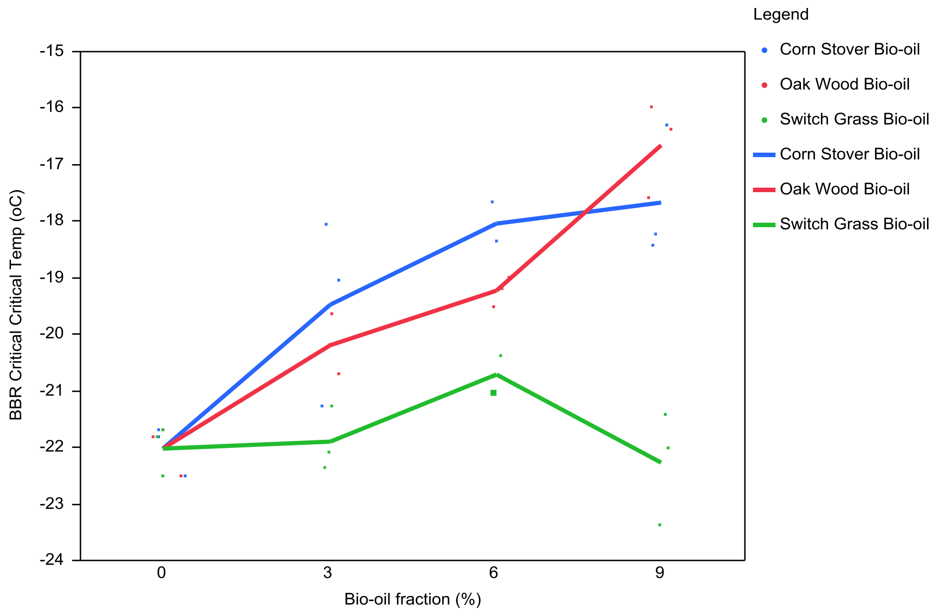


Figure 14. Low Critical Temp for LPMB vs. Bio-oil fraction (%) by Bio-oil types

Table 40. Model ANOVA and effect tests for LPMB DSR data

Analysis of variance						Effect tests				
Source	**DF**	**Sum Squares**	**Mean Square**	**F Ratio**	**Prob > F**	**Source**	**DF**	**Sum Squares**	**F Ratio**	**Prob > F**
Model	11	127.27	11.57	19.11	<.0001	**Bio-oil type**	2	43.22	35.69	<.0001
Error	24	14.53	0.61			**Bio-oil fraction**	3	53.32	29.35	<.0001
C. Total	35	141.81				**Interaction**	6	30.74	8.46	<.0001

Tukey HSD tests (Table 41) demonstrate that the corn stover and oak wood bio-oil treatment levels have significantly higher critical low temperature means than switch grass bio-oil. No difference between the corn stover and oak wood bio-oil treatments and is consistent with the trending similarity illustrated in Figure 14.

Table 41. HSD (Tukey-Kramer) multiple comparisons for bio-oil type

Bio-oil Type Level			**Mean**
Corn Stover Bio-oil	A		-19.30
Oak Wood Bio-oil	A		-19.53
Switch Grass Bio-oil		B	-21.73

Levels not connected by same letter are significantly different.

The same letter "A" is a sign that both fraction levels 9% and 6% (Table 42) have no significant difference.

Table 42. HSD (Tukey-Kramer) multiple comparisons for bio-oil fraction

Bio-oil Fraction Level				Mean
9%	A			-18.87
6%	A			-19.33
3%		B		-20.52
0			C	-22.01

Levels not connected by same letter are significantly different.

For applying the bio-oil modification to the LPMB binder, switch grass bio-oil does not produce a statistically different critical low temperature than the LPMB binder alone.

Table 43. HSD (Tukey-Kramer) multiple comparisons for treatment combination

Treatment Level						Mean
Oak Wood Bio-oil,9	A					-16.66
Corn Stover Bio-oil,9	A	B				-17.66
Corn Stover Bio-oil,6	A	B	C			-18.04
Oak Wood Bio-oil,6		B	C	D		-19.24
Corn Stover Bio-oil,3		B	C	D		-19.47
Oak Wood Bio-oil,3			C	D	E	-20.18
Switch Grass Bio-oil,6				D	E	-20.71
Switch Grass Bio-oil,3					E	-21.91
Neat LPMB Binder					E	-22.01
Switch Grass Bio-oil,9					E	-22.28

Levels not connected by same letter are significantly different.

5.2.1.10 <u>Summary of Performance Grade</u>

After bio-oil modification, all binders became softer at the unaged stage. In asphalt specifications, to ensure that asphalt binders, especially modified ones can be pumped and handled at the hot plant mixing facility, a maximum viscosity requirement should be met for the unaged binder. This value is 3 kPa*s at 135 ^{o}C. The specified test procedure is documented in AASHTO T316, *Viscosity Determination of asphalts Binders Using*

Rotational Viscometer. Due to the softening effect on unaged modified binders via adding bio-oil, the bio-oil modified binders would be pumped and handled more easily than the initial binder.

A statistically significant increase in the high critical temperature was observed for every bio-oil modified binder after the RTFO aging except the switch grass ESP bio-oil modified AAD-1 binder as shown in Figures 15, 16, and 17. The larger high critical temperature grade for the bio-oil modified binder indicates hardening of the asphalt during the simulated construction aging process. This could imply the HMA mixtures being less susceptible to rutting after field construction, due to the stiffer asphalt binder and the higher dynamic modulus of the HMA mixtures (Xiang Shu, Baoshan Huang 2007).

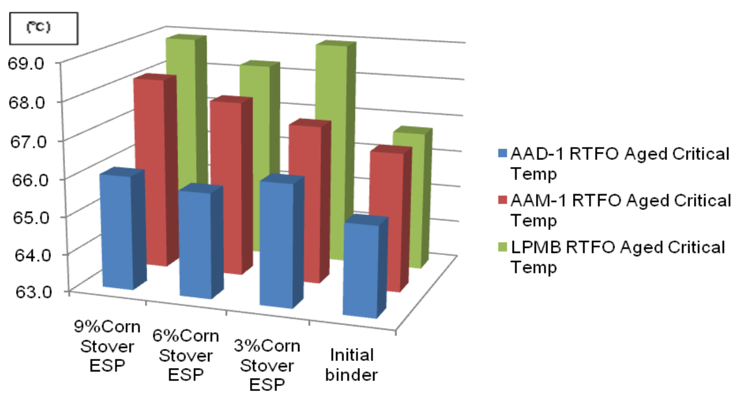


Figure 15. Corn stover bio-oil modified binder RTFO aged high critical temperatures

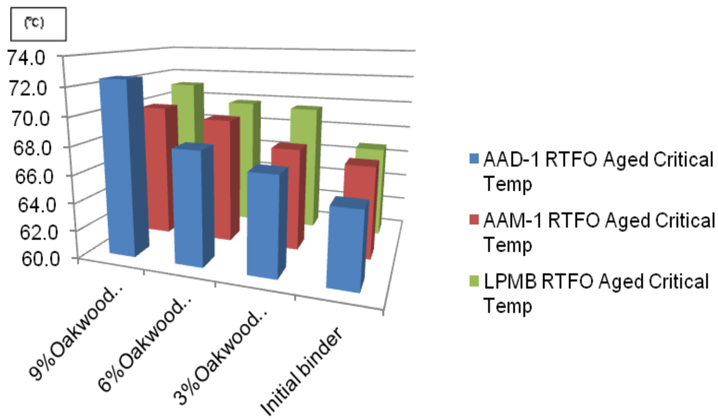


Figure 16. Oak wood bio-oil modified binder RTFO aged high critical temperatures

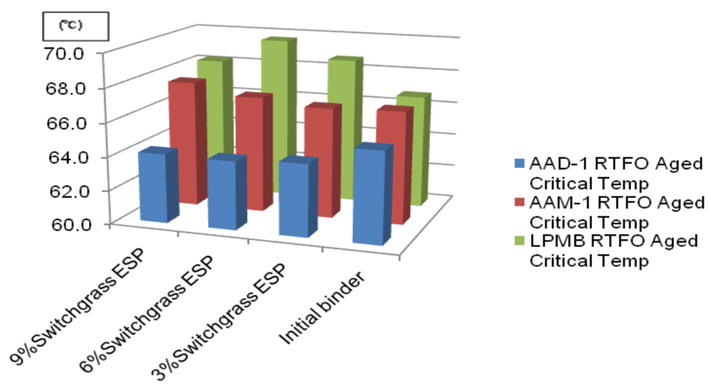


Figure 17. Switch grass bio-oil modified binder RTFO aged high critical temperatures

A trend for the intermediate critical temperature was not prominent for the PAV aged residuals. Long-term aging effects were more complex than the short-term aging and the results varied with the binder and bio-oil types. As shown in Figures 18, 19, and 20, an increase in the intermediate critical temperature grade was detected for every bio-oil modified AAD-1 binder. But the intermediate critical temperature for bio-oil modified binder AAM-1 slightly decreased, since AAM-1 is less susceptible to oxidative aging (Mortazavi and Moulthrop 1993). The results for the bio-oil modified LPMB binder was complex, likely due to the LPMB's SBS modification. The rheological properties for polymer modified asphalt during the aging processes are dependent upon the structural characteristics of the incorporated polymer (M.S Cortizo *et al*. 2004). However, the size exclusion chromatography technique can be applied to analyze the molecular size of the polymer modified asphalt to explain the rheological phenomena for a future study.

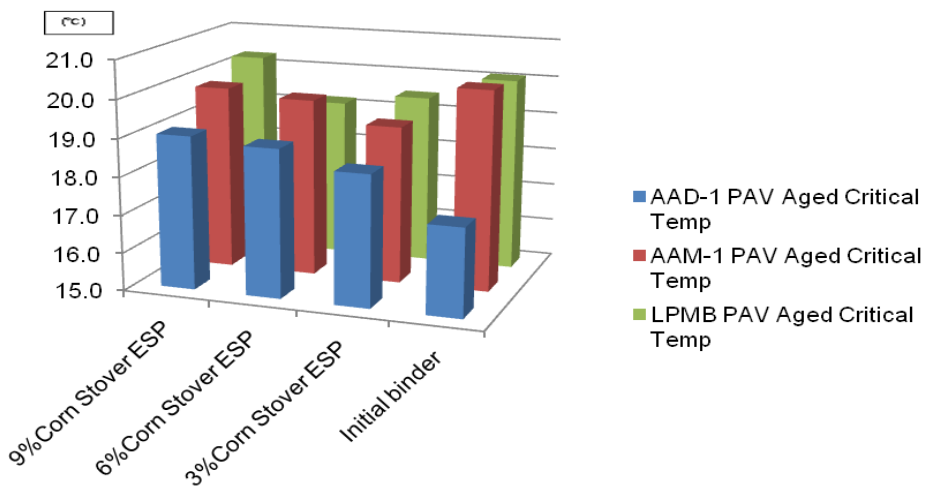


Figure 18. Corn stover bio-oil modified binder PAV aged intermediate critical temperatures

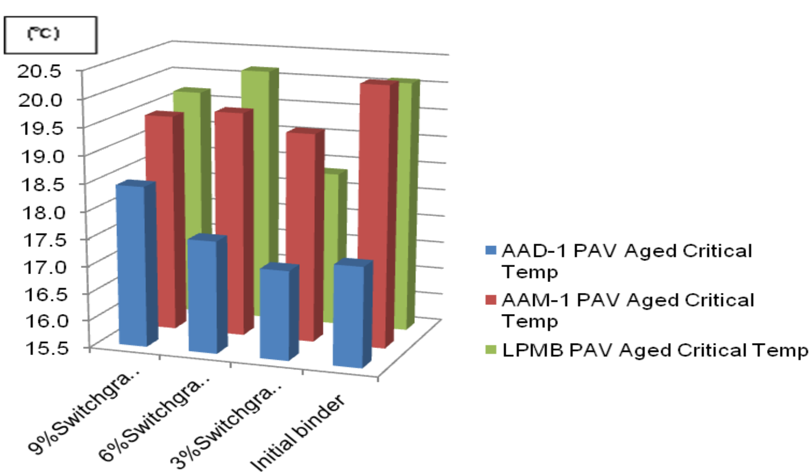


Figure 19. Switch grass bio-oil modified binder PAV aged intermediate critical temperatures

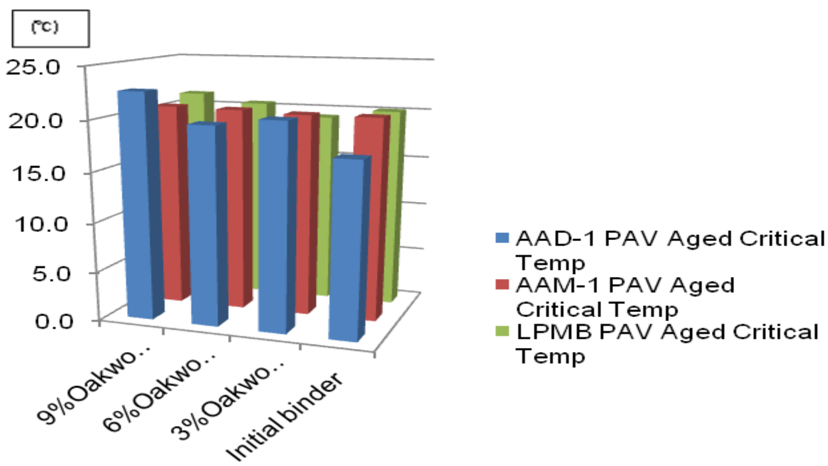


Figure 20. Oak wood bio-oil modified binder PAV aged intermediate critical temperatures

For most of the oak wood and corn stover bio-oil treatment combinations, the low critical temperature grades were increased in different amounts by the variation of the binder percentage and the fraction of the added bio-oil. The order in which performance grade scales decreased was AAM-1 then LPMB followed by AAD-1. The stiffening effect benefits the high temperature properties and adversely affects the low temperature performance. In addition, the more bio-oil added, the greater the increase in the critical low temperature. However, the switch grass bio-oil added in all three binders did not adversely affect the rheological properties at low temperatures as much as the other two bio-oils, especially for the LPMB binder. The 3%, 6%, and 9% switch grass modified LPMB, the 3% and 6% switch grass modified AAM-1, and the 3% switch grass modified AAD-1 maintained similar critical low temperatures as the initial binder without a statistically significant difference. The statistical analysis consisted of student t-tests with an $\alpha = 0.05$.

The overall effects of the bio-oil additive were estimated by the PG range difference. Table 44 presents a summary of bio-oil treatment combinations demonstrating positive or neutral effects on the PG range. A student-t least significant difference (LSD) with a type 1 error of 0.05 was used to determine the statistically significant difference between the average mean values of performance grades.

Table 44. Summary of bio-oil treatment combination effect

Binder	Positive Effect	ΔT°C	Neutral Effect
AAD-1	None		Possible 9% Oak wood
AAM-1	9% Oak wood	+1.13	3% Switch grass 6% Switch grass 9% Switch grass 6% Oak wood
LPMB	3% Switch grass 6% Switch grass 9% Switch grass 3% Oak wood	+1.86 +1.63 +1.71 +0.95	6% Oak wood 9% Oak wood 3% Corn stover

For the AAD-1 binder, no combination of bio-oils showed an extension of the performance grade. Adding oak wood bio-oil yielded a relevant increase in the critical high temperature, but the greater decrease in the critical low temperature mitigated the benefit of the asphalt hardening by long-term aging.

For the AAM-1 binder, no bio-oil combinations increased the PG range. The switch grass bio-oil slightly increases the critical high temperature, and nearly maintains the critical low temperature range, which is detected as not a statistically significant increase in the PG.

The bio-oil can be applied to the SBS modified binder, LPMB. Switch grass and oak wood are also suitable for the bio-oil modification.

All Fit models are tested to be useful with a high R square value. The interaction term for all models is tested and found to be significantly important to explain the variations. The modification effect is significantly dependent on the amount of bio-oil and the bio-oil types. When the interaction term is detected to be significantly important in the Fit model, the interaction affects the experimental response. Since the scale of the interaction effective is varying, the general conclusions that can be used to address the bio-oil treatment effect are hard to identify.

5.2.2 Tall oil fatty acids treatment effect evaluation

This one-way completely randomized experiment was designed for evaluating each binder individually by adding tall oil fatty acids at two different percentages, 0.18% and 0.36%. Three asphalt binders (AAD-1, AAM-1, and LPMB) were the experimental materials. The treatment factor was the tall oil fatty acids with two levels, 0.18% and 0.36%. The critical high, intermediate, and low cracking temperatures were measured, and two PG ranges were calculated as the experimental response. The random block design was not selected to apply in this research because of the anticipated significant interaction between the block factor (asphalt type) and the tall oil fatty acids was considered. The LPMB binder is a SBS polymer modified binder, and the tall oil fatty acids is usually used as an emulsifier in the polymerization procession. The interactions were proved to be significant by an analysis and thus their effects could not be ignored.

The two tall oil dosage treatments were randomly assigned to the asphalt binder. Three blends were prepared for each treatment combination. The same way to conduct the performance grading for evaluating the bio-oil modified binder was applied as well. Analysis of variance (ANOVA) using the method of least squares was used to analyze the results of the experiment. Statistical differences between the treatment levels were tested, and the statistically important factor was determined. A Type I error (α) of 0.05 was used for all statistical analysis and effect tests.

The experiment results are summarized in Figure 21. The dash lines are used to mark the RTFO critical temperature or RTFO critical temperature range, the soild lines are used to describe the unaged critical temperature or unaged critical temperature range. For each binder column in Figure 21, the points on the extreme left side are the experimental results collected from the control group containing 0% tall oil. The neat binder results were compared with the treatment means for evaluating the tall oil effect.

For this research, the first stage was to evaluate the bio-oil modified binder's properties, indentify the critical factor, and establish the model that can fit the experimental data. When the first stage was done, the experiment results indicated that bio-oil modification could raise the binder's critical high temperatures but meanwhile increased the critical low temperature. The overall performance grade range varied depending on the combination of binders and bio-oils. Most bio-oil treatments applied to the AAD-1 and AAM-1 binders reduced or maintain the high to low temperature interval resulting from the discrepancy or balancing between the decrease in the low critical temperature and the smaller to equal increments from the high critical temperature. The stiffening of the bio-oil modified binders benefits the rutting resistance but decreases the low temperature cracking. Therefore, how the binders behave at BBR low critical temperatures is important to this research since their performance at low temperatures will determine how the binders can be applied to pavement materials. Because tall oil fatty acids are widely used in the tire and rubber industries as emulsifiers to make the product softer, utilizing the tall oil fatty acids to optimize the bio-oil binder modification was the second research stage. For the second research stage, the tall oil fatty acids modification effects on the neat binder were studied at first, and then the tall oil modification effects on the bio-oil modified binder were evaluated.

As shown in Figure 21, the addition of tall oil fatty acids at all levels caused a decrease in unaged and RTFO critical temperature for the AAD-1 and AAM-1 binder. Tall oil caused binder AAD-1 and AAM-1 to soften. Based on the graph, the more tall oil added, the greater drop in the high critical temperatures with a reducing/changing slope. It seems even by adding tall oil to the AAD-1 and AAM-1 binders with higher dosage, the unaged critical temperature ranges are maintained. However, adding the tall oil to the polymer modified binder LPMB ended up increasing the critical high temperatures. But since the plot shown in Figure 21 (on the top right) has the parabola curve trending downwards, it is hard to predict the effect when more than 0.36% tall oil fatty acids are added. Future testing using higher amounts of tall oil should be considered. This parabola shaped plot also can be seen with the BBR critical low temperature plots.

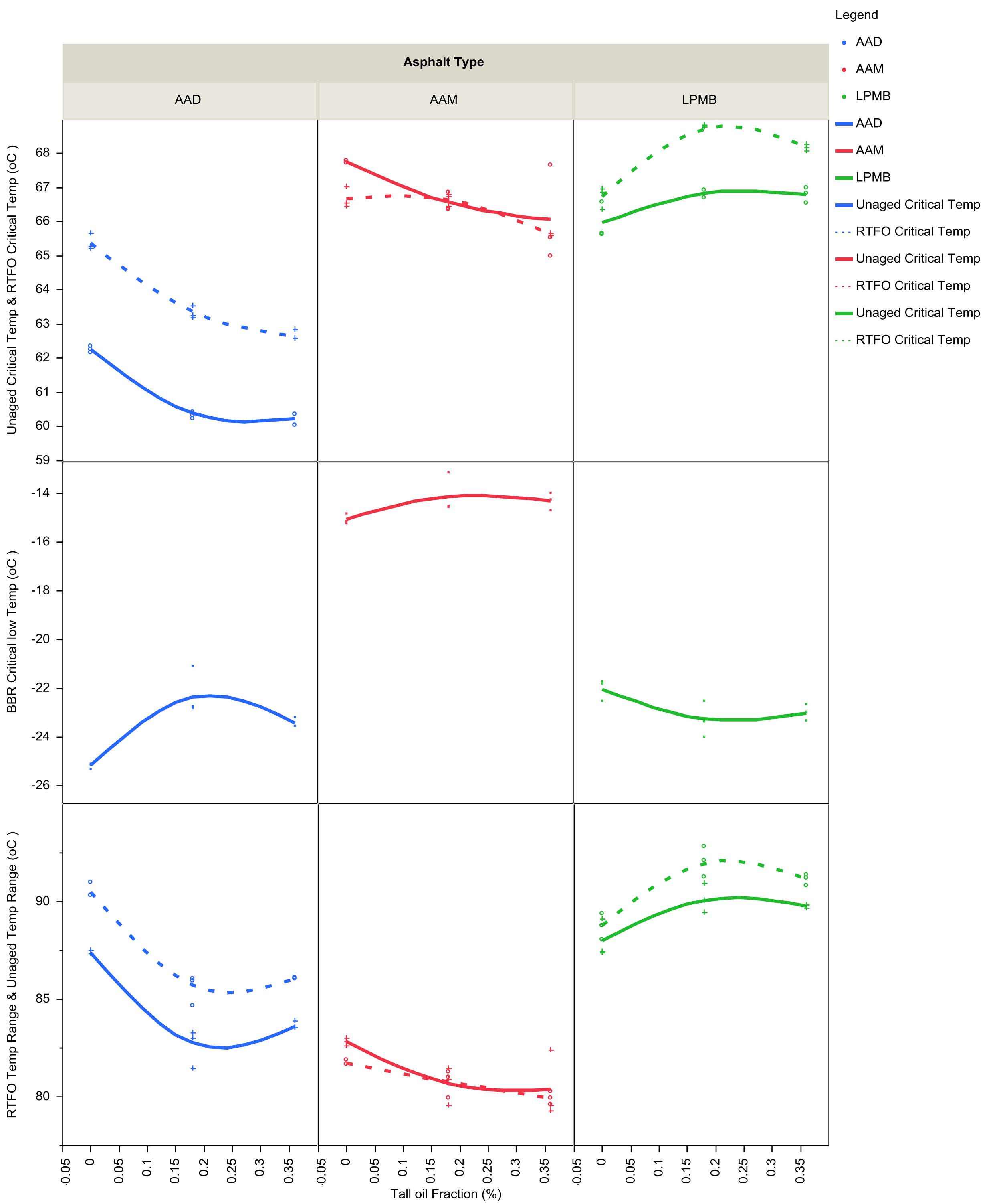


Figure 21. Experiment summary by critical temp vs. tall oil fatty acids fraction

For the AAD-1 binder, the critical low temperature goes up when treated by 0.18% tall oil and drops down when treated by adding larger amounts. The same changing manner was observed for the AAM-1 binder. So far, by treating the AAM-1 binder with tall oil in the range from 0% to 6% by asphalt weight, the tall oil adversely increases the BBR critical temperature and is statistical significant. However, adding tall oil has no significant effect on the BBR critical temperature for the LPMB binder. The tests with higher dosage should be carried out in future research.

The summary for the effect tests and Tukey-Kramer HSD comparison are listed in Table 45. The traditional letter-coded report indicates where means do not share the same letter are significantly different. Table 45 is used to verify whether the change in critical temperature that has been illustrated in Figure 21 is statistically significantly different.

Table 45. The effect tests for tall oil additive in binder AAD-1, AAM-1 and LPMB

	AAD-1 Binder			AAM-1 Binder			LPMB Binder		
	Level		Mean	Level		Mean	Level		Mean
Unaged Critical Temp	0	A	62.27	0	A	67.77	0.18	A	66.87
	0.18	B	60.34	0.18	A	66.55	0.36	A B	66.80
	0.36	B	60.25	0.36	A	66.08	0	B	65.97
RTFO Critical Temp	0	A	65.38	0	A	66.68	0.18	A	68.81
	0.18	B	63.33	0.18	A	66.68	0.36	B	68.18
	0.36	C	62.67	0.36	B	65.62	0	C	66.74
PAV Critical Temp	0	A	17.32	0	A	20.26	0	A	20.09
	0.18	A B	17.06	0.18	A	19.00	0.18	B	18.12
	0.36	B	16.38	0.36	B	18.59	0.36	B	17.91
BBR Critical Low Temp	0.18	A	-22.23	0.18	A	-14.07	0	A	-22.01
	0.36	A	-23.42	0.36	B	-14.32	0.36	A	-22.98
	0	B	-25.18	0	B	-15.06	0.18	A	-23.28
Unaged PG Range	0	A	87.45	0	A	82.83	0.18	A	90.14
	0.36	B	83.67	0.36	A	80.63	0.36	A	89.78
	0.18	B	82.57	0.18	A	80.39	0	B	87.98
RTFO PG Range	0	A	90.56	0	A	81.74	0.18	A	92.09
	0.36	B	86.09	0.18	B	80.76	0.36	A	91.16
	0.18	B	85.56	0.36	B	79.94	0	B	88.75

Levels not connected by same letter are significantly different.

The interaction plots in Figures 22, 23 and 24 demonstrate the general tendencies for unaged critical high temperature, RTFO critical high temperature, BBR critical low temperature, and RTFO PG Range by treating the AAD-1, AAM-1, and LPMB binder with varying amounts of tall oil.

Interaction for between binder types and tall oil was detected and is seen is Figure 22. As the tall oil fraction is increased, the effect on the unaged critical high temperature does not have the same effect. This explains the variation among the unaged critical temperature means. The tall oil treatment effects are consistent across binders AAD-1 and AAM-1 but different for the LPMB binder. This indicates that tall oil behaves differently in the LPMB binder compared to the AAD-1 and AAM-1 binders.

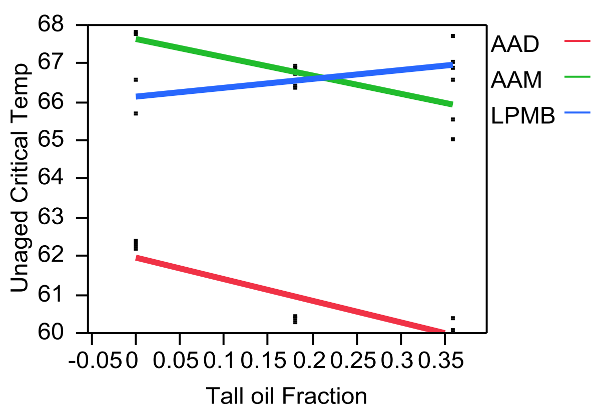


Figure 22. Tendency for uaged critical temperature by varying tall oil treatments

Figure 23 shows the tendencies for RTFO critical temperature when changing the tall oil treatment dosage. Generally, in the dosage range from 0% to 0.36%, the RTFO critical temperature decreases for the AAD-1 and AAM-1 binder, but increases if it is blended with LPMB binder. The difference in temperature changes for all binders was found to be statistically significant.

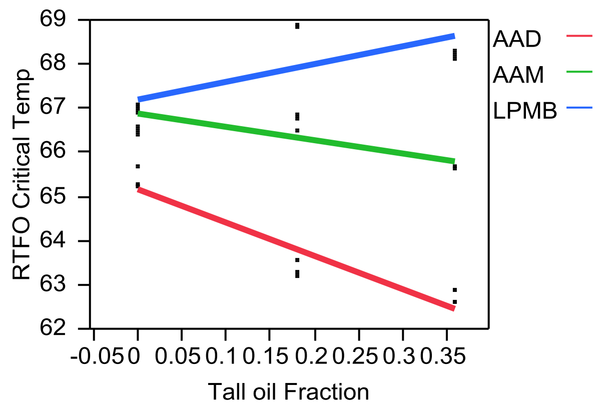


Figure 23. Tendency for RTFO critical temperature by varying tall oil treatments

Figure 24 illustrates the effect for tall oil resulting on the BBR critical low temperature for different binders. The tall oil additive causes a statistically significant increase in BBR low temperature when applied to binder AAD-1 and AAM-1 and has no significant effect on the LPMB binder.

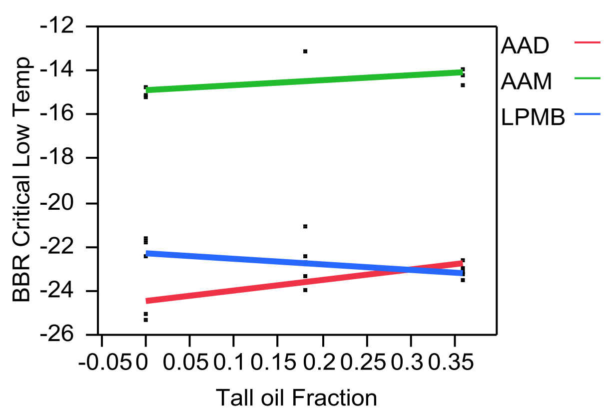


Figure 24. Tendency for BBR critical low temperature by varying tall oil treatments

There are no positive outcomes by adding tall oil in the range from 0% to 0.36% by weight, comparing with the neat binder. Just introducing the tall oil to the neat binder cannot enhance or benefit the binder properties at low temperatures. By reviewing the BBR raw data, the reason that the binder could not be graded at a lower critical low temperature was because most of the tall oil modified binders failed to meet the minimum m-value specification, however the majority of the modified binders satisfied the maximum stiffness requirement. The additives for tall oil modified binder that are able to accelerate the creep rate may solve the problem and improve the binder's low temperature performance. Additionally, even though adding the tall oil to the neat binder does not improve the low temperature properties, the tall oil rehabilitation effect to the bio-oil modified binder at low temperature properties is observed and more details are discussed in Section 5.2.3 Bio-oil and tall oil fatty acids mixture modification effect evaluations.

The overall effect for tall oil is revealed in Figure 25. The tall oil treatment produces a statistically significant positive effect to extend the PG range for LPMB binder, but shrinks the PG range for binder AAD-1 and AAM-1 statistically.

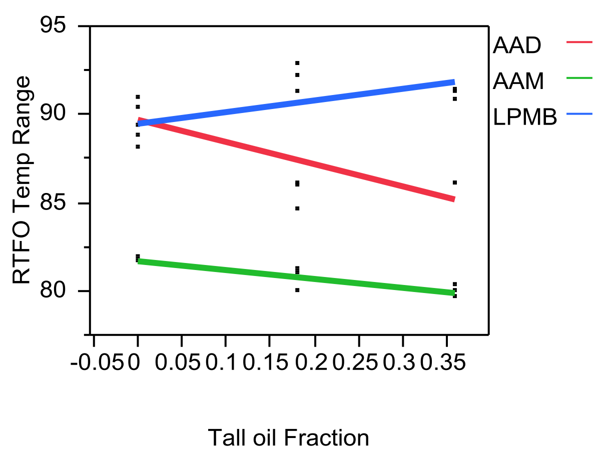


Figure 25. Tendency for RTFO PG range by varying tall oil treatments

5.2.3 Bio-oil and tall oil fatty acids mixture modification effect evaluation

The two–way factorial experiment was designed to evaluate the modification by adding bio-oil and tall oil fatty acids in the binders AAD-1, AAM-1and LPMB. Asphalt binder is the experimental unit. The three types of bio-oil (corn stover, oak wood and switch grass) were combined with one type of tall oil and were blended with the three asphalt binders. The critical high, intermediate, and low cracking temperatures were measured as the experimental responses and two PG ranges were calculated as well. The two conditions are:

- **Factor A-** tall oil fraction by weight, 0% and 0.18%.
- **Factor B-** bio-oil fraction by weight, 0% and 6%.

This two-way experiment was repeated nine times to evaluate all the asphalt binder with bio-oil and tall oil blends. The nine experiments were analyzed individually.

There are four treatment combinations for each individual experiment. Asphalts were randomly assigned to those treatment combinations and blended with the bio-oil and tall oil in varying fractions. Each blend was tested in triplicate to provide a good measure of random error. The JMP statistic software was used to analyze the data. The ANOVA model is mainly applied to detect whether the main effects of the factors and the interaction effect are statistically significant. ANOVA was used to detect the significant difference between the means of treatment responses.

Generally, the factors effects were detected to be significant if there were some significant differences among the means that can be found between factor levels. Those significant differences indicate the factor "did" something amongst different levels, if the interaction is not significant. The interaction effects were significant when the effects of one factor depend on the other factor. Therefore if there is significant interaction, the main factor effect detected to be significant on the condition of other factor's presence does not have to be significant when the other factor is not present.

In this research, since one of the levels for both factors is 0% treatment, the effect test on Factor A addresses whether adding small amounts of tall oil at 0.18% by weight is related to critical temperature shifting. The effect test on Factor B addresses whether 6 % bio-oil affects the critical temperature. The interaction effect tests indicate whether the bio-oil modified asphalt binder behaves differently depending on the presenting with a small amount of tall oil. The treatment performance for adding bio-oil or tall oil individually has been already studied and evaluated in previous sections. If the interaction effect between the bio-oil and tall oil is not significant, the statement and the conclusion about the Factor A tall oil effect and the Factor B bio-oil effect should have no difference to what were generated and presented separately in the bio-oil analysis and tall oil evaluation sections. In ensuing subsections, more attention will focus on the discussion of the interactions between the bio-oil and the tall oil in different binders.

5.2.3.1 The notion of an interaction

Since the two-way factorial design experiment has effect tests on two main factors and the interaction, there are eight possible outcomes of what could be significant from the ANOVA effect analysis. What could occur in the bio-oil with tall oil fatty acids experiment is listed below:

- **Nothing** - non effects of tall oil, bio-oil or interaction between them are significant,
- **Effect of Factor A -** tall oil effect is significant,
- **Effect of Factor B -** bio-oil effect is significant,
- **Both main effect (Factor A and B) -** both of tall oil and bio-oil are significant,
- **Interaction –** interaction effect between tall oil and bio-oil is significant,
- **Interaction and effect of Factor A - interaction** and tall oil effects is significant,

- **Interaction and effect of Factor B -** interaction and bio-oil oil effects are significant,
- **Interaction and effect of Factor A, B -** all factors and interaction are significant

The first possibility is that nothing is significant to affect the critical temperatures. As an example, the treatment of adding switch grass bio-oil and tall oil into binder AAM-1 does not significantly affect the RTFO critical temperature. The ANOVA effect test result is shown in Table 46. As summarized in Table 46, the fact that neither the cell means nor the marginal means show any significant difference among the RTFO critical temperatures indicates that none the of tall oil, bio-oil, or interaction effects between them significantly affected the RTFO critical temperature. After adding the switch grass bio-oil and tall oil mixture into AAM-1 binder, the RTFO critical temperature did not change significantly.

Table 46. RTFO critical temp for AAM-1 treated with switch grass bio-oil and tall oil

RTFO Critical Temp for AAM-1 Binder treated with switch grass bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	66.68	66.91	66.80
	0.18% (by weight)	66.68	67.00	66.84
B marginals		66.68	66.96	

In graphical form:

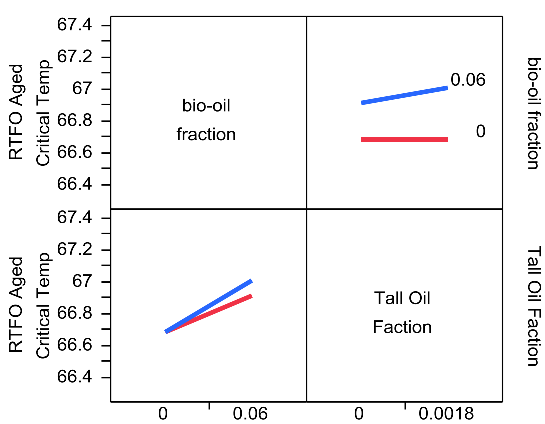


Figure 26. Interaction plots for switch grass bio-oil and tall oil in AAM-1 binder

In Figure 26, the parallel lines indicate there is no interaction. The lack of difference for the average RTFO critical temperature between the 0% and 6% level for factor B (switch grass bio-oil) signifies no significant effect for adding switch grass bio-oil to the AAM-1 binder. This is also applied to factor A (tall oil). The small increase in the RTFO critical temperature may be noticed by adding switch grass bio-oil, but the ANOVA effect test concludes that the difference was not statistically to be significant.

The evaluation conclusion for modifying the AAM-1 binder by adding switch grass bio-oil mixture with tall oil is that neither the switch grass bio-oil at 6% dosage nor the tall oil demonstrates any effect on the RTFO critical temperature of the AAM-1 binder. In addition, the switch grass bio-oil's treatment effect on RTFO critical temperature does not relate to the presence of tall oil at the small dosage of 0.18%. In other words, blending switch grass bio-oil with AAM-1 binder does not demonstrate any effect on the RTFO critical temperature is not due to the a small amount tall oil in the blend. Later in the fifth and sixth possibilities, the cases present two situations that the reason why serving bio-oil at a small amount with the binder does not demonstrate any effect is because the tall oil is added, and the interaction overrides the bio-oil main effects.

The second possibility is that only the main effect of factor A (tall oil) is significant. The treatment of adding switch grass bio-oil and tall oil into binder LPMB gives an example of how only factor A significantly affects the PAV critical temperature. The ANOVA effect test result is shown in Table 47. Table 47 shows the significant difference between the tall oil levels in the A marginals cell, which indicates that the main effect of factor A (tall oil) is significant. No significant difference that can be detected in B marginals suggests switch grass bio-oil (factor B) has no effect on PAV critical temperature when added to the LPMB binder at 6% by weight. The fact that, no matter whether the 6% switch grass bio-oil is added or not, the tall oil effect is consistent across both levels of factor B demonstrates there is no interaction between the tall oil and the switch grass bio-oil for measuring the PAV critical temperature for the LPHB binder. A decreasing PAV critical temperature for LPMB binder causing by serving tall oil at a small dosage of 0.18% is not dependent on the presence of the switch grass treatment.

Table 47. PAV Critical Temp for LPMB treated with switch grass bio-oil and tall oil

PAV Critical Temp for LPMB Binder treated with switch grass bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	20.09	20.16	20.13
	0.18% (by weight)	18.12	19.09	18.61
B marginals		19.11	19.63	

In graphical form:

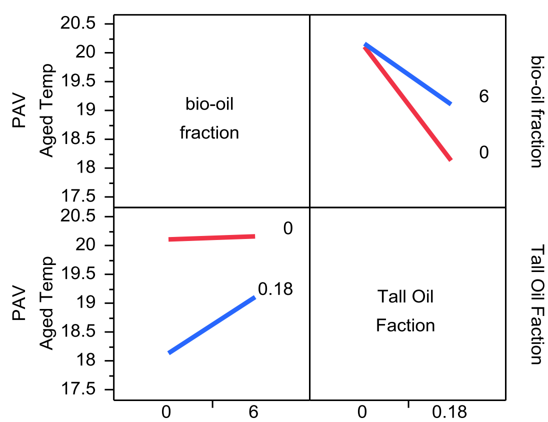


Figure 27. Interaction plots for switch grass bio-oil and tall oil in LPMB binder

Graphically, if the red line and the blue line are parallel or the slopes of two lines are not significantly different, there is no interaction. If the red and blue lines are combined together to form an average line representing the average changing tendency, and also the average line is found to keep parallel to the experiment variable axis, there is no effect for the experimental variable (factor).

The third possibility is that only the main effect of factor B (bio-oil) is significant. There is a treatment of adding oak wood bio-oil and tall oil into binder AAM that provides an example of how only factor B (oak wood bio-oil) significantly affects the BBR critical temperature. The ANOVA effect test result is shown in Table 48. As summarized in Table 48, a significant difference between the two levels of the bio-oil factor in the B marginals indicates that oak wood bio-oil (factor B) has significant effect on increasing the BBR critical low temperature. No significant difference can be detected in A marginals, which means the tall oil had no effect. The fact that the bio-oil effect is fairly consistent across both levels of factor A (tall oil) signifies no interaction between the oak wood bio-oil and the tall oil. In Figure 34, if effects of the oak wood bio-oil are perfectly consistent across the two levels of factor A, the red line and the blue line should be perfectly parallel showing in the left corner. The lines shown in Figure 28 look virtually unparallel, but the ANOVA effect test suggests they are fairly parallel and changing towards the same direction.

Table 48. BBR Critical Temp for AAM-1 treated with oak wood bio-oil and tall oil

BBR Critical Temp for AAM-1 Binder treated with oak wood bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	-15.06	-12.76	-13.91
	0.18% (by weight)	-14.07	-12.86	-13.47
B marginals		-14.57	-12.81	

In graphical form:

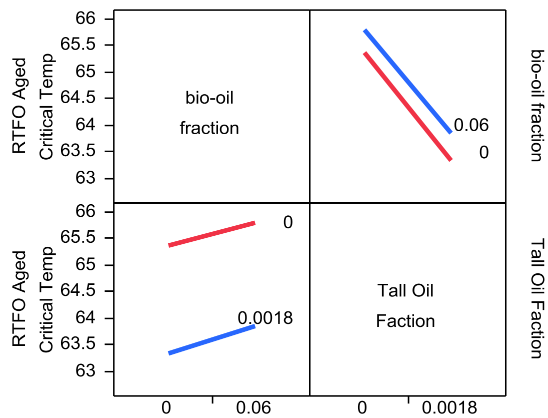


Figure 28. Interaction plots for oak wood bio-oil and tall oil in AAM-1 binder

The fourth possibility is that both main effects of factors (tall oil and bio-oil) are significant. The treatment of adding corn stover bio-oil and tall oil into binder AAD-1 gives an example of how both bio-oil and tall oil factors significantly affect the RTFO critical temperature without having significant interaction effects. The ANOVA effect test result is shown in Table 49. Notice that both sets of marginals (Table 49) show a statistically significant difference of the two levels, so both of the main effects are significant. The corn stover bio-oil significantly increases the RTFO critical temperature by adding a small amount. The tall oil decreases the RTFO critical temperature significantly. The fact that both of these main effects are consistent across the levels of the remaining factor implies that there is no interaction. As illustrated in Figure 29, with a increasing dosage of corn stover bio-oil that added to the AAD-1 binder, the effects on the RTFO critical temperature are fairly equal for both of the neat binder and the tall oil treated binder. This can be addressed other around as well. The effect is significant as shown by the parallel lines.

Table 49. RTFO Critical Temp for AAD treated with corn stover bio-oil and tall oil

RTFO Critical Temp for AAD Binder treated with corn stover bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	65.38	65.80	65.59
	0.18% (by weight)	63.33	63.86	63.60
B marginals		64.36	64.83	

In graphical form:

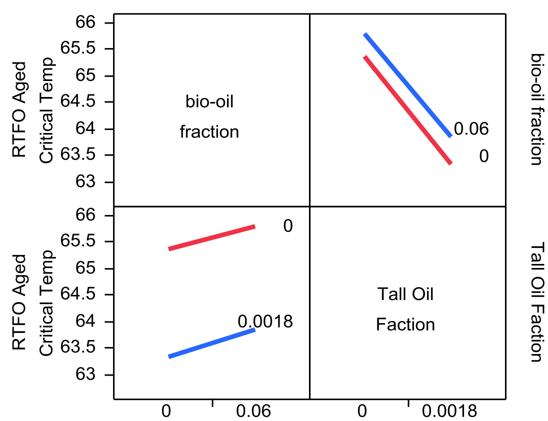


Figure 29. Interaction plots for corn stover bio-oil and tall oil in AAD-1 binder

The fifth possibility is that only the interaction is significant. The treatment of adding switch grass bio-oil and tall oil into binder AAD-1 gives an example for nothing but only interaction significantly affects the BBR critical temperature. The ANOVA effect test result is shown in Table 50. Neither in A marginals nor B maitinals is a significant difference detected, as shown in Table 50. However, some means of the four treatment combination do differ significantly. The switch grass bio-oil does increase the BBR critical temperature significantly when no tall oil is added, and decreases the BBR critical temperature when the tall oil is served. Whenever the effect of one factor depends upon the levels of another, there is an interaction. In other words, the effects to the BBR critical temperature of adding switch grass bio-oil to the AAD-1 depends on the presences of tall oil at a small dosage. The tall oil decreases the BBR critical temperature significantly, if the bio-oil is added. The interaction effect between the switch grass bio-oil and tall oil is significant on the AAD-1 binder when measuring the BBR critical temperature.

Table 50. BBR Critical Temp for AAD-1 treated with switch grass bio-oil and tall oil

BBR Critical Temp for AAD-1 Binder treated with switch grass bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	-25.18	-21.84	-23.51
	0.18% (by weight)	-22.23	-25.54	-23.89
B marginals		-23.71	-23.69	

In graphical form:

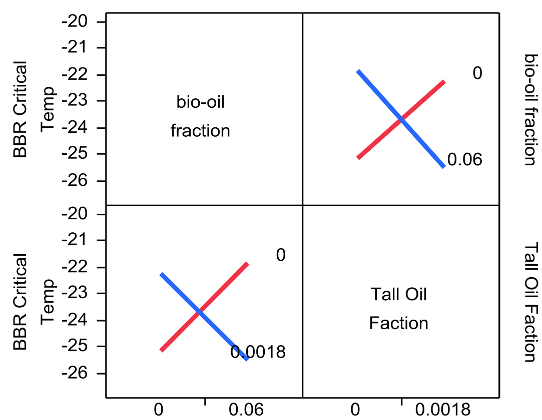


Figure 30. Interaction plots for switch grass bio-oil and tall oil in AAD-1 binder

The sixth possibility is that only the main effect of factor A (tall oil) and interaction are significant. The treatment of adding corn stover bio-oil and tall oil into binder LPMB gives an example about how the tall oil and the interaction with corn stover bio-oil significantly affect the RTFO critical temperature. The ANOVA effect test result is shown in Table 51. The B marginals show no significant difference, thus the main effect of corn stover bio-oil has no significant effect. The A marginals do show a difference between the two levels, which demonstrates a significant effect of factor A (tall oil). When adding tall oil into the

LPMB binder, the RTFO critical temperature increases. However, the treatment combination cell means reveals the real story. The bio-oil increases the RTFO critical temperature without the presence of tall oil, and the RTFO critical temperature decreases with adding tall oil. There is strong interaction between the bio-oil and the tall oil. The addition of the tall oil could significantly increase the RTFO critical temperature but only when the bio-oil is not added. The interaction produces some reverse effect. More importantly, the interaction effect overrides the main factor in different scales. The interaction overrides the bio-oil effect more than the tall oil effect, which in results the bio-oil not having a significant effect. But if the interaction effect overrides the tall oil effect and enhances the bio-oil effect, it would result in the seventh case discussed next.

Table 51. RTFO Critical Temp for LPMB treated with corn stover bio-oil and tall oil

RTFO Critical Temp for LPMB Binder treated with corn stover bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	66.74	68.29	67.52
	0.18% (by weight)	68.81	67.63	68.22
B marginals		67.78	67.96	

In graphical form:

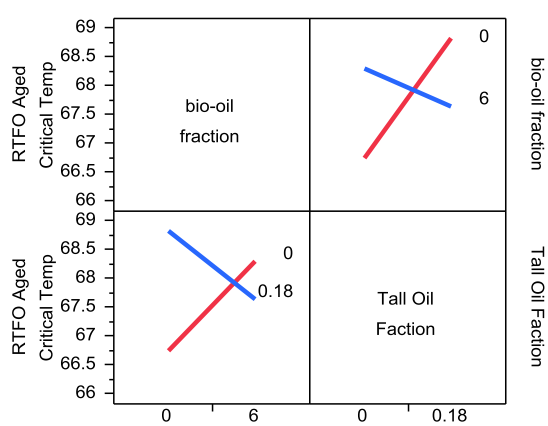


Figure 31. Interaction plots for corn stover bio-oil and tall oil in LPMB binder

The seventh possibility is that only the main effect of factor B (bio-oil) and interaction are significant. The treatment of adding oak wood bio-oil and tall oil into the LPMB binder gives an example for how the oak wood bio-oil and interaction significantly affect the unaged critical temperature. The ANOVA effect test result is shown in Table 52. No difference in A marginals indicates that the factor A (tall oil) has no significant effect. The oak wood bio-oil significantly decreases the unaged critical temperature. However, the cell means tell the whole story. Adding the oak wood bio-oil to the LPMB binder decreases the unaged critical temperature significantly only when the tall oil is added. Adding tall oil enhances the decrease in the RTFO temperature decreasing. The factor A (tall oil) has the effect on increasing the RTFO critical temperature, but this effect is overridden by presenting the oak wood bio-oil. Then the tall oil effect is not demonstrated.

Table 52. Unaged Critical Temp for LPMB treated with oak wood bio-oil and tall oil

Unaged Critical Temp for LPMB Binder treated with oak wood bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	65.97	65.36	65.67
	0.18% (by weight)	66.87	65.08	65.98
B marginals		66.42	65.22	

In graphical form:

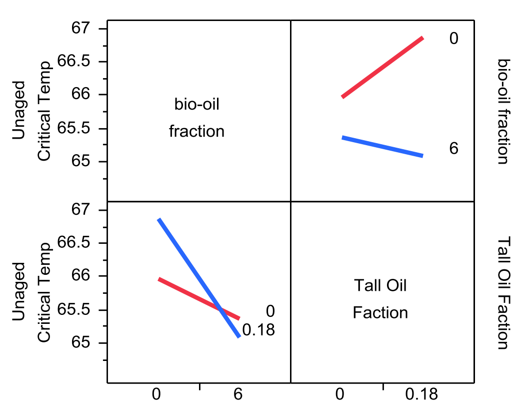


Figure 32. Interaction plots oak wood bio-oil and tall oil in LPMB binder

The final possibility is that both main effect of factor A and B and interaction are significant. The treatment of adding oak wood bio-oil and tall oil into binder AAD-1 gives an example for how bio-oil and tall oil and their interaction significantly affect the unaged critical temperature. The ANOVA effect test result is shown in Table 53. Both of marginals A and B have some significant differences, which means that the main effect A and effect B are significant. The cell means reveal the details. For the bio-oil factor, it only significantly decreases the uanged critical temperature when the tall oil is not added. For the tall oil factor, it only drops the unaged critical temperature significantly without the oak wood bio-oil. The interaction has some overriding effect to both factors, but it is not large enough for them to demonstrate their effects.

Table 53. Unaged Critical Temp for AAD-1 treated with oak wood bio-oil and tall oil

Unaged Critical Temp for AAD-1 Binder treated with oak wood bio-oil and tall oil		Factor B (Bio-oil)		A marginals
		0% (by weight)	6% (by weight)	
Factor A (Tall oil)	0% (by weight)	62.27	59.80	61.04
	0.18% (by weight)	60.34	59.64	59.99
B marginals		61.31	59.72	

In graphical form:

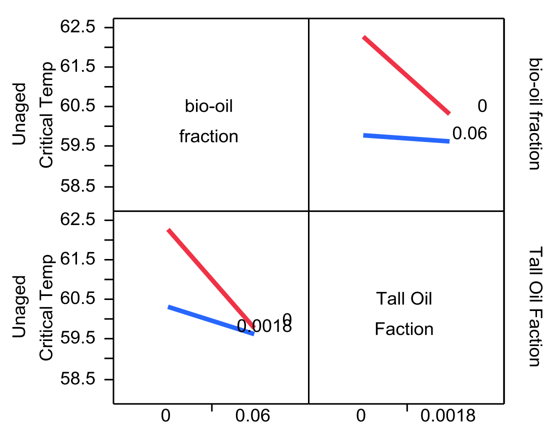


Figure 33. Interaction plots for oak wood bio-oil and tall oil in AAD-1 binder

The ANOVA is good at evaluating the treatment effect. But once the significant interaction gets involved, the phenomenon becomes complex. The critical temperatures vary with the amount of bio-oil and tall oil fatty acids, and the interaction effect is not obvious. Based on the ANOVA effect tests results and their outputs, it is not convenient to correctly make interpretations about the experimental data and reveal changing relationship between the factors with the experimental responses

First, the ANOVA effect tests of the factors and the interaction (Table 40 or Table 54) does not directly describe what happens to the experimental response when the experimental variables are changing. The significant effect is of limited value without checking the interaction plots (Figure 14 or Figure 26) to find out what direction of the effect to the experimental response. This is because the "significant effects" statement does not describe whether it is a "significant increase effect" or "significant decrease effect" to the experimental response. Even after checking the interaction plot to and find the general tendency between the factors with the experimental responses, it is not safe to address "the factor A has significant effect to decrease the experimental response", if the interaction is significant. One more question needs to be asked: "the significant increase depends on what condition?" Take the seventh case for example, shown in page 99. The factor B effect (oak wood bio-oil) is detected to be significant (Table 64) in the ANOVA model for unaged critical temperature for the LPMB binder. Then the oak wood bio-oil is detected to decrease the unaged critical temperature for the LPMB binder from interaction plot (Figure 32), the "conclusion" is that the oak wood bio-oil significantl decreases the unaged critical temperature of the LPMB binder. Finally, it is found that this conclusion only happens when the tall oil is added when checking the cells means in Table 52. Evidence shows in Table 19 that the treatment of 6% oak wood bio-oil does not decrease the unaged critical temperature significantly when compared to the neat binder. The connection between the ANOVA effect tests report and these outcomes with the experimental responses is strong but hard to view directly. In order to comprehensively understand the experimental phenomena, the ANOVA effect tests (Figure 40 or Figure 54), the interaction plots (Figure 14 or 26) and the means differences tests (Table 52) are needed.

Second, when analyzing the treatment effect for the application of bio-oil and tall oil fatty acids into asphalt, the interaction plot shown in Figure 26 can not reveal the relationship between the experimental responses with two variables changing simultaneously. The critical temperatures vary with the amount of bio-oil and tall oil fatty acids. The optimization of the binder modification cannot be done if one can only change one factor at a time while holding everything else constant.

In the next section, the contour plot and the response surface plot concept are introduced to illustrate the experimental phenomena as shown in Figure 35—"A picture is worth one thousand words". The contour plots can comprehensively exhibit the relationships between experimental responses and two variables by adding bio-oil and tall oil fatty acids. It is useful for visualizing the changing tendencies, but the changing rate displayed via the contours lines is difficult to detect. The 3D plots, from which the contour plot is derived, were applied to those plots having complex patterns to help understand the experimental reactions by exhibiting the shape of the response surface.

5.2.3.2 Bio-oil and tall oil fatty acids treatment effect on binder AAD-1

To evaluate the binder modification method by adding different bio-oils and tall oil into asphalt AAD-1, a two-way factorial experiment was performed three times. The experiment tested corn storver bio-oil additive with tall oil, oak wood bio-oil additive with tall oil, and switch grass bio-oil additive with tall oil. All three tests had the same experimental structure.

Binder AAD-1 is the experimental unit. The critical high, intermediate, and low cracking temperatures were measured as the experimental responses, and two PG ranges were calculated as well. The two conditions are:

- **Factor A-** tall oil fraction by weight, 0% and 0.18%, and
- **Factor B-** bio-oil fraction by weight, 0% and 6%.

There are four treatment combinations. Asphalt AAD-1 was randomly assigned to the treatment combinations and blended with the bio-oil and tall oil in varying percentages. Each blend was tested in triplicate to provide a measurement of random error. The JMP statistic software was used to analyze the data. The ANOVA model is mainly applied to detect whether the main effects of factors and the interaction effect are statistically significant. The ANOVA analysis of variance was used to detect the significant difference between the means of treatment responses.

The effect tests results for the model includes two main factors, Factor A (Tall oil fraction), Factor B (Bio-oil fraction), and the interaction (Tall oil fration *Bio-oil faction). These factors are summarized in Table 54 for all three ANOVA models established for unaged critical high temperature, the RTFO critical high temperature, PAV critical intermediate temperature, and BBR critical low temperature. The Type I error (α) of 0.05 was used for all statistical analysis and effect tests. An alpha value of 0.05 states that there is a five percent chance of rejecting the null hypothesis when it is in fact true.

Table 54. Effect tests results for the factors and the interaction term for AAD-1 binder

Binder AAD-1		Corn Stover Bio-oil	Oak Wood Bio-oil	Switch Grass Bio-oil
Effect on Unaged Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*sig*	*sig*
Effect on RTFO Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*sig*	*sig*	*non*
	Interaction	*non*	*non*	*sig*
Effect on PAV Critical Temp	Tall oil fraction	*sig*	*non*	*sig*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*non*	*sig*
Effect on BBR Critical Temp	Tall oil fraction	*non*	*non*	*non*
	Bio-oil fraction	*sig*	*sig*	*non*
	Interaction	*sig*	*sig*	*sig*

Sig : Significant effect on the response
Non : non significant effect on the response

The first order Fit model including the two main factors and the interaction term was used to predict the other combination treatment effects so that the response surface plot could be generated. Additionally, the Fit model does not only fit the two-way factorial experimental data, but also fits all experiment data as shown in Figure 34. The crossing symbol marks the data imported to the Fit model. The blank box means that no data was obtained for that treatment combination. In this way, two benefits may be accessed: 1. More data increases the ability and probability for forming the Fit model to make accurate predictions, and thus the probability to generate the incorrect conclusion because of the data outliers or bias could be reduced. 2. More testing data extends the application range.

		Factor B (Bio-oil Fraction)			
		0%	3%	6%	9%
Factor A (Tall oil Fraction)	0%	X	X	X	X
	0.09%		X		
	0.18%	X		X	
	0.27%				X
	0.36%	X			

Figure 34. Data resources for response surface plot and contour plot

The contour plots for the unaged critical temperature and RTFO critical temperatures (Figure 35) were created by assigning the bio-oil variable to the y-axes and tall oil to the x- axes.

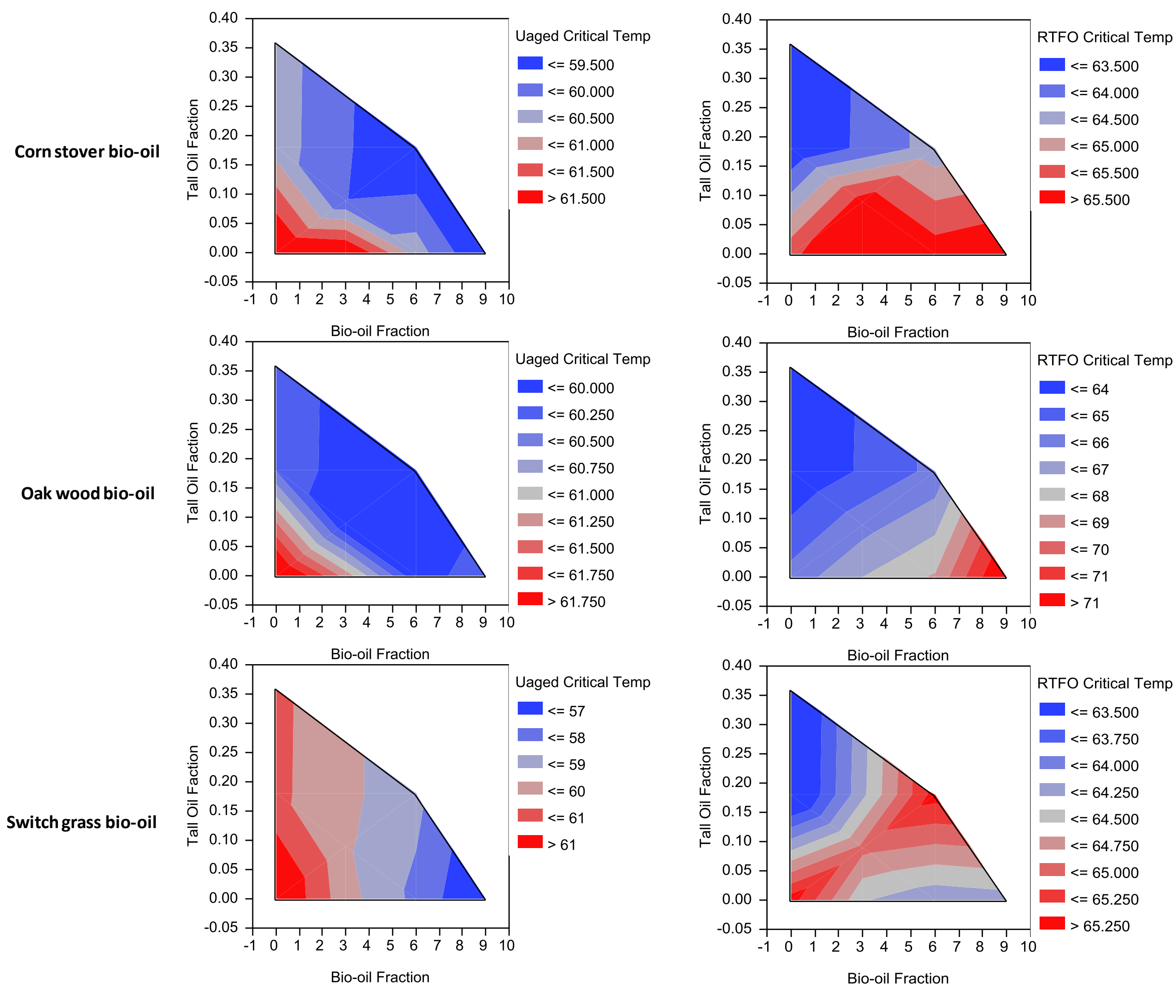


Figure 35. Unaged & RTFO Critical Temp contour plots for binder AAD-1

The color scheme depicted in the legend shows the temperature levels. The redder color represents higher temperature, and the bluer region marks the lower temperatures in degrees in temperature. The changing tendency from blue to grey to red indicates the temperature varying from relatively low to relatively high.

The contour maps in Figure 35 show the critical temperature changing tendency with the varying amount of bio-oil and tall oil fatty acids. Just as normal contour maps, the contour lines or curves have the same temperature level. Evenly spaced isotherm lines indicate the constant temperature changing rate. With a space between contours is as a sign of a gentle slope. Whereas closer contours indicate that temperature is changing at a great rate with the varying bio-oil/tall oil treatment combinations. The vector perpendicular to isotherms, so called gradient (∇f), represents a direction that the temperature changes most rapidly. The gradient that applied in this research exposes the bio-oil/tall oil dosage ratio resulting in the most rapid changes to the critical temperature. This can be used to find the most effective formula for adding bio-oil/ tall oil blends to increasing the RTFO critical temperature or performance grade. Additionally, on the other hand, the contrary application is to minimize the critical temperature grade change. The vector (u) perpendicular to the gradient (∇f) provides the bio-oil/tall oil dosage ratio that can minimize the temperature grade change. This can be applied to the situation when adding a bio-oil/tall oil blend is not possible to improve the low temperature property by decreasing the low critical cracking temperature, yet bio-oil can still be added to enhance the rutting resistant, which may cause the low critical cracking temperature to increase. Actually, it reveals a recipe for designing a bio-oil /tall oil blend which can maximize benefits at the high temperature and minimize the adverse side-effect for low temperatures. Another economic application of adding the bio-oil to minimize the material cost in a road paving project and at the same time to keep the same critical temperature as the neat binder, since the bio-oil could be more economical than asphalt binder. The application is easy to execute for the binder whose response surface is a slanted or oblique plane, since the gradient (∇f) and the vector (u) are constant numbers. If the response surface is a curved surface, then the surface model should be created and the gradient field can be generated. The gradient field can be used to optimize the binder modification.

With the exception of the switch grass bio-oil/ tall oil contour map for RTFO critical temperature having a saddle-shaped response surface, the other plots all have fairly planar surfaces for the experimental data. The parallel contour lines that are evenly spaced indicate a planar response surface that can be used to describe the temperature change. The estimated gradients (∇f) for each planar or fairly planar response surface are listed in Table 55.

Table 55. Estimate gradients (∇f) for AAD-1 binder

AAD-1	Unaged Temp Response Surface	RTFO Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , 2.5)	(100 , -7.5)
Oak Wood Bio-oil	(100 , 3.8)	(100 , -3)
Switch Grass Bio-oil	(100 , 0.8)	Not Flat

Since the contour plots set the x-axis as the amount of the bio-oil, and the y-axis as the amount of tall oil, the gradient (100, 2.5) suggests that by adding or reducing the amount of the bio-oil/tall oil in this ratio (2.5 gram of tall oil per 100 gram bio-oil)can result the maximum beneficial change in temperature. The negative ratio means that if one component is added, the other one should be reduced by that ratio, if the desire is to create the maximum temperature change.

Figure 36 illustrates the response surface representing the PAV and BBR critical temperatures when the AAD-1binder is treated with bio-oil /tall oil by varying amounts. All PAV response surfaces are fairly planar. The BBR response surfaces, however, are more complex.

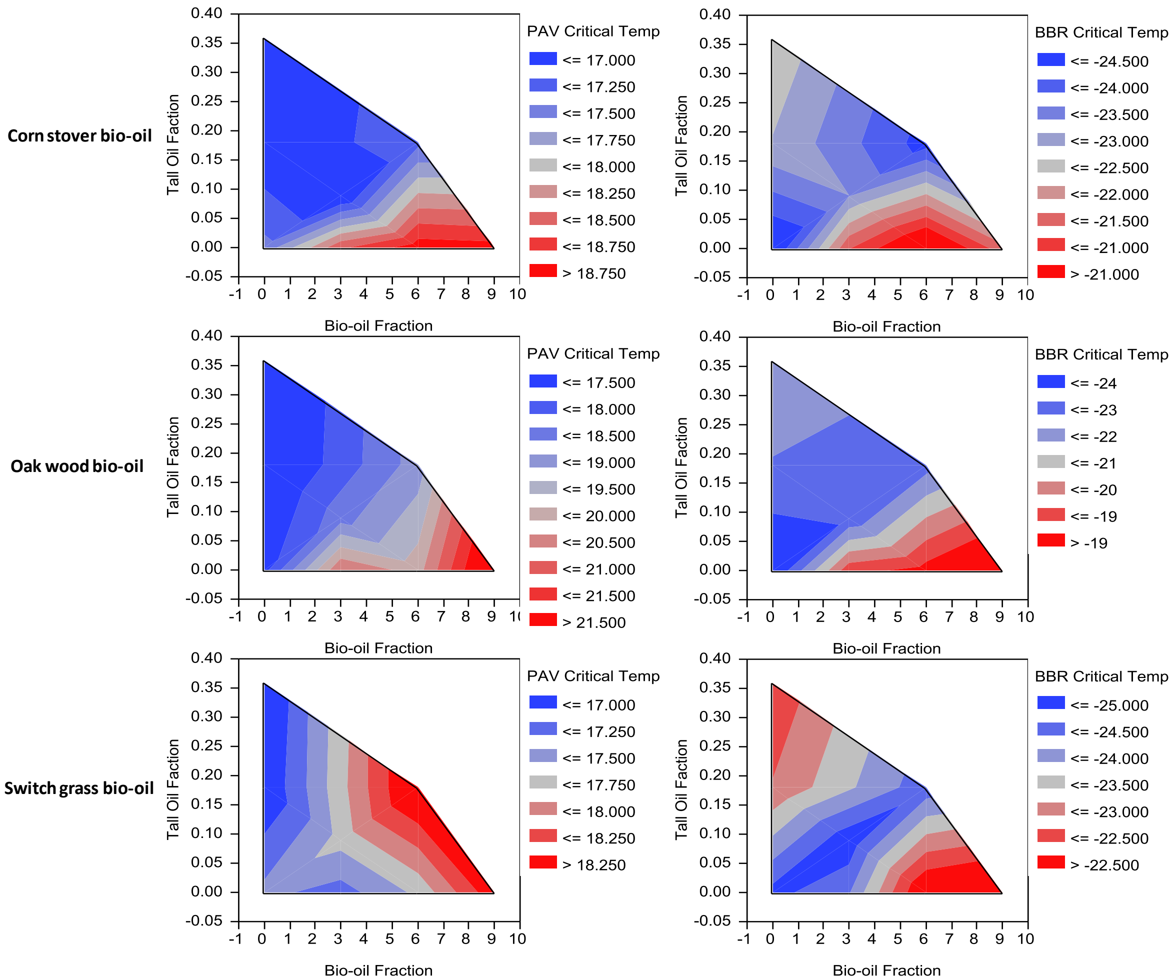


Figure 36. PAV & BBR Critical Temp contour plots for binder AAD-1

The BBR critical temperature data obtained from the corn stover and switch grass bio-oils with the tall oil blend modification treatment fit a saddle-shaped response surface with maximum and minimum values encountered at various combinations of bio-oil and tall oil. Table 56 shows the estimated gradients

Table 56. Estimate gradients (∇f) for AAD-1 binder

AAD-1	PVA Temp Response Surface	BBR Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , -3.8)	Not Flat
Oak Wood Bio-oil	(100 , -2.8)	Not Flat
Switch Grass Bio-oil	(100 , 2.3)	Not Flat

The overall performance grade ranges vary depending on the combinations of bio-oil/ tall oil. As shown in Figure 37, all contour plots for the AAD-1 binder modified by the bio-oil and tall oil present a saddle-shaped response surface with maximum RTFO PG range at appropriate bio-oil/tall oil rate which is about 100 to 3. This phenomenon does make sense. When just adding bio- oil, the BBR critical temperature increases, which could reduce the PG range. But by adding bio-oil, the RTFO high critical temperature increases, then the PG range does not change until increasing in high temperature by adding bio-oil, which eventually causes the PG range to decrease approximately at 2% bio-oil dosage.Only adding the bio-oil or tall oil, the PG range starts to decrease at small dosage. However, the tall oil extends the acceptability of the AAD-1 binder to take more bio-oil; adding to the binder makes the PG range less sensitive to the bio-oil.

Based on the 3D surface plots from JMP, none of the response surfaces are planar. In other words, constant gradients do not exist or cannot be detected. Table 57 lists the estimations.

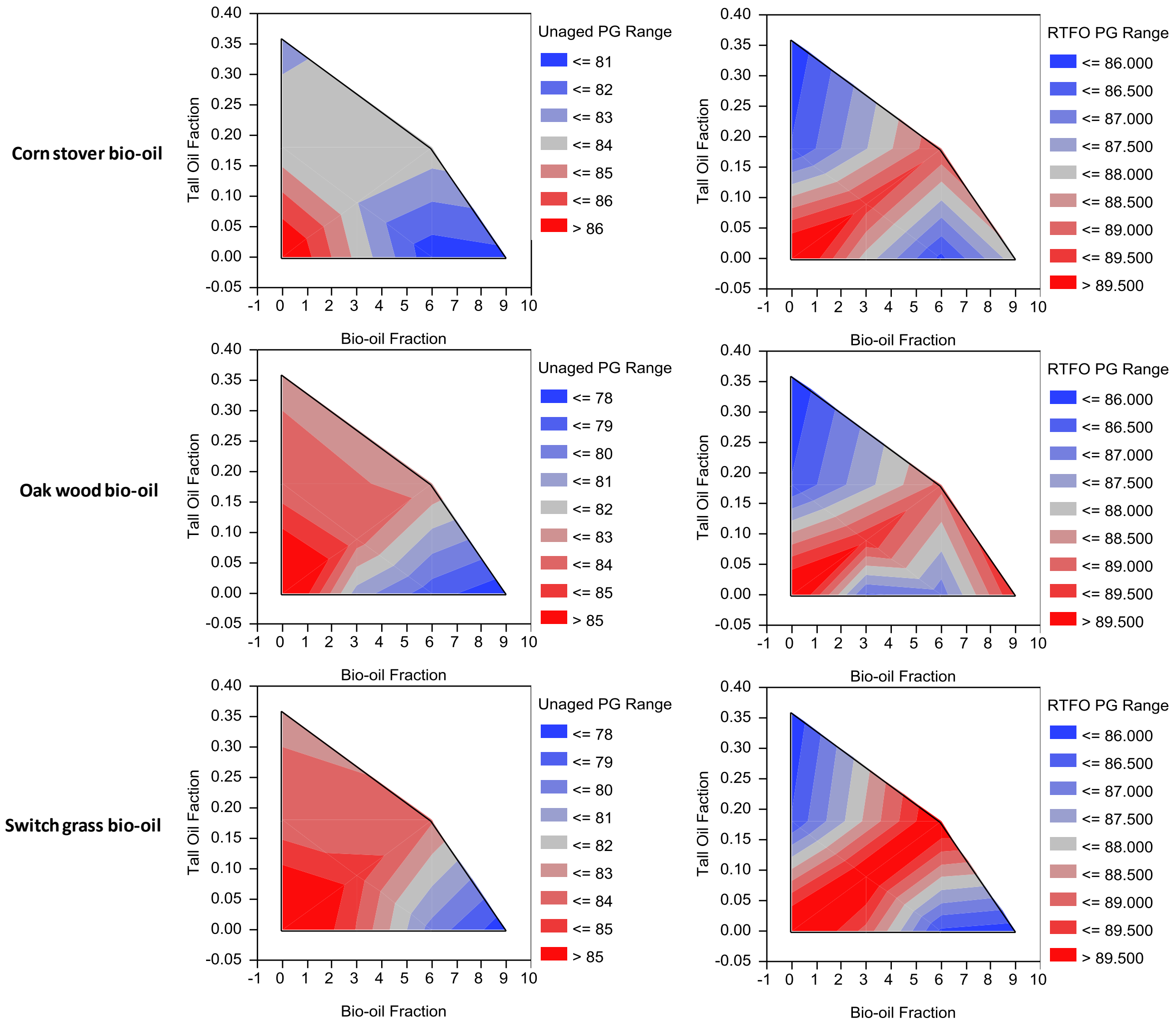


Figure 37. Unaged & RTFO Critical Temp Range contour plots for binder AAD-1

Table 57. Estimate gradients (∇f) for AAD-1 binder

AAD-1	Unaged Temp Range Response	RTFO Temp Range Response
Bio-oil Type Level	**Gradient ∇f**	**Gradient ∇f**
Corn Stover Bio-oil	Not Flat	Not Flat
Oak Wood Bio-oil	Not Flat	Not Flat
Switch Grass Bio-oil	Not Flat	Not Flat

The contour plots provide a method to visualize what happens to the experimental response individually. However, the general effect of adding tall oil to bio-oil modified binder is still of interest. The Fit model with two blockings and one variable is formed to evaluate whether the presence of a small amount of tall oil has a significant effect on the bio-oil modified binder. Therefore, the bio-oil modified binders are set as the benchmark to comparing with the tall oil treated bio-oil modified binders. The bio-oil with three levels (corn stover, oak wood and switch grass) is one experimental block and the bio-oil fraction with two levels (6% and 9%) is the second experimental block. Four critical temperatures and the PG range were evaluated as experimental responses. The testing results are presented in Table 58.

Table 58. Tall oil effect for adding in bio-oil modified binder AAD-1

AAD-1		No Tall Oil	Tall oil Presence
Effect on Unaged Critical Temp	Factor Level	A	B
	Mean oC	60.08	59.16
Effect on RTFO Critical Temp	Factor Level	A	B
	Mean oC	65.91	65.17
Effect on PAV Critical Temp	Factor Level	A	B
	Mean oC	18.72	17.84
Effect on BBR Critical Temp	Factor Level	A	B
	Mean oC	-21.00	-24.26
Effect on Unaged PG Range	Factor Level	B	A
	Mean oC	81.08	83.43
Effect on RTFO PG Range	Factor Level	B	A
	Mean oC	86.91	89.44

Levels not connected by same letter are significantly different.

As illustrated in Table 58, the tall oil has a pronounced effect on the AAD-1bio-oil modified binder, even despite the interaction between the bio-oil and the tall oil. The tall oil significantly makes the AAD-1 boil-oil modified binder softer at all aging stages, and results in decreasing the BBR critical temperature dramatically, meanwhile extending the unagd range as well as RTFO PG performance grade.

5.2.3.3 *Bio-oil and tall oil fatty acids treatment effect on binder AAM-1*

A similar experiment as the one testing the AAD-1 binder with bio-oil and tall oil was conducted using the AAM-1 binder. The experimental data were analyzed using the same approach used with the AAD-1 blends. Table 59 illustrates the results.

Table 59. Effect tests results for the factors and the interaction term for AAM-1 binder

Binder AAM-1		Corn Stover Bio-oil	Oak Wood Bio-oil	Switch Grass Bio-oil
Effect on Unaged Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*sig*	*sig*
Effect on RTFO Critical Temp	Tall oil fraction	*non*	*sig*	*non*
	Bio-oil fraction	*sig*	*sig*	*non*
	Interaction	*non*	*sig*	*non*
Effect on PAV Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*non*	*sig*	*non*
	Interaction	*sig*	*sig*	*sig*
Effect on BBR Critical Temp	Tall oil fraction	*sig*	*non*	*sig*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*non*	*sig*

Sig : Significant effect on the response
Non : non significant effect on the response

The contour maps illustrate the experimental results in Figure 38. With the exception of the response surface for the RTFO critical temperature obtaining from switch grass bio-oil mixture with tall oil treatments, the other unaged or RTFO temperature response surfaces are all fairly planar. Table 60 lists the gradients. The negative gradients indicate that between the bio-oil and tall oil, an increasing dosage for one of them, and reducing the amount of the other can result in a maximum temperature change. The relationship between the two factors is negative. The oak wood bio-oil and tall oil RTFO temperature surface plot is a good example. In order to increase the RTFO critical temperature, the most efficient way is to increase the bio-oil amount and using less tall oil. The switch grass bio-oil blends with the tall oil does not affect the RTFO critical temperature at the interval from 0 to 5% for bio-oil and 0 to 0.18% for tall oil.

Table 60. Estimate gradients (∇f) for AAM-1 binder

AAM-1	Unaged Temp Response Surface	RTFO Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , 0.6)	(100 ,-3.1)
Oak Wood Bio-oil	(100 , 1.9)	(100 , -2.8)
Switch Grass Bio-oil	(100 , -2.8)	Not Flat

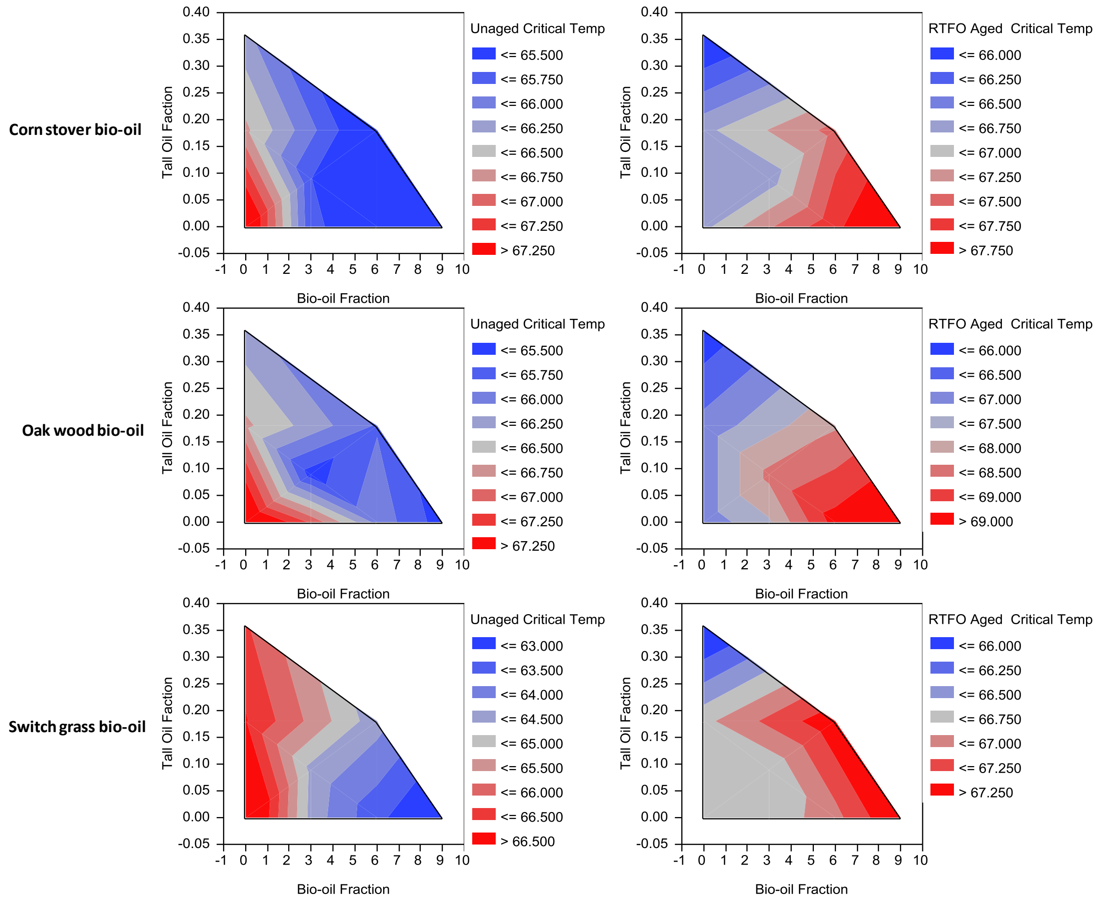


Figure 38. Unaged & RTFO Critical Temp contour plots for binder AAM-1

The response surfaces for the PAV and BBR critical temperatures are presented in Figure 39.

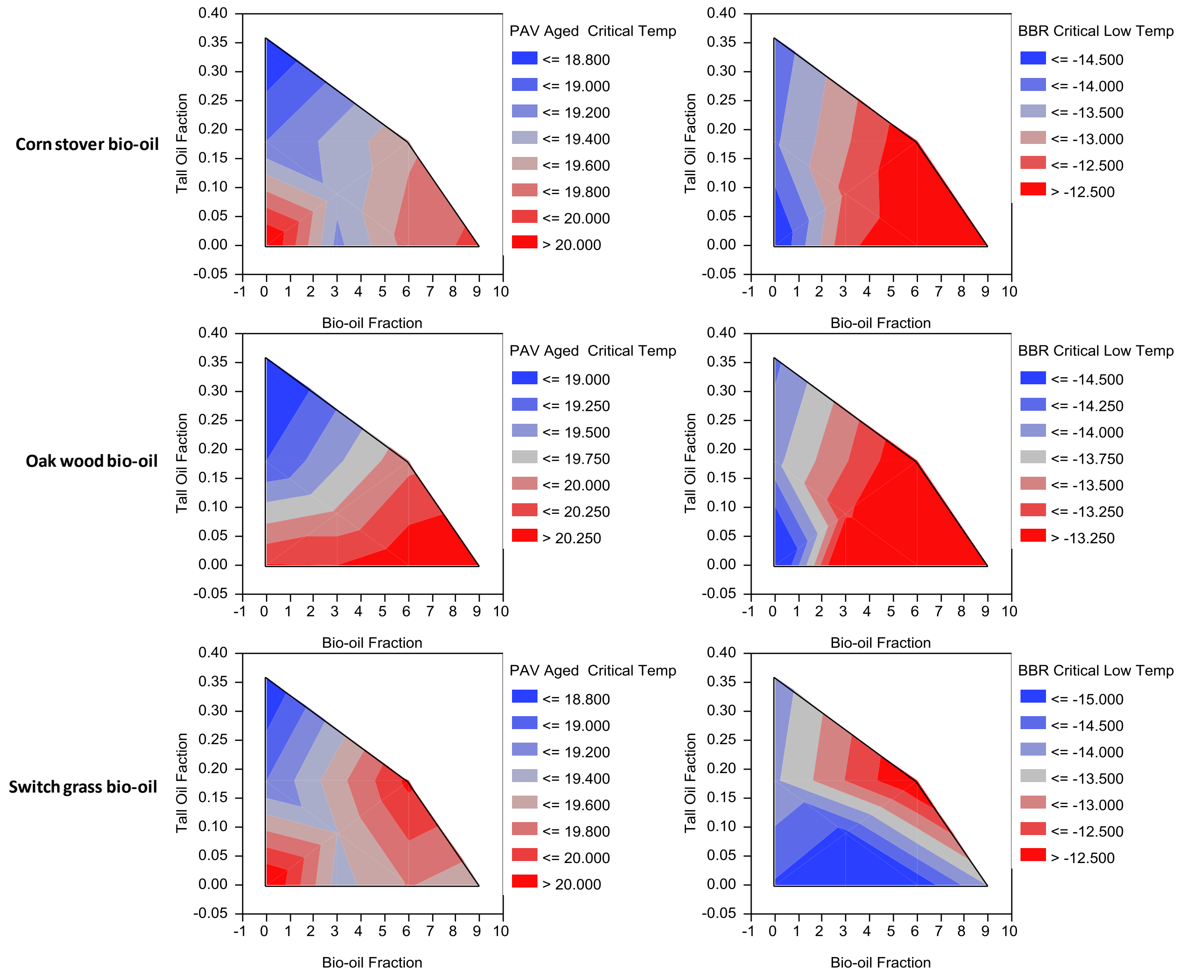


Figure 39. PAV & BBR Critical Temp contour plots for binder AAM-1

Table 61 lists the gradients. Except for the switch grass bio-oil could decreasing the BBR critical temperature by increasing the bio-oil dosages, the others two types of bio-oils (corn srover and oak wood) must reduce the dosage of bio-oil and add more tall oil to improve the low temperature properties. The most effective way to soften the AAM-1 binder and decrease the BBR critical temperature is to serve more tall oil and reduce the usage of the bio-oil at the same time. The corn stover and switch grass bio-oil blends with tall oil generate the saddle-shaped response surface for the PAV critical temperatures, which indicates the strong interactions between the bio-oil and the tall oil.

Table 61. Estimate gradients (∇f) for AAM-1 binder

AAM-1	PVA Temp Response Surface	BBR Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	Not Flat	(100 , -2.5)
Oak Wood Bio-oil	(100 , -3.3)	(100 , -2.5)
Switch Grass Bio-oil	Not Flat	(100 , 5.6)

The response surfaces for the unaged and RTFO critical temperature ranges are presented in Figure 40. Table 62 lists the gradients.

Table 62. Estimate gradients (∇f) for AAM-1 binder

AAM-1	Unaged Temp Range Response	RTFO Temp Range Response
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , -0.4)	(100 , 1.0)
Oak Wood Bio-oil	(100 , 2.6)	Not Flat
Switch Grass Bio-oil	(100 , 2.1)	(100 , 3.5)

The common method to extend the PG range for AMM-1 binder is using less tall oil. Adding corn stover bio-oil with or with tall oil will not benefit the binder's performance grade. Oak wood and switch grass bio-oil could widen the RTFO PG range with a low amount of tall oil. Modifying the AAM-1 binder without the tall oil may even do a better job in increasing the PG range, but the loss of the low temperature cracking resistance should be considered.

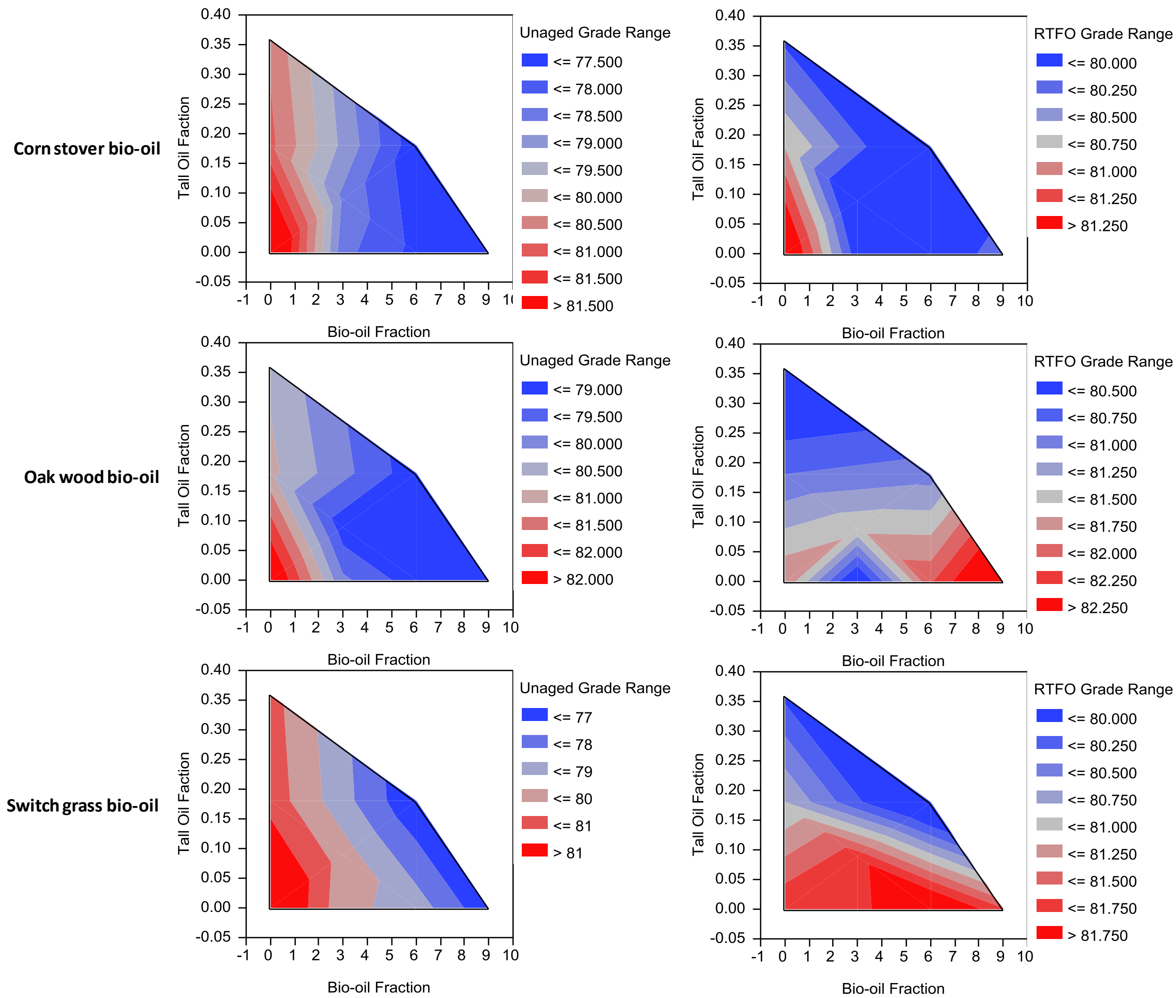


Figure 40. Unaged & RTFO Critical Temp Range contour plots for binder AAM-1

The contour plots provide the approach to visualizing what happens to the experimental response individually. But one should still be interested in the general effect by adding tall oil to bio-oil modified binder. No significant effects are detected by adding tall oil into AAM-1 bio-oil modified binder (Table 63). Many possible reasons can cause this result. But at least one conclusion can be made: the tall oil effect is not obvious.

Table 63. Tall oil effect for adding in bio-oil modified binder AAM-1

AAM-1		No Tall Oil	Tall oil Presence
Effect on Unaged Critical Temp	Factor Level	A	A
	Mean oC	65.18	65.04
Effect on RTFO Critical Temp	Factor Level	A	A
	Mean oC	67.50	67.34
Effect on PAV Critical Temp	Factor Level	A	A
	Mean oC	19.74	19.66
Effect on BBR Critical Temp	Factor Level	A	A
	Mean oC	-13.03	-13.42
Effect on Unaged PG Range	Factor Level	A	A
	Mean oC	78.61	78.07
Effect on RTFO PG Range	Factor Level	A	A
	Mean oC	80.93	80.37

Levels not connected by same letter are significantly different.

5.2.3.4 Bio-oil and tall oil fatty acids treatment effect on binder LPMB

The additions of the bio-oil/tall oil to the LPMB binder were analyzed similar to AAD-1 and AAM-1 as binder as the experimental design was exactly the same. The effect tests results are presented in Table 64.

The response surfaces for original unaged and RTFO aged critical high temperatures are presented in Figure 41. For the unaged critical temperatures, the bio-oil makes the LPMB binder softer. However the tall oil has limited effect on the unaged critical high temperatures.

Table 64. Effect tests results for the factors and the interaction term for LPMB binder

Binder LPMB		Corn Stover Bio-oil	Oak Wood Bio-oil	Switch Grass Bio-oil
Effect on Unaged Critical Temp	Tall oil fraction	*non*	*non*	*non*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*sig*	*sig*
Effect on RTFO Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*non*	*sig*	*sig*
	Interaction	*sig*	*sig*	*sig*
Effect on PAV Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*non*	*sig*	*non*
	Interaction	*sig*	*sig*	*non*
Effect on BBR Critical Temp	Tall oil fraction	*sig*	*sig*	*sig*
	Bio-oil fraction	*sig*	*sig*	*sig*
	Interaction	*sig*	*non*	*non*

Sig : Significant effect on the response
Non : non significant effect on the response

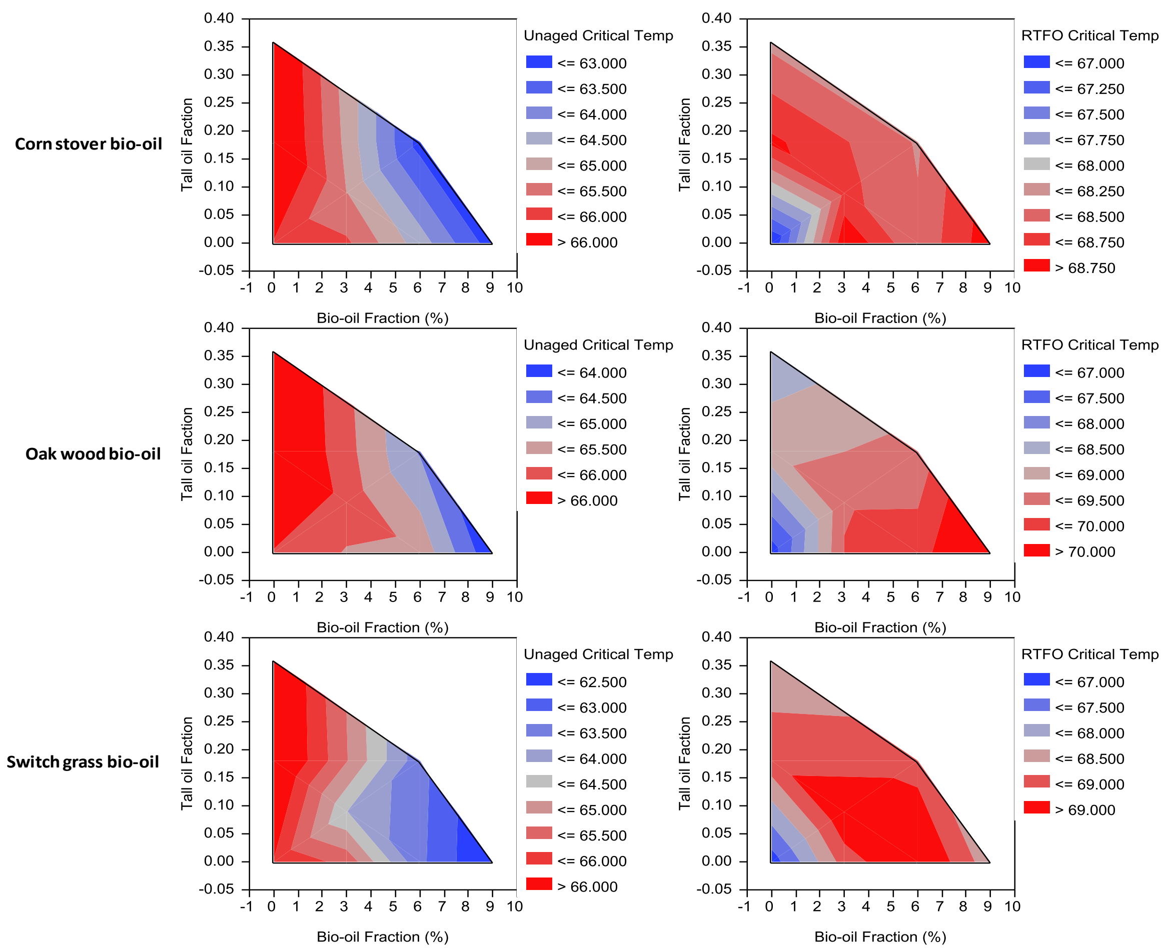


Figure 41. Unaged & RTFO Critical Temp contour plots for binder LPMB

The gradients (Table 65) are all positive for all bio-oil in RTFO temperature response surface. This indicates that the bio-oil and tall oil have some common effects in changing the RTFO critical temperature. Higher amounts of bio-oil with more tall oil at certain percentages result in increasing the RTFO critical temperature.

Table 65. Estimate gradients (∇f) for LPMB binder

LPMB	Unaged Temp Response Surface	RTFO Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , 2.9)	(100 , 2.9)
Oak Wood Bio-oil	(100 ,-1.3)	(100 , 1.4)
Switch Grass Bio-oil	(100 , -1.9)	(100 , 1.1)

The response surfaces for PAV and BBR critical temperature are presented in Figure 42 and Table 66 lists the gradients.

Table 66. Estimate gradients (∇f) for LPMB binder

LPMB	PVA Temp Response Surface	BBR Temp Response Surface
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	Not Flat	(100 , -1.4)
Oak Wood Bio-oil	(100 , -2.5)	(100 , -1.9)
Switch Grass Bio-oil	Not Flat	Not Flat

As shown in Figure 42, notice that there is a temperature decrease with the 3% bio-oil treatment to the LPMB binder without adding tall oil, and it happens for all three diffident bio-oils. It indicates the bio-oils could first soften the LPMB binder at small dosage and then harden the binder when more than 3% dosages are added. But the tall oil additive has a constant softening effect to the LPMB binder. Then combination effect to the PAV critical temperature depends on the bio-oil and tall oil ratio.

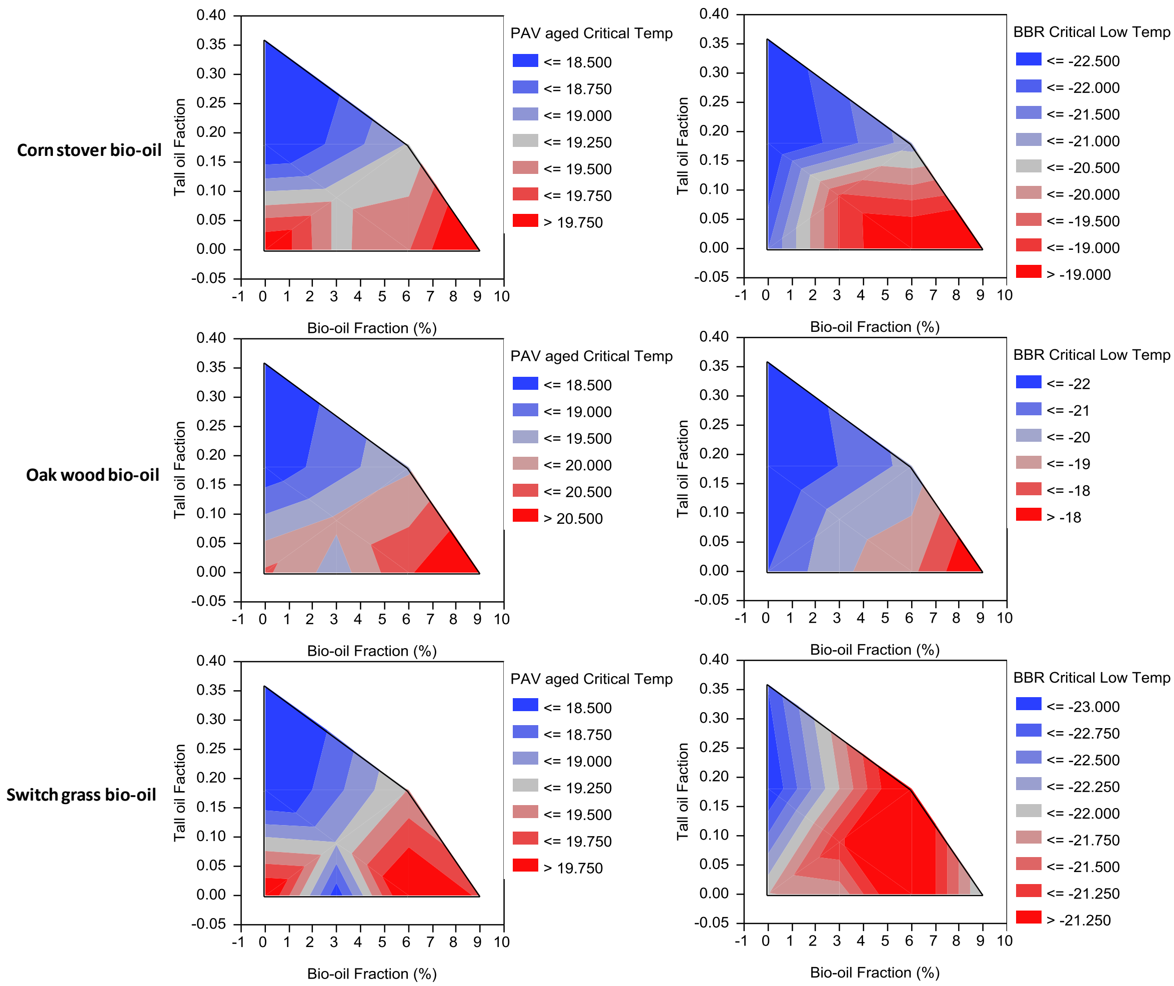


Figure 42. PAV & BBR Critical Temp contour plots for binder LPMB

The response surfaces for unaged and RTFO critical temperature are presented in Figure43 and Table 67 lists the gradients. The gradients are the entire negative for uanged and RTFO critical temperature response surfaces. The most effective way to not use the PG range is to decline the bio-oil dosage and increasing the tall oil percentage in the blend.

Table 67. Estimate gradients (∇f) for LPMB binder

LPMB	Unaged Temp Range Response	RTFO Temp Range Response
Bio-oil Type Level	**Gradient f**	**Gradient f**
Corn Stover Bio-oil	(100 , -1.9)	(100 , -4.3)
Oak Wood Bio-oil	(100 , -1.9)	(100 , -2.7)
Switch Grass Bio-oil	Not Flat	Not Flat

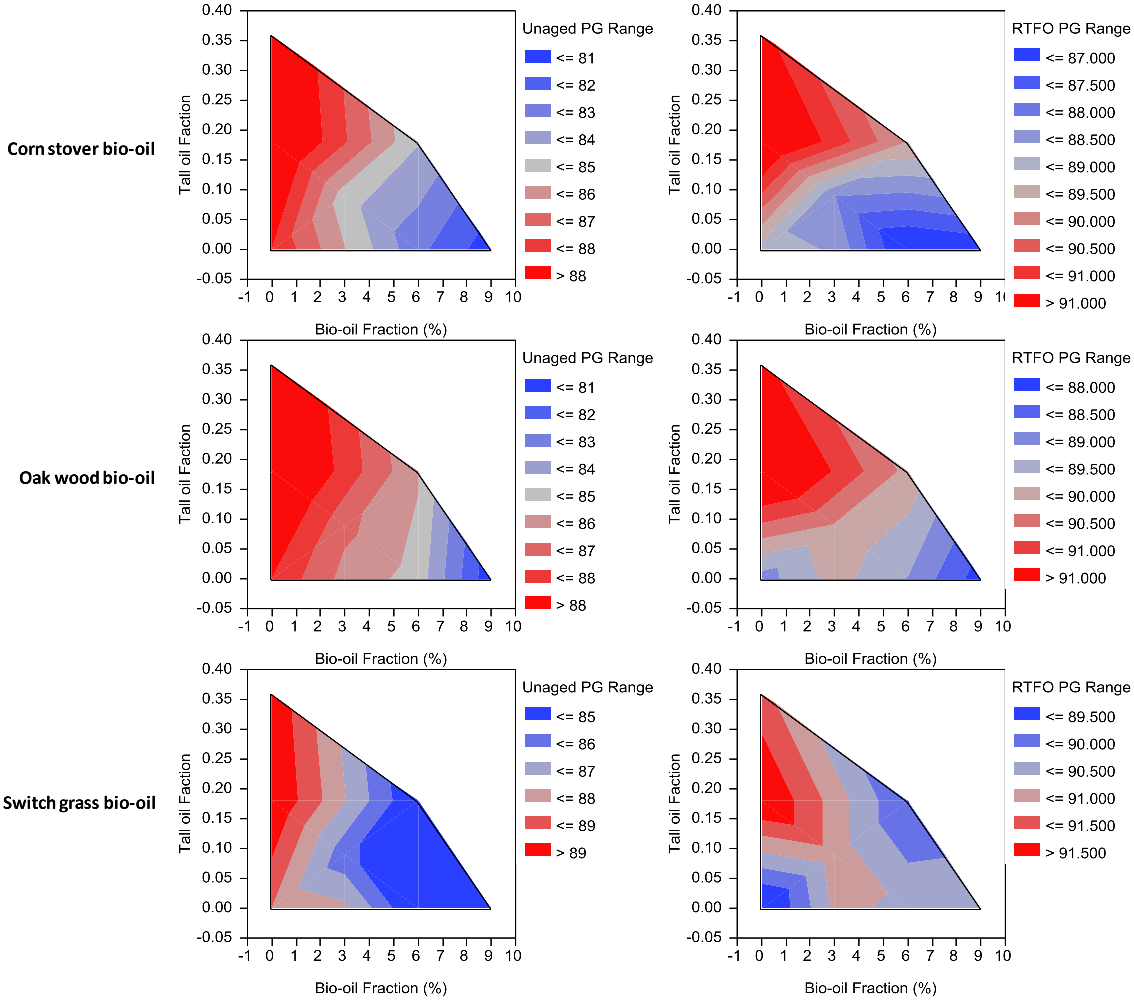


Figure 43. Unaged & RTFO Critical Temp Range contour plots for binder LPMB

The contour plots provide the approach to visualizing what happens to the experimental response individually. But one should still be interested at the general effect by adding tall oil to bio-oil modified binder. The tall oil demonstrates a significant effect to the bio-oil polymer modified LPMB binder, which softens the bio-oil modified LPMB at the un-aged critical temperature and lowers the BBR critical temperature. The tall oil displays some recovery ability to heal the decrease in the BBR critical temperature through bio-oil modification.

Table 68. Tall oil effect for adding in bio-oil modified binder LPMB

LPMB		No Tall Oil	Tall oil Presence
Effect on Unaged Critical Temp	**Factor Level**	A	B
	Mean oC	64.85	64.21
Effect on RTFO Critical Temp	**Factor Level**	A	A
	Mean oC	65.91	65.17
Effect on PAV Critical Temp	**Factor Level**	A	A
	Mean oC	19.48	19.25
Effect on BBR Critical Temp	**Factor Level**	A	B
	Mean oC	-19.92	-20.64
Effect on Unaged PG Range	**Factor Level**	A	A
	Mean oC	84.85	84.77
Effect on RTFO PG Range	**Factor Level**	A	A
	Mean oC	89.59	89.07

Levels not connected by same letter are significantly different.

5.2.3.5 <u>Summary of effect evaluation</u>

The tall oil behaves as a low temperature performance enhancement for the bio-oil modified AAD-1 binder. The LPMB modified by bio-oil and tall oil extends the overall PG grade not only by enhancing the rutting resistance but also by improving low-temperature cracking performance.

6 ASPHALT MIXTURE PHYSICAL PERFORMANCE

6.1 Dynamics modulus

To evaluate the HMA mixture using bio-oil modified binder, the 9% oak wood bio-oil modified binder, which is commonly beneficial or neutral for every binder, was selected to mix with aggregate for dynamic modulus testing. Figures 44, 45, and 46 present the 21ºC dynamic modulus master curves for the 9% oak wood bio-oil modified binders (AAD-1, AAM-1, and LPMB).

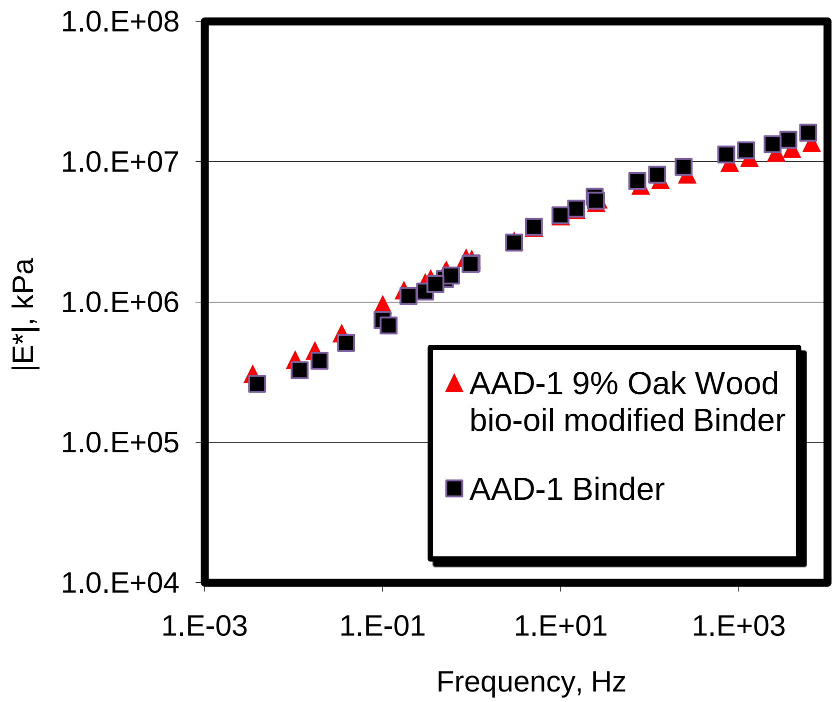


Figure 44. AAD-1 master curve

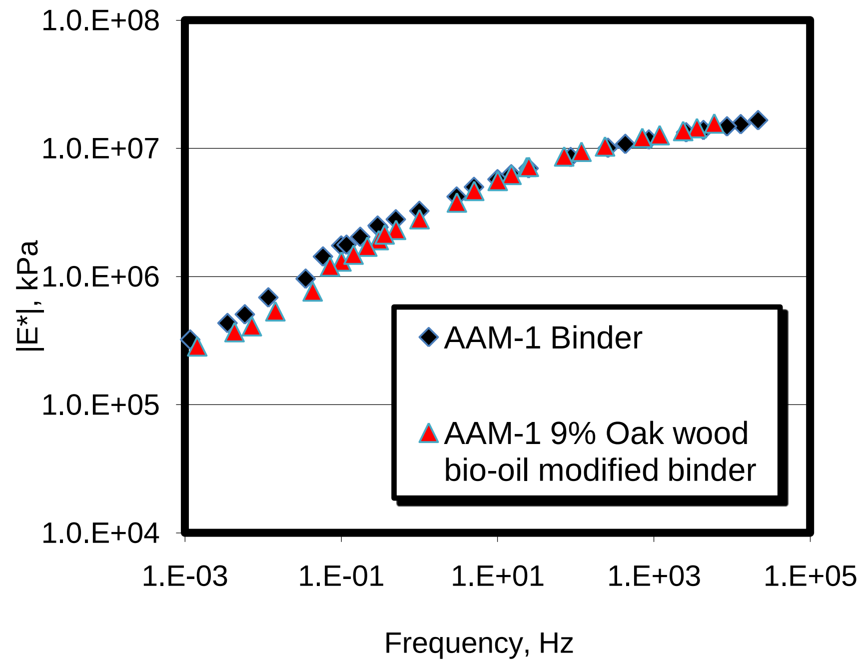


Figure 45. AAM-1 master curve

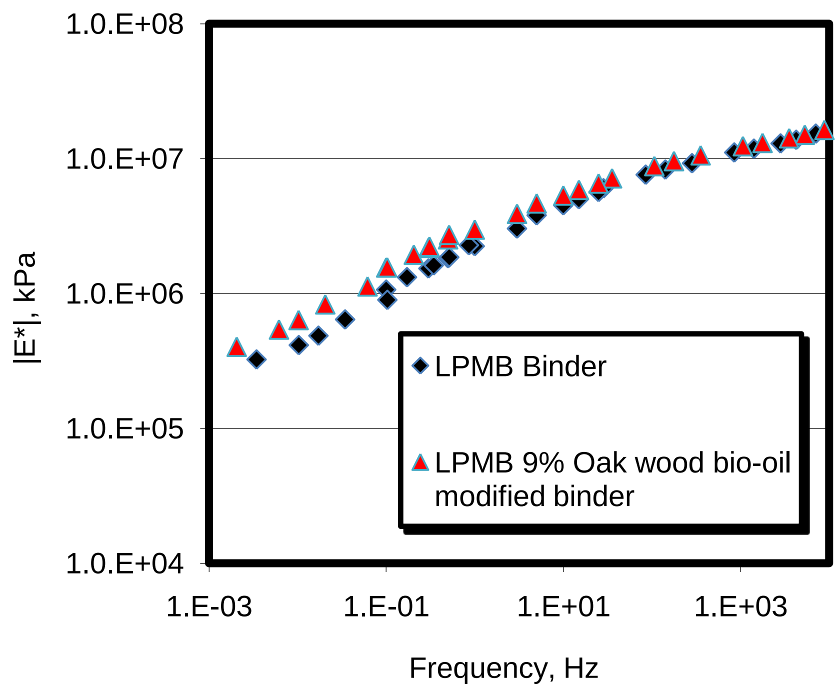


Figure 46. LPMB master curve

The differences for the E* values between initial binder and the bio-oil modified binder can be seen from the master curves. As shown in Table 5 in chapter 4, the 9% oak wood treatment improved the RTFO critical high temperatures by 7.1°C for AAD-1, 3.0°C for AAM-1, and 4.9°C for LPMB. Based on the sensitivity analysis, using stiff asphalt binders is an effective way to increase the dynamic modulus values (Xiang Shu, Baoshan Huang 2007). This statement is true for the AAD-1 and LPMB, but not for the AAM-1 binder mixture. The stiffer binder, AAM-1, modified by 9% oak wood has a relatively smaller modulus than initial AAM-1 binder. One possible explanation is that the 3°C increment in critical temperature is not sufficient. It is clear that bio-oil modified LPMB mixtures have advantages in low frequency or high temperature environments. Additionally, the bio-oil modified AAD-1 mixture seems to have potential benefit for resisting fatigue at intermediate-temperatures and thermal cracking at low temperatures. The AAD-1 mixture also has high frequency ambience, since the E* for the bio-oil modified AAD-1is smaller than that of the initial one (Qunshan Ye *et al*. 2009).

6.2 Flow number

A statistical analysis of the flow number mean for the asphalt mixtures were performed on the different binder comparisons. An alpha level of 0.05 was selected for the two-sample student's t-test.

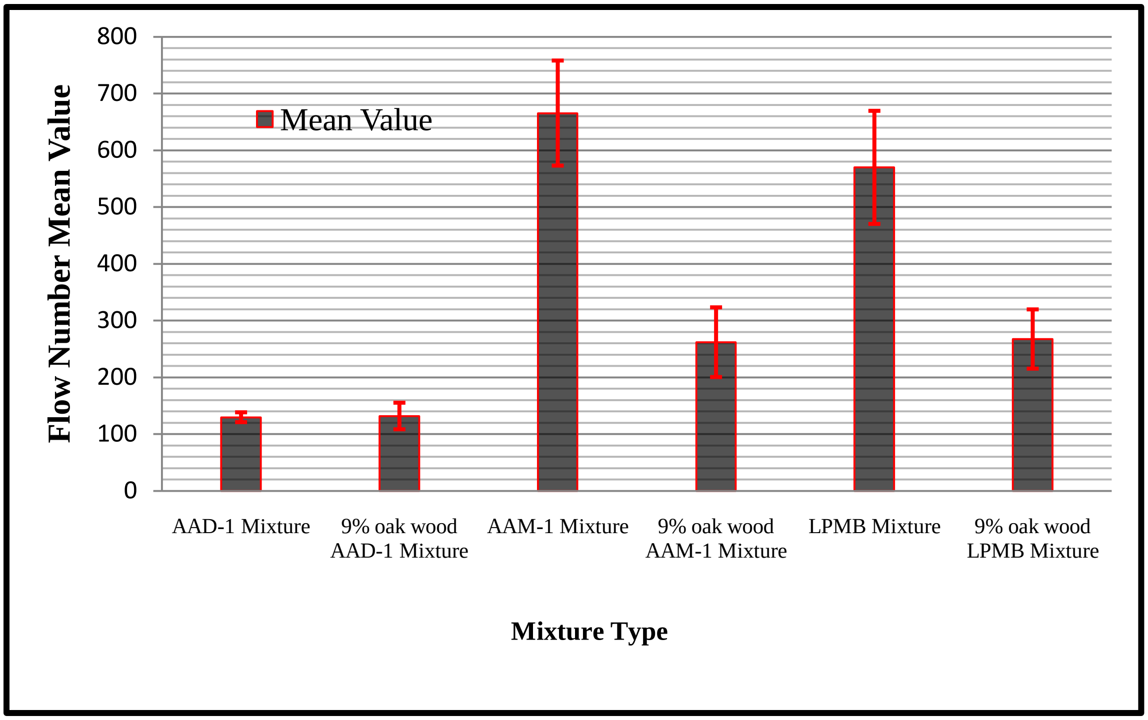


Figure 47. Summary of flow number mean value and standard deviation

Figure 47 summarized the average flow number performance test results for each oak wood bio-oil/binder combination mixture group. The red lines showed one standard deviation from the sample mean.

Table 69 provides the details for the t- test results for the flow number sample means comparison. The bi-oil modified binder AAD-1 mixture has no different flow number valuse than the neat AAD-1 binder mixture. However, the bio-oil modified AAM-1 and LPMB binder mixture had statistically significant smaller flow number values than the mixtures containing the AAM-1 and LPMB binders without bio-oils. This illustrates that the mixtures with the bio-oil modified AAM-1 and LPMB binders on average moved into the tertiary flow earlier and reached the minimum strain rate faster than the mixtures with the original binders. All mixtures were compacted to +/- 1% air void and for the same aggregate gradation at this effective experiment testing temperature. However, this statistic only presents the correlations, not the consequences between the bio-oil modified binders with flow numbers. The only conclusion that could be generated based on the students' t-test for comparing flow number mean values was that the discrepancy for the average flow number was statistically significant, which means the difference was not the result of random error but the experimental treatment. It might be the treatment of the different binders, or the treatment of different air voids, or some other variables not included in the control. It was confirmed that there was some difference for the flow number; however, the reason was not clear. The possible explanations are given later in this report, when talking about the impact of air voids on the flow number test results.

Table 69. Students' test data for flow number mean value comparison

Sample Name	FN Value	t Ratio	Prob-value	Statistically Significant
AAD-1 Mixture	129.4	-0.19707	0.8487	No
9% oak wood AAD-1 Mixture	131.6			
AAM-1 Mixture	665.25	7.885724	0.0001	**YES**
9% oak wood AAM-1 Mixture	261.6			
LPMB Mixture	569.6	6.012035	0.0009	**YES**
9% oak wood LPMB Mixture	267.2			

Another way to look at the flow number test data was to find the number of cycles for the 10,000 micro strains. This indicates for the loading criteria used, 60 Kpa, the number of load cycles a test sample can tolerate prior to obtaining 10% strain. As can be seen in the Table 8, it coincides with Figure 70, but just in different cycles scale.

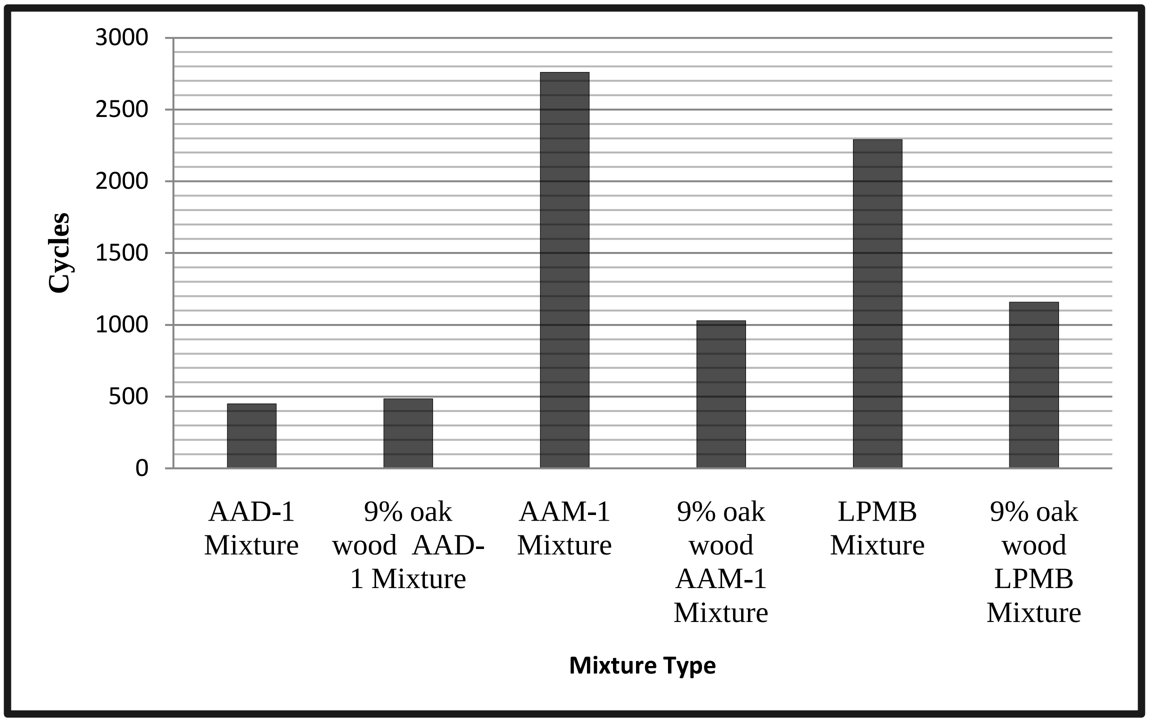


Figure 48. Loading Cycle at 10,000 micro-strain

According to the flow number testing data, the plots for the accumulated strain versus loading cycle number are illustrated in Figure 49 through 51.

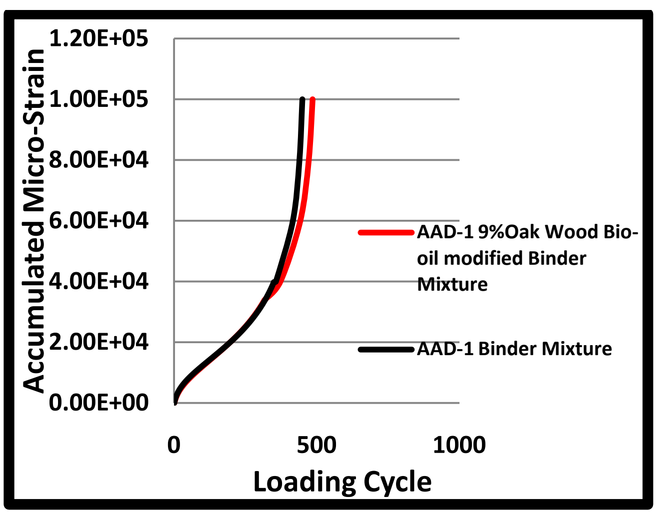


Figure 49. Accumulated Micro-Strain Curve for AAD-1

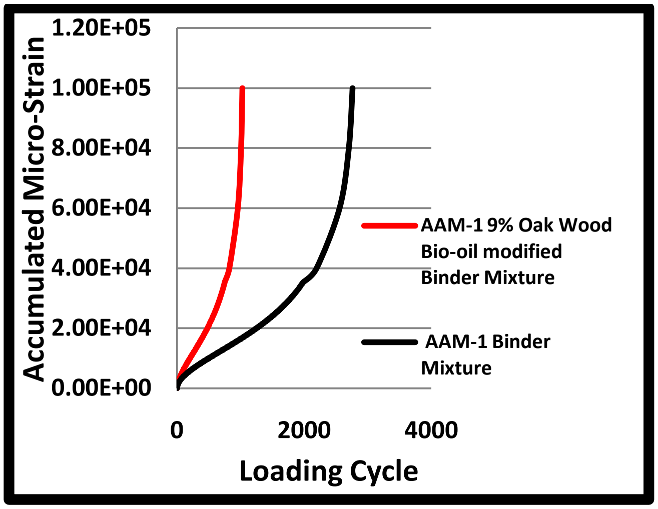


Figure 50. Accumulated Micro-Strain Curve for AAM-1

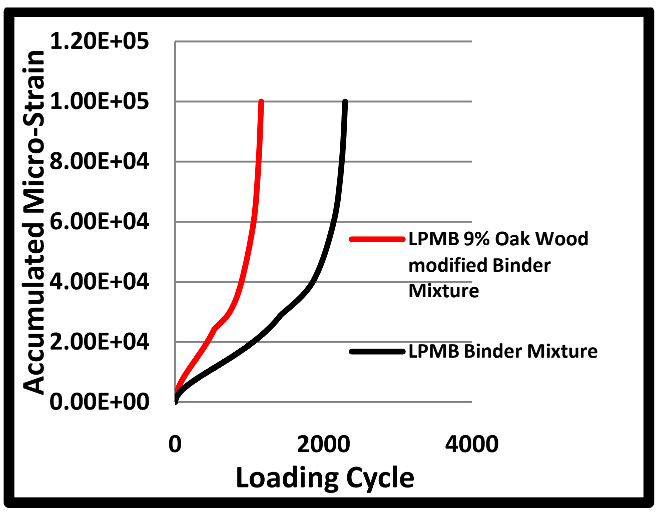


Figure 51. Accumulated Micro-Strain Curve for LPMB

With some limited variability in air voids (+/- 1%) which could not be controlled in specimen preparation, Figures 49, 50 and 51 exhibited that the asphalt mixtures composed of bio-oil modified binders were more sensitive to the loading and tended to yield larger deformation at the 37^{o}C effective experimental testing temperature, except the bio-oil modified AAD-1. This *conclusion* was not compatible with the dynamic modulus test data shown in Figures 44, 45, and 46, which specified after blending with bio-oil, the modified LPMB binder mixtures should be stiffer at high temperature condition and the modified

AAM-1 binder mixtures may become softer but did not statistically significantly decrease. Moreover, this *conclusion* for LPMB did not show any relationship to the DSR binder test data. The DSR data indicated a higher critical temperature for bio-oil modified LPMB binder than the LPMB binder alone.

Very important backgrounds should document out and mentioned again were that those accumulated micro-strain curves were graphed based on the average data values and those testing SPT cone specimens had some variations on the air voids around 1% difference. In the ensuing paragraphs, the conflict between the results and thus conclusions for the flow number, DSR and dynamic modulus tests are explained, mainly due to the variability of the air voids.

After plotting the air voids versus flow number, as can be seen in Figure 52, three main relationships (correlations) are clearly presented. Furthermore, the correlations were confirmed to be statistically important by conducting a JMP fit model analysis.

First, those minor differences in air voids (~0.5%) were able to influence the measured flow number tremendously. When the air voids increase, the flow numbers decrease if the other factors like the binder rheological properties and aggregate size were eliminated by utilizing exactly the same materials in the experiment or at least constrained the outside influence by using homogeneous materials. Second, the stiffer binder had higher flow number values if the air voids for the testing samples were the same. The red line indicates the mixtures whose binder critical temperature was above 64 ^{o}C. The blue line reflects the mixtures whose binder critical temperature was below 62 ^{o}C. A fair relationship between DSR critical temperatures representing the binder rheological properties with the mixture's properties was observed. The red line was above the blue line. Additionally, those asphalt mixtures whose binders have higher critical temperatures tend to be more sensitive to the air voids than those using softer binders. For the red line, a 0.5 % air voids change was correlated with a change of 500 load cycles in flow number. For the blue line, a 0.5 % air voids difference had approximately a change of 50 flow number load cycles.

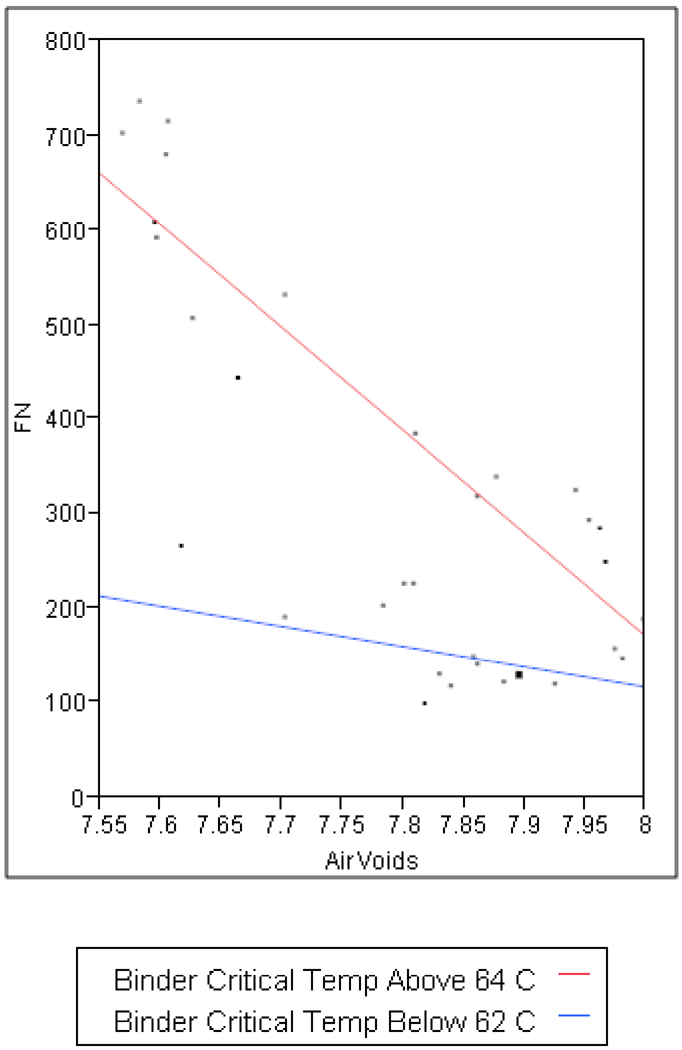


Figure 52. Flow Number versus Air Voids

Therefore, comparing the flow number was only applicable if the asphalt mixtures possessed very similar air void content. If the air voids are different for each comparison group, the results can be complex. Both effects of the binder rheological properties and mixture air voids on the flow number test results should be considered. The outcomes depend upon the scale of the differences in the air voids and binder critical temperature together. This can be used to explain the differences between the flow number test results with the DSR and dynamic modulus test data. It is fair for the higher critical temperature binder mixtures to have lower flow number value, if the air voids for the mixtures are not the same. The *conclusion* shown in the Figure 49, 50 and 51 is thus misleading.

At this moment, attention should highlight on whether the bio-oil modification treatment benefits the asphalt mixture and increases the flow number if the specimens all have same air void and gradation. After plotting out the graph of flow number verses air voids for each binder (AAD-1, AAM-1and LPMB), the positive answers were found and the exciting and interesting relationships are illustrated in Figures 53 and 54.

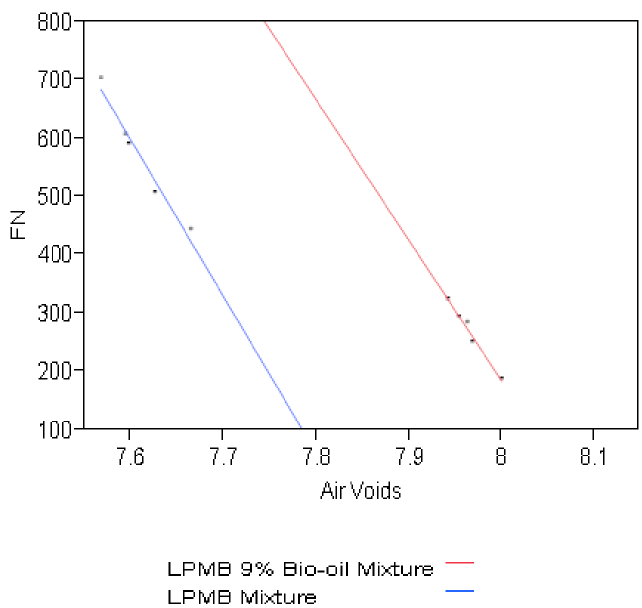


Figure 53. Flow Number versus Air Voids

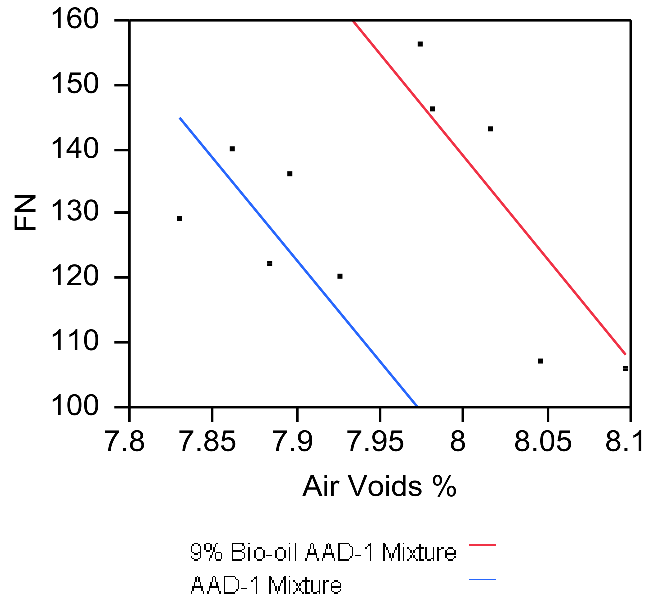


Figure 54. Flow Number versus Air Voids

LPMB binder's data is examined for an example. From the Figure 53, the red line is formed by the bio-oil modified binder mixture points and the blue line is given by the neat binder mixtures. The points for the blue line are located around 560 FN (flow number) and the points for the red line are focused about 250 FN. As the flow number comparison documented in previous paragraphs, the mean flow number for the bio-oil modified binder mixtures is lower than the neat binder mixtures. However, just as be discussed above, this is because of the difference in the air voids. The average air voids for the blue line points is about 7.61 % and 7.95% for the red line points.

It means that if both of the bio-oil modified mixture and neat binder mixture have the same air voids, the flow number for the bio-oil modified mixture would be higher. The Figures 53 and 54 indicate the benefits provided by the bio-oil modified binder to the asphalt mixture.

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The bio-oil modified binders are stiffer than the initial “base” binders when subjected to the aging process and this shows benefits for rutting resistance. Conversely, the stiffer bio-oil modified asphalt usually sacrifices some ability to prevent low-temperature thermal cracking. The overall performance grade ranges vary depending on the combinations of three different binders and bio-oils. However, HMA testing results initially do not appear to agree with the binder test results.

The tall oil demonstrates some beneficial ability to heal the increase in the BBR critical temperatures introduced by bio-oil modification when adding to bio-oil modified binder AAD-1 and LPMB. This effect is not apparent in bio-oil modified AAM-1 binder.

Both of the effects coming from binder rheological properties and mixture air voids should be considered when comparing the flow number test results. The one dominates the outcomes depending on the scale of the difference in air voids and binder critical temperature together. The bio-oil modification is estimated to increase a mixture’s flow number and improve the performance.

7.2 Recommendations

In the asphalt industry, the desired experimental outcomes are to maximize the high critical performance temperatures, minimize low critical performance temperatures, or widen the range of the performance grades for the asphalt binder balancing economics. For the asphalt mixtures, the desired results are complex, depending on the other considerations.

Processing the multiple comparisons tests from the ANOVA model identifies the "best" bio-oil and tall oil fatty acids treatment combinations. The "best" treatment combination considered from one perspective may inhibit other properties or benefits that might be important. Based on the design criteria and other desires such as economic opportunity, a more flexible binder modification design guide can be provided. The prediction and the contour profilers should be introduced to assist in the guide. RSM is a mathematical and statistical method developed for modeling phenomena and to find combinations of multiple experimental factors that will possibly lead to optimum responses and was first developed by Box and Wilson in 1951.

When the bio-oil and tall oil fatty acids are administered to the asphalt binder for achieving certain criteria, the response surface contour map (Figure 55) generated by JMP based on the mathematical model illustrate the "sweet" spot where all specifications are met.

This constraint shading map (contour map) can identify the possible bio-oil and tall oil combinations to satisfy different desired criteria. Based on this map, other researchers are able to locate the possible treatment combinations and modify the asphalt binder to maximize the economical interests without sacrificing the asphalt performance quality. Basically, the constraint shading map combines the contour plots of desired experimental responses and shade area that do not meet the desired criteria. Take for example, identifying the possible treatment combination zones for producing a better AAD-1 binder by adding tall oil ranging from 0% to 0.36% by weight and corn stover bio-oil in the fraction varying from 0% to 9% by weight. The desired modification is described as obtaining the higher RTFO critical temperature and the lower BBR critical cracking temperature compared with the initial neat binder. The initial AAD-1 binder has an average RTFO critical temperature of 65.38 °C and a low BBR cracking temperature at -25.18 °C. As illustrated in Figure 50, when the 65.38 °C is set as the low limit for RTFO critical temperature on the constraint shading map, the area where the treatment combinations for the RTFO critical temperature lower than 65.38 °C will be shaded by one color. The white region indicates the recommended treatment combinations that result in the RTFO critical temperatures being higher than the lower limit settings.

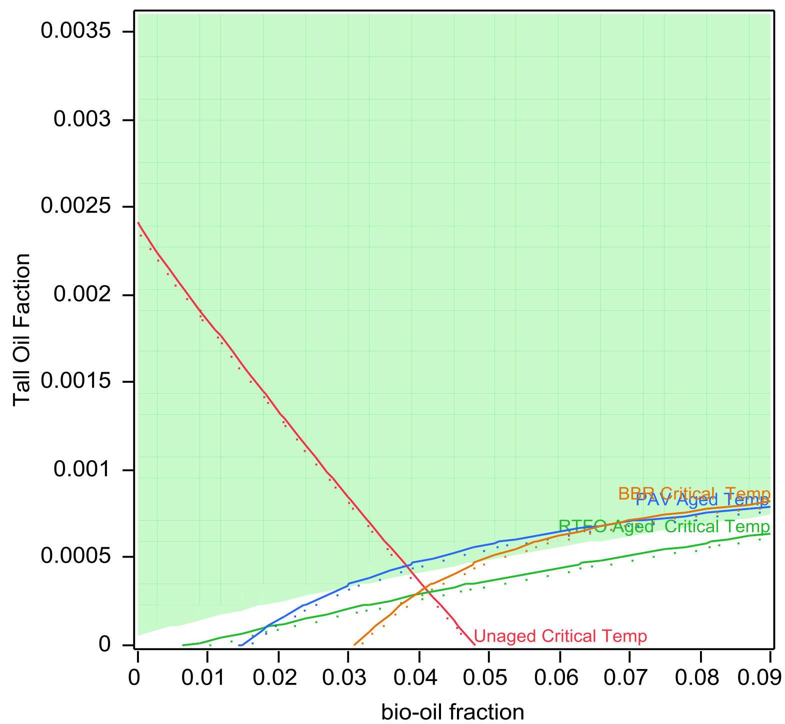


Figure 55. Constraint shading map for AAD-1 with corn stover bio-oil and tall oil

After the other constraint for the BBR critical temperature is imported into Figure 56, no blank area was identified as a result of none of feasible zone that can meet both desired criteria. Figure 52 illustrates the feasible zone representing the possible bio-oil with tall oil treatment combination that can decrease the BBR critical temperature. As one can see, there is no overlap between the Figure 55 and Figure 57 for the blank area.

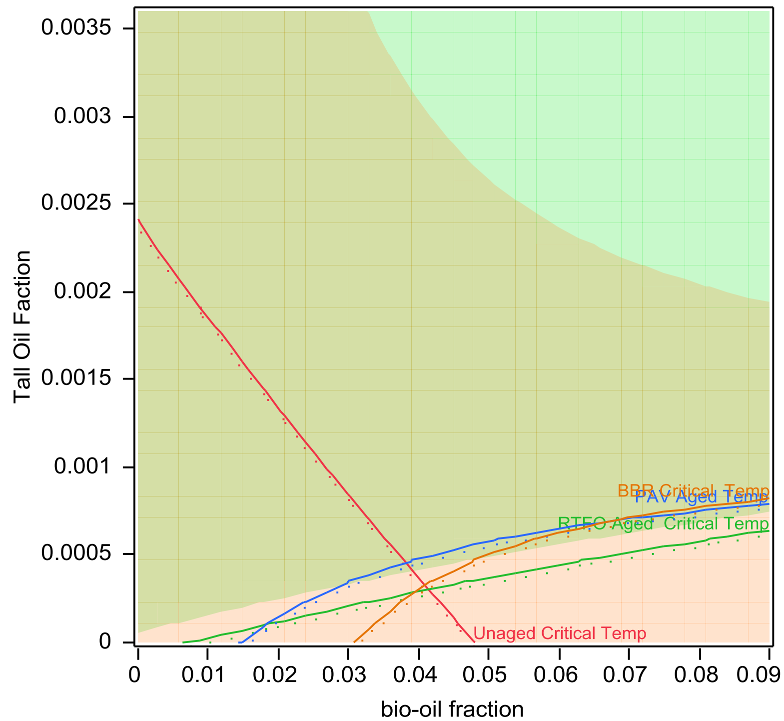


Figure 56. Constraint shading map for AAD-1 with corn stover bio-oil and tall oil

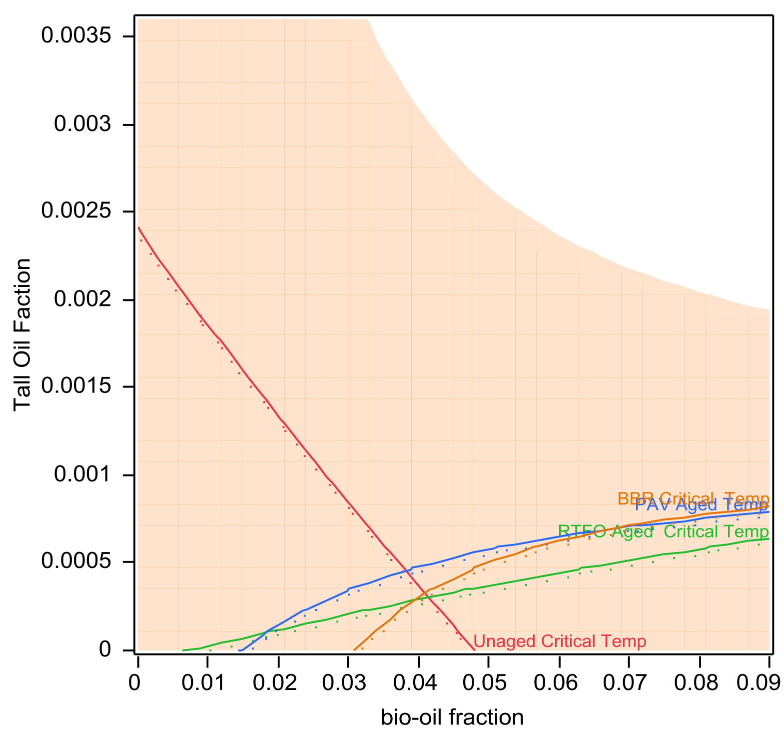


Figure 57. Constraint shading map for AAD-1 with corn stover bio-oil and tall oil

Figure 58 reveals the feasible zone (blank areas) where both constraint conditions are met. The RTFO critical temperature of the modified binder should be higher than the initial value of the neat binder for the modified binder's BBR critical temperature (lower than the neat binder). The combinations with more than 6% corn stover bio-oil and more than 0.25% tall oil are recommended.

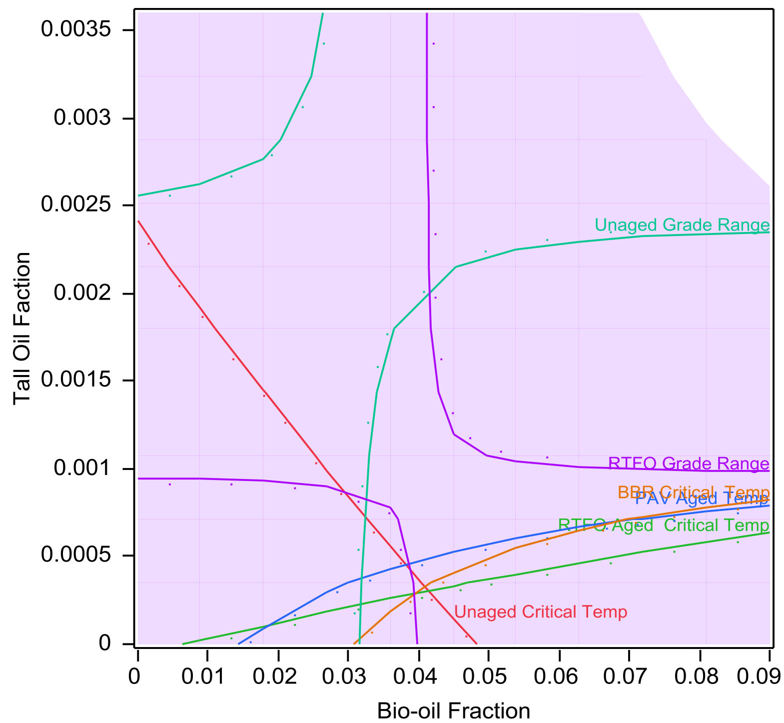


Figure 58. Constraint shading map for AAD-1 with corn stover bio-oil and tall oil

Figure 59 reveals the feasible zones for utilizing the oak wood bio-oil and tall oil to modify the AAD-1 binder where two constraint conditions are met. The RTFO critical temperature of the modified binder should be higher than the initial value of the neat binder at the same time that the modified binder's BBR critical temperature is "asked" to be lower than the neat binder. Approximately, the combinations with more than 6.5% corn stover bio-oil and adding tall oil in the range from 0.2% to 0.25% by weight are suggested.

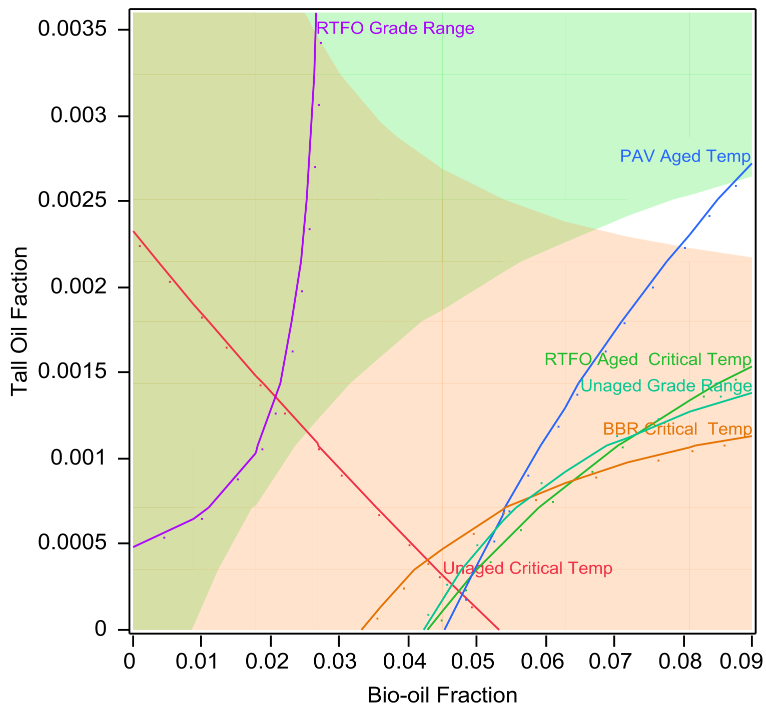


Figure 59. Constraint shading map for AAD-1 with oak wood bio-oil and tall oil

Figure 60 displays the practical zones by the blank area where the two constraint conditions about the RTFO and BBR critical temperatures are satisfied. The RTFO critical temperature of the modified binder should be higher than the initial value of the neat and the modified binder's BBR critical temperature is required to be lower than the neat binder. The combinations approximately with more than 5.5% corn stover bio-oil added with more than 0.17% tall oil are suggested.

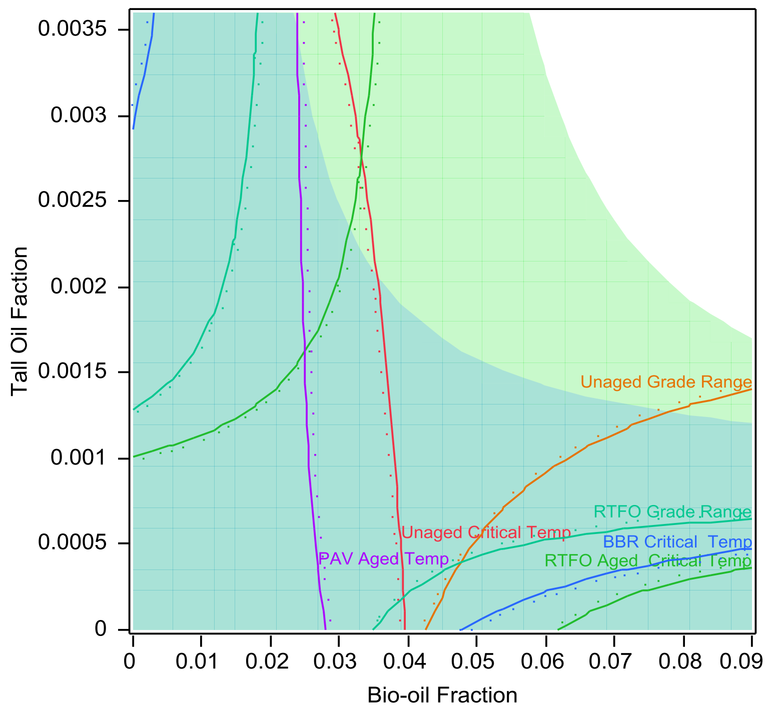


Figure 60. Constraint shading map for AAD-1 with switch grass bio-oil and tall oil

No recommendations can be made to modify AAM-1 binder using corn stover bio-oil in the interval between 0% to 9% and tall oil from 0% to 0.36% by weight. Enhancing the high temperature performance and the low temperature property cannot be achieved at the same time with the AAM-1 binder by adding bio-oil and tall oil. Even the RTFO PG range extension cannot be detected. The Figure 61 illustrates that there is no feasible treatment combination.

The same results with the corn stover bio-oil modification with tall oil occur with the oak wood bio-oil with tall oil enhancing the high temperature performance and the low temperature property at same time does not occur. The Figure 62 illustrates that there is no feasible treatment combination.

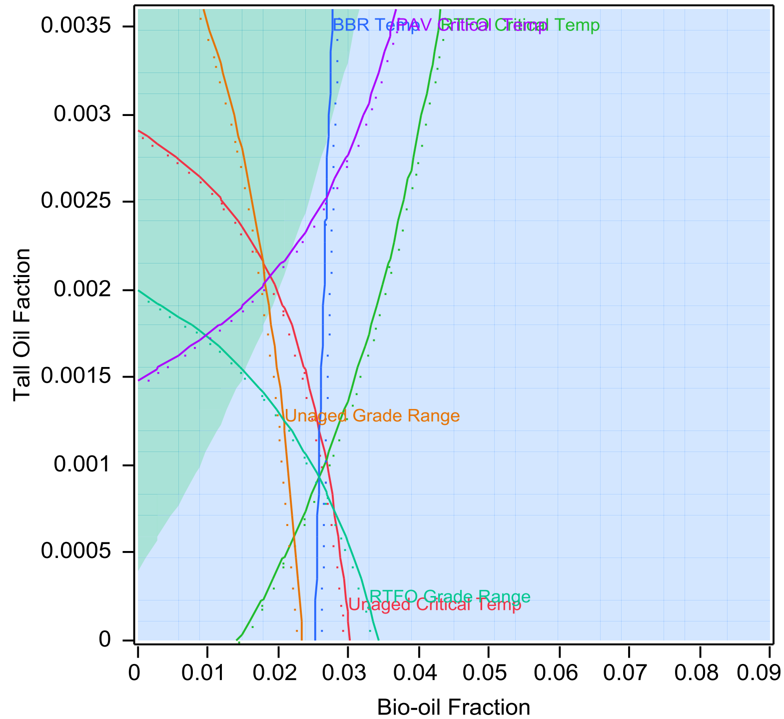


Figure 61. Constraint shading map for AAM-1 with corn stover bio-oil and tall oil

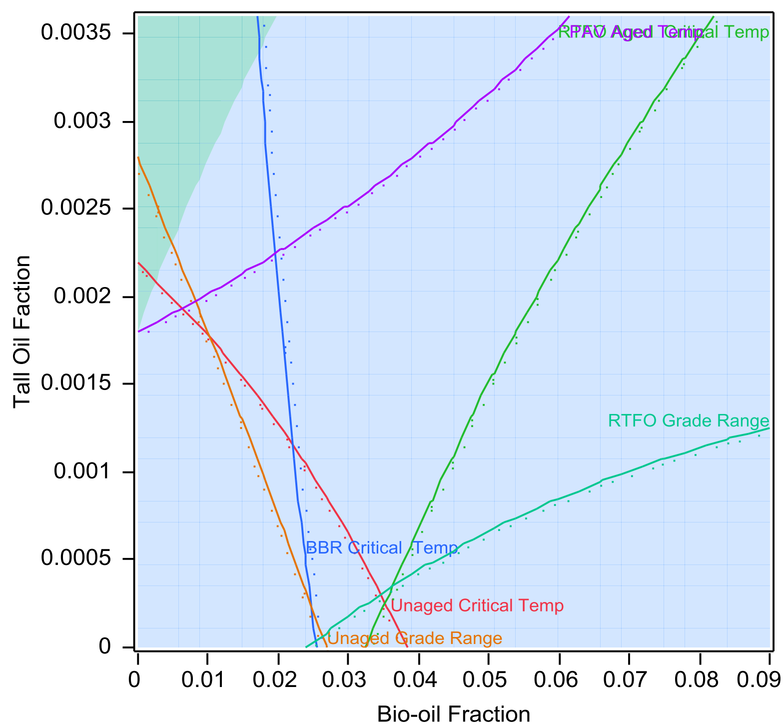


Figure 62. Constraint shading map for AAM-1 with oak wood bio-oil and tall oil

However, by adding oak wood bio-oil with tall oil into the AAM-1 binder, there are some combinations that extend the RTFO critical temperature range, as shown in Figure 63. This application area is form by relatively higher increments in RTFO high critical temperature than the increments in BBR critical temperature.

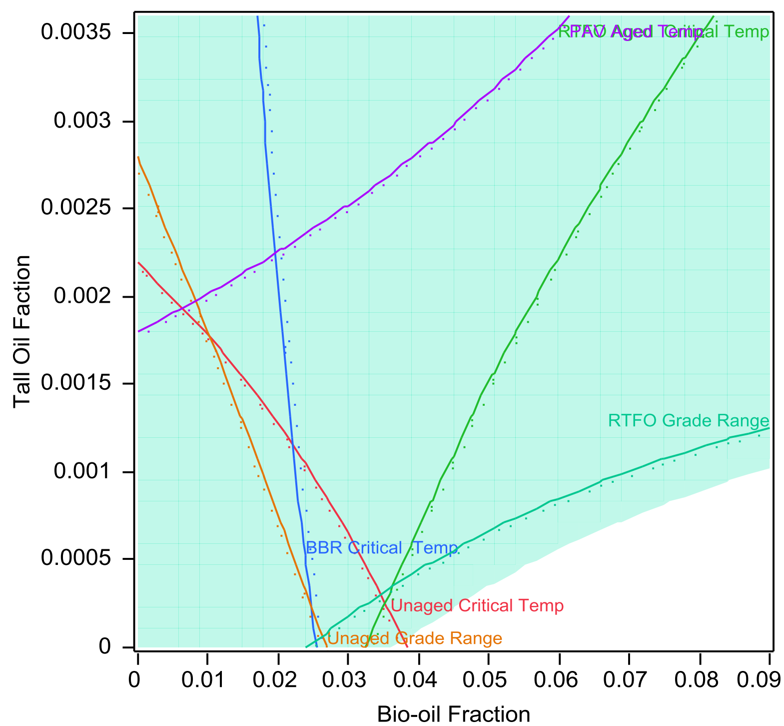


Figure 63. Constraint shading map for AAM-1 with oak wood bio-oil and tall oil

When applying the switch grass bio-oil with tall oil into the AAM-1 binder, there is a small area that can benefit both the high and low temperature properties, as showing in Figure 64. The suggested treatment combinations for extending the RTFO PG range are illustrated in Figure 65.

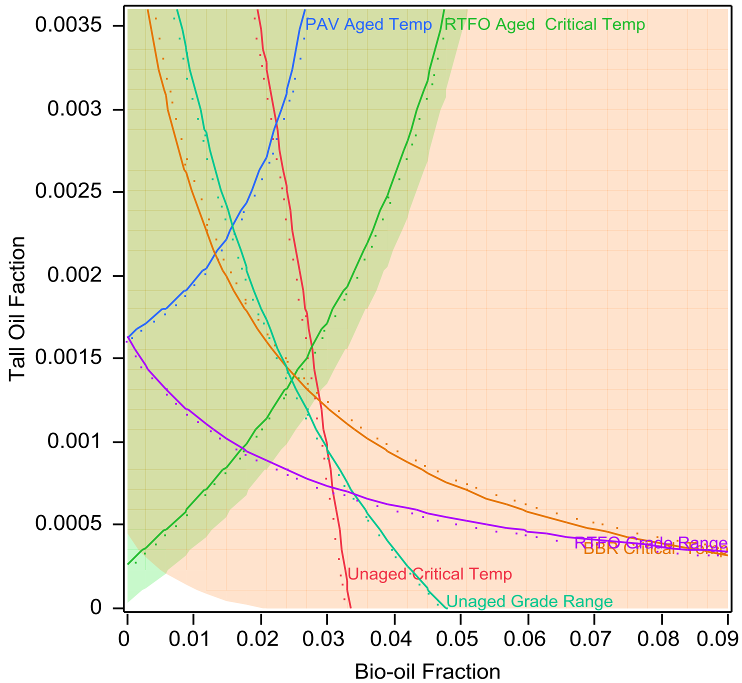


Figure 64. Constraint shading map for AAM-1 with switch grass bio-oil and tall oil

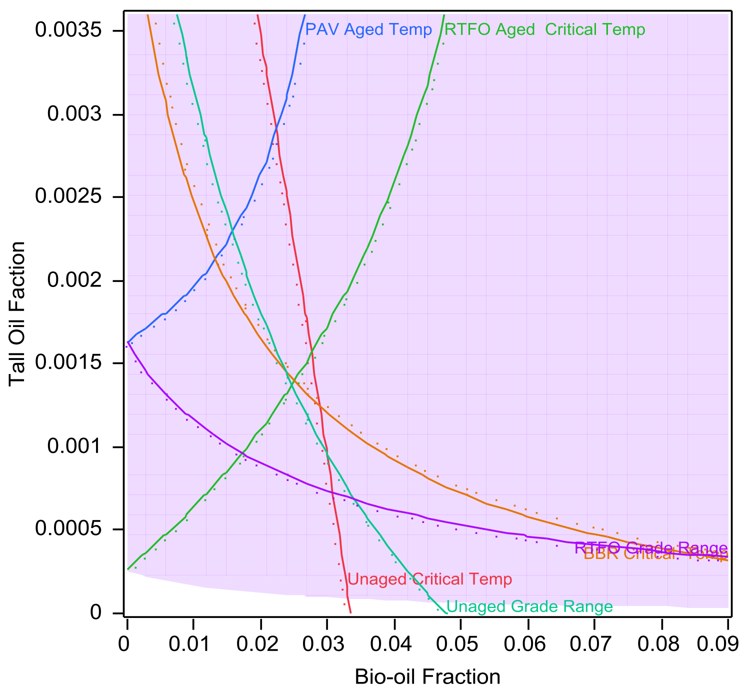


Figure 65. Constraint shading map for AAM-1 with switch grass bio-oil and tall oil for RTFO PG range

LPMB is the best base asphalt material to producing the bio-oil tall oil modified binder. It has a wide set of treatment combination that can improve the high and low temperature performance. As shown in Figure 66, it is the shading map for adding the corn stover bio-oil into LPMB binder with tall oil that can enhance both the high and low temperature performance.

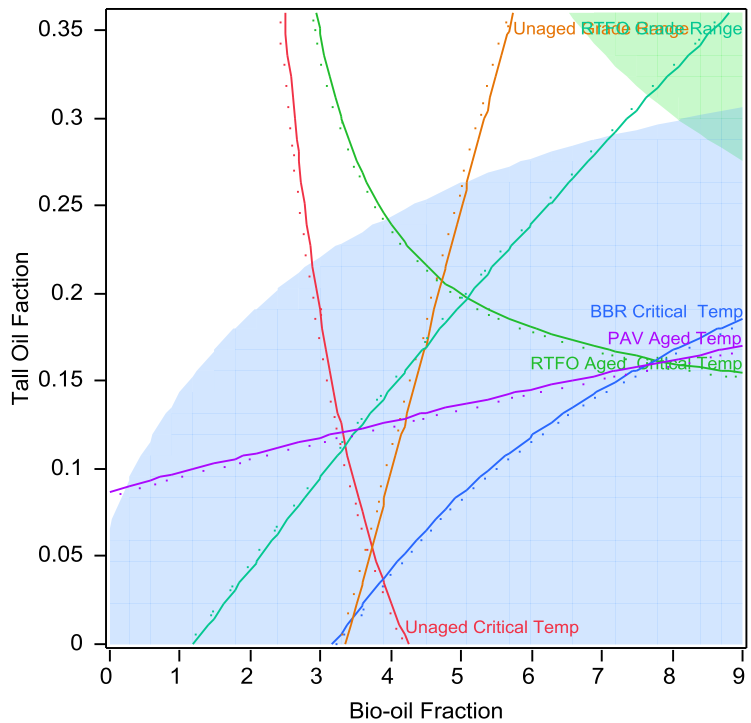


Figure 66. Constraint shading map for LPMB with corn stover bio-oil and tall oil

Figure 67 the oak wood bio-oil mixture with tall oil has relatively smaller application range than the other two bio-oil/ tall oil mixture. The dosage for oak wood bio-oil which should be less than 2% is recommended to blend with more than 0.2% tall oil.

The constraint shading graph (Figure 68) clearly illustrates the switch grass bio-oil with tall oil treatment combinations zones that can benefit both the high and low temperature properties.

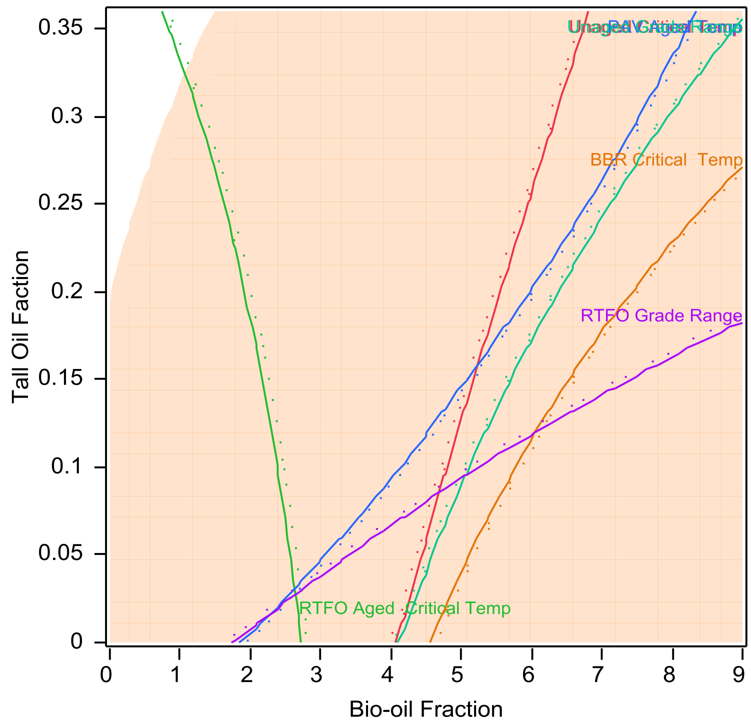


Figure 67. Constraint shading map for LPMB with oak wood bio-oil and tall oil

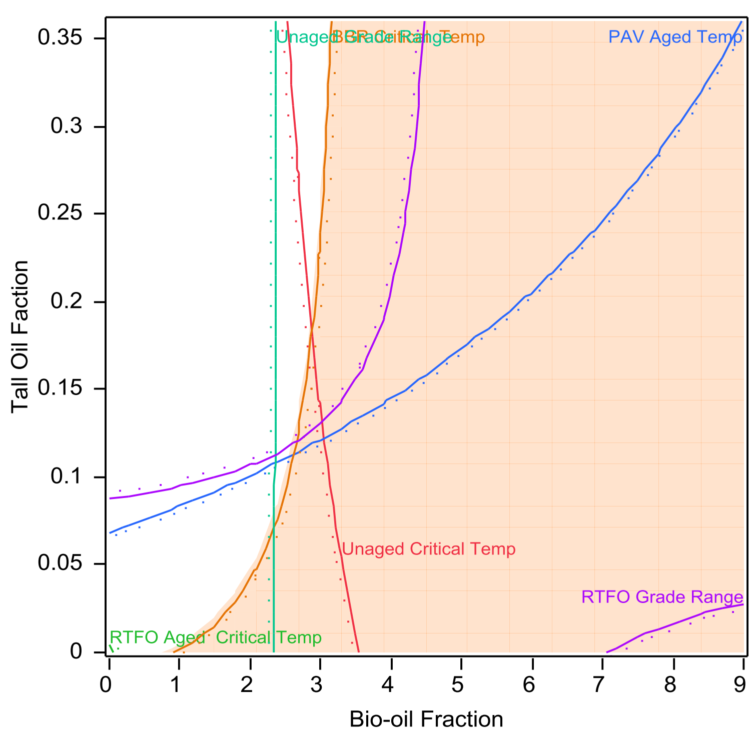


Figure 68. Constraint shading map for LPMB with switch grass bio-oil and tall oil

7.3 Final remarks and future work

Future research should examine other bio-oils (switch grass and corn stover) in the same or different asphalt binders. Also, tall oil fatty acids should be used to examine their effect on mix performance testing including low temperature mix fracture testing such as the semi-circular bend test.

Considering the flow number decrease for applying the bio-oil modified binder in asphalt mixture, the maximum theoretical specific gravity tests (ASTM D 2041) should be planned to be conducted in order to verify whether adding bio-oil changes the asphalt absorption of the aggregate. The reduction of the asphalt absorption could result in an increase in the amount of effective asphalt content leading to softer asphalt mixtures if other factors remain the same.

The higher amounts of tall oil fatty acids, much more than the amounts that had been tested in this research should be evaluated. There is a trend and possibility for the AAD-1 and AAM-1 binders to achieve the lower BBR critical temperature when tall oil fatty acids are added at more than 0.36% by weight. The tall oil fatty acids recover the performance grade loss in the low temperature criteria by applying the bio-oil binder modification.

In this research, the experimental data obtained from the two-level factorial test may not provide sufficient information to adequately model the true surface. However the response surface and contour plots based on the testing data do reveal the relationship between the binders with the bio-oil and tall oil, and indicates the changing trend when varying the amount of the additive (bio oil and/or tall oil).

If the bio-oil and tall oil treatment effects would like to be accurately stimulated (predicted), standard response surface methodology (RSM) experiment designs such as the central composite design (CCD) or Box-Behnken design (BBD) are recommended to generate the contour maps that can be directly applied for formulation in practice.

The response surface methodology (RSM) has great potential to be introduced in the modeling and optimization of asphalt binder modification processes.

APPENDIX

Table 70. DSR and BBR data

Asphalt ID	Bio-oil (%)	Tall-oil (%)	Bio-oil (type)	Average Critical Temperatures (oC) Average Unaged High T_c	Average RTFO Aged High T_c	Average PAV aged Int T_c	Average PAV Aged Low T_c	Grade Range, (°C) Unaged High Tc - Low Tc	RTFO Aged Tc - Low Tc
AAD-1	6	0.18	Corn Stover ESP	59.06	63.86	16.49	-24.19	83.25	88.05
	6	0.18	Oakwood ESP	59.64	66.21	19.63	-23.17	82.81	89.38
	6	0.18	Switchgrass ESP	57.93	64.78	18.38	-25.54	83.47	90.32
	3	0.09	Corn Stover ESP	62.16	66.23	18.45	-21.53	83.69	87.76
	3	0.09	Oakwood ESP	61.15	67.01	20.48	-19.39	80.54	86.40
	3	0.09	Switchgrass ESP	59.36	64.27	17.14	-24.54	83.90	88.81
	0	0	Initial binder	62.27	65.38	17.33	-25.18	87.46	90.56
AAM-1	6	0.18	Corn Stover ESP	65.84	67.68	19.77	-12.66	78.50	80.34
	6	0.18	Oakwood ESP	65.88	68.04	19.84	-12.86	78.74	80.90
	6	0.18	Switchgrass ESP	63.27	67.00	19.92	-11.40	74.67	78.41
	3	0.09	Corn Stover ESP	65.50	66.62	19.25	-12.87	78.38	79.49
	3	0.09	Oakwood ESP	65.38	68.15	19.79	-13.29	78.67	81.44
	3	0.09	Switchgrass ESP	64.35	66.54	19.40	-15.11	79.45	81.65
	0	0	Initial binder	67.77	66.68	20.26	-15.06	82.83	81.75
LPMB	**6**	**0.18**	**Corn Stover ESP**	**62.91**	**67.63**	**18.80**	**-21.13**	**84.05**	**88.77**
	6	**0.18**	**Oakwood ESP**	**65.08**	**69.82**	**19.82**	**-20.08**	**85.15**	**89.89**
	6	**0.18**	**Switchgrass ESP**	**62.43**	**68.72**	**19.10**	**-21.42**	**83.85**	**90.14**
	3	0.09	Corn Stover ESP	65.01	68.58	19.18	-19.44	84.45	88.02
	3	**0.09**	**Oakwood ESP**	**65.81**	**69.46**	**19.59**	**-20.48**	**86.29**	**89.94**
	3	**0.09**	**Switchgrass ESP**	**64.01**	**69.49**	**19.02**	**-21.29**	**85.30**	**90.78**
	0	0	Initial binder	65.97	66.74	20.09	-22.01	87.98	88.75

Asphalt ID	Bio-oil (%)	Bio-oil (type)	Average Critical Temperatures (oC) Average Unaged High T_c	Average RTFO Aged High T_c	Average PAV aged Int T_c	Average PAV Aged Low T_c	Grade Range (^oC) Unaged High Tc - Low Tc	RTFO Aged Tc - Low Tc
AAD-1	9	Corn Stover ESP	58.91	66.04	19.04	-21.77	80.68	87.81
	9	Oakwood ESP	60.23	72.49	22.63	-17	77.23	89.49
	9	Switchgrass ESP	55.78	64.12	18.44	-21.52	77.3	85.65
	6	Corn Stover ESP	60.26	65.8	18.9	-20.06	80.32	85.85
	6	Oakwood ESP	59.8	68.12	19.76	-18.6	78.4	86.72
	6	Switchgrass ESP	57.77	64.06	17.56	-21.84	79.6	85.9
	3	Corn Stover ESP	62.16	66.23	18.45	-21.53	83.69	87.76
	3	Oakwood ESP	61.15	67.01	20.48	-19.39	80.54	86.4
	3	Switchgrass ESP	59.36	64.27	17.14	-24.54	83.9	88.81
	0	Initial binder	62.27	65.38	17.33	-25.18	87.46	90.56
AAM-1	9	Corn Stover ESP	64.96	68.16	19.86	-11.97	76.94	80.13
	9	**Oakwood ESP**	**65.37**	**69.83**	**20.56**	**-13.04**	**78.4**	**82.87**
	9	**Switchgrass ESP**	**62.24**	**67.54**	**19.47**	**-13.98**	**76.22**	**81.52**
	6	Corn Stover ESP	65.26	67.69	19.69	-12.08	77.34	79.77
	6	**Oakwood ESP**	**65.92**	**69.2**	**20.46**	**-12.76**	**78.69**	**81.96**
	6	**Switchgrass ESP**	**63.15**	**66.91**	**19.61**	**-15.39**	**78.53**	**82.3**
	3	Corn Stover ESP	65.56	67.22	19.15	-12.6	78.16	79.82
	3	Oakwood ESP	66.96	67.44	20.25	-12.66	79.62	80.1
	3	Switchgrass ESP	64.27	66.57	19.32	-15.05	79.32	81.61
	0	Initial binder	67.77	66.68	20.26	-15.06	82.83	81.75
LPMB	9	Corn Stover ESP	62.73	68.91	20.31	-17.66	80.39	86.58
	9	Oakwood ESP	63.59	71.07	21.26	-16.66	80.25	87.73
	9	**Switchgrass ESP**	**61.87**	**68.19**	**19.7**	**-22.28**	**84.14**	**90.47**
	6	Corn Stover ESP	64.25	68.29	19.48	-18.04	82.28	86.33
	6	**Oakwood ESP**	**65.36**	**69.74**	**20.44**	**-19.24**	**84.6**	**88.98**
	6	**Switchgrass ESP**	**63.12**	**69.68**	**20.16**	**-20.71**	**83.83**	**90.39**
	3	Corn Stover ESP	65.58	68.97	19.19	-19.47	85.05	88.44
	3	**Oakwood ESP**	**65.46**	**69.52**	**19.26**	**-20.18**	**85.64**	**89.7**
	3	**Switchgrass ESP**	**65.33**	**68.7**	**18.34**	**-21.91**	**87.24**	**90.61**
	0	Initial binder	65.97	66.74	20.09	-22.01	87.98	88.75

Asphalt ID	Tall-oil (%)	Average Critical Temperatures (oC)				Grade Range, (°C)	
		Average Unaged High T_c	Average RTFO Aged High T_c	Average PAV aged Int T_c	Average PAV Aged Low T_c	Unaged High Tc - Low Tc	RTFO Aged Tc - Low Tc
	0.36	60.35	62.58	16.12	-23.53	83.88	86.11
	0.36	60.04	62.61	16.10	-24.61	84.65	87.22
	0.36	60.37	62.84	16.91	-23.20	83.57	86.04
AAD-1	0.18	60.34	63.55	17.07	-21.11	81.45	84.66
	0.18	60.43	63.26	17.10	-22.82	83.25	86.08
	0.18	60.24	63.19	17.00	-22.76	83.00	85.95
	0	62.27	65.38	17.33	-25.18	87.45	90.56
	0.36	65.68	65.61	17.88	-14.69	80.37	80.30
	0.36	65.01	65.67	18.95	-14.26	79.27	79.93
	0.36	65.54	65.59	18.93	-14.00	79.54	79.59
AAM-1	0.18	66.88	66.47	19.18	-14.55	81.43	81.02
	0.18	66.41	66.82	19.06	-13.15	79.56	79.97
	0.18	66.37	66.76	18.75	-14.52	80.89	81.28
	0	67.77	66.68	20.26	-15.06	82.83	81.74
	0.36	**66.54**	**68.08**	**17.91**	**-23.32**	**89.86**	**91.40**
	0.36	**67.01**	**68.19**	**17.74**	**-22.65**	**89.66**	**90.84**
	0.36	**66.85**	**68.26**	**18.09**	**-22.98**	**89.83**	**91.24**
LPMB	**0.18**	**66.93**	**68.80**	**18.10**	**-22.50**	**89.43**	**91.30**
	0.18	**66.73**	**68.78**	**18.31**	**-23.35**	**90.08**	**92.13**
	0.18	**66.94**	**68.85**	**17.95**	**-23.98**	**90.92**	**92.83**
	0	65.97	66.74	20.09	-22.01	87.98	88.75

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