

The Utilization of Agriculturally Derived Lignin as an Antioxidant in Asphalt Binder

Nicolaus S. McCready
Department of Civil, Construction, and Environmental Engineering
Iowa State University
174 Town Engineering
Ames, IA 50011
nmccrea@iastate.edu

R. Christopher Williams
Department of Civil, Construction, and Environmental Engineering
Iowa State University
482A Town Engineering
Ames, IA 50011
rwilliam@iastate.edu

ABSTRACT

Asphalt pavements undergo long-term aging due to oxidation of the asphalt binder. As a pavement oxidizes, it stiffens and eventually cracks. The use of an antioxidant in an asphalt binder could retard aging, thus increasing the pavement's service life. Lignin is a known antioxidant and is highly available from timber and many agricultural products. A wet-mill ethanol process produces several co-products, some of which contain lignin. The utilization of lignin from an ethanol plant could provide benefit to asphalt pavements, along with increasing the value of these lignin containing co-products. Three different lignin containing co-products were added to four asphalt binders with varying amounts to find the optimum amount of lignin that would provide the greatest benefit to the asphalt binders. The asphalt-lignin blends were evaluated according to Superpave specifications and performance-graded on a continuous scale. The blends were also tested for separation tendencies. The results illustrate that the addition of lignin has a slight stiffening effect on the binder. The more lignin added, the greater the stiffening. However, separation effects are significant at high lignin levels. Binder stiffening increases the high-temperature properties, while the low-temperature properties are slightly decreased. However, the low-temperature stiffening effects are small and do not change the actual performance grade. The lignin has an overall effect of widening the performance grade range of the asphalt binders.

Key words: antioxidant—asphalt—ethanol—lignin

INTRODUCTION

As the world demand for energy increases, the United States looks to establish a more bio-based economy (Van Dam et al. 2005). A bio-based economy has several advantages to traditional reliance on fossil fuels. First, energy derived from agricultural products is renewable. Crops such as corn, soybeans, switch grass, and sugar cane are common in the United States and are excellent for producing reliable and efficient biofuels. Second, fuels created from agricultural products burn with fewer toxic emissions and a reduction in the amount of green house gases produced (Demirbas and Balat 2006). Carbon neutrality is becoming ever more important as the world's concern for global warming increases. Finally, a bio-based economy provides the United States and other agricultural nations with a large economic opportunity. Crops would have greater value giving rural America an economic boost. New markets will need to develop to utilize co-products derived from biofuel production. However, research of co-products from fuel production needs more attention.

Ethanol is the nation's largest and most popular biofuel. Ethanol has existed for over 100 years, but is increasing in popularity as the United States tries to liberate itself from dependence upon foreign oil (over 62% imported) (Bothast and Schlicher 2005). Ethanol production is an efficient process. However, many co-products are produced as the entire corn kernel cannot be used to make fuel (Gulati et al. 1997). These co-products have uses, mostly acting as livestock feed. Further market opportunities for co-products could greatly benefit ethanol producers.

With wet-mill ethanol production, co-products are produced that contain lignin. Lignin is a well studied biological polymer and is a known antioxidant. The antioxidant effects of lignin are derived from the scavenging action of phenolic structures on oxygen containing free radicals (Dizhbite et al. 2004). Lignin contains large amounts of phenolic structures enabling it to be an effective antioxidant. The use of lignin in asphalt pavements could provide substantial benefit. The primary cause of long-term aging in asphalt pavements is oxidation of the asphalt binder. The complex reaction of binder with atmospheric oxygen causes the binder to age and stiffen. As a binder stiffens, it becomes brittle and eventually cracks, usually by means of thermal and fatigue stresses (Roberts et al. 1996). Fixing distressed pavements is costly, so delaying oxidative aging would be valuable.

Antioxidants have been previously researched in asphalt binders. Chemicals such as zinc dialkyldithiophosphate (ZDDP) and naphthenoid oil have proven successful at retarding asphalt binder oxidation and age hardening (Ouyang et al. 2006). However, practical limitations have prevented their incorporation into the industry. Wood lignin has also been researched and proven beneficial to asphalt. The high- and low-temperature properties of the binder were increased at four and seven percent by weight lignin content (Bishara et al. 2005). Yet, wood lignin is a waste product of the paper industry, so it carries a negative stigma. The idea of using roads as a "horizontal landfill" is unattractive to many in the asphalt industry. However, if a low-cost, environmentally friendly antioxidant could be used as a performance modifier, then that chemical would have a much greater chance of being incorporated into the industry. Lignin derived from ethanol production has positive value, so its potential use in asphalt pavements is high. No published asphalt research has been performed on ethanol-derived lignin.

EXPERIMENTAL PLAN

This study examined four asphalt binders, each combined with three different corn lignin samples at four percentages. The binders used were two local (one polymer modified and one unmodified) and two well-studied binders from the National Materials Research Laboratory (AAD-1 and AAM-1). The two local binders were obtained from a local supplier in Tama, Iowa. The corn lignin samples

were acquired from Grain Processing Corporation in Muscatine, Iowa. The samples vary slightly in their lignin content due to different processing methods. After processing, the samples range from around 10 to 15% lignin. The remainder is a combination of inert fillers consisting of cellulose and hemi-cellulose. Lignin A and B are modified corn hull which contain more lignin than C. The lignin samples were dried to approximately 10% moisture and then ground into a fine powder. Each binder was blended with each lignin sample at 3.0, 6.0, 9.0, and 12.0% by weight. Also, each binder was tested without the addition of lignin. A total of 52 asphalt/lignin blends were produced, each tested in triplicate.

Each asphalt/lignin blend was performance graded on a continuous scale according to Superpave specifications (AI 2003). First, the unaged samples were tested in a dynamic shear rheometer (DSR) to determine the high-temperature visco-elastic properties. Next, a rolling thin film oven (RTFO) was used to short-term age the binders. The RTFO simulates the aging the binder goes through while being mixed and constructed in the field. The RTFO residue was then tested in the DSR to verify the high-temperature visco-elastic properties. Next, the RTFO residue was long-term aged in a pressure aging vessel (PAV). The PAV mimics 8 to 10 years of actual in-service pavement aging (Roberts et al. 1996). The PAV residue was tested in the DSR to determine the intermediate-temperature visco-elastic properties. Low-temperature properties were determined by examining the PAV residue test properties with a bending beam rheometer (BBR).

Separation testing was performed according to ASTM D 7173-05. Asphalt/lignin blends were examined to determine the maximum amount of each lignin that was able to remain suspended in solution after 48 hours.

RESULTS AND DISCUSSION

Initially, the samples were blended using a high-speed shear mixer. Each blend was mixed at 155°C for one hour. We used 155°C because it closely resembles the temperatures the binder will be subjected to while being mixed in the field. Once the asphalt reached temperature, the mixer was initiated and set to 5,000 rotations per minute (RPM). We used 5,000 RPM because it was the lowest speed that produced a sufficient vortex to properly blend the lignin into the binder. If a higher mixing speed was used, sufficient friction was produced by the mixing head to increase the heating of the asphalt beyond 155°C. Using speeds of 6,000 RPM or more increased the heat of the blends well beyond the desired mixing temperature.

First, the asphalt/lignin blends were studied for separation effects in accordance with ASTM D 7173-05. The blends were poured into aluminum cigar tubes and stored vertically in an oven at 155°C for 48 hours. Theoretically, the denser particles settle to the bottom while the lighter particles stay suspended. Immediately after heating, the samples were frozen. The frozen tubes were cut into three equal-size portions. The middle fraction was discarded, while the top and bottom portions were heated and poured into separate containers. The top and bottom portions were tested separately in a rotational viscometer. The viscosities of each sample were tested at 135.0°C, 150.0°C, and 165.0°C. Results showed large viscosity differences at the 12% level. The top and bottom portions differed by an average of 13.3%. This amount of separation is undesirable and would cause problems for future binder handling and construction. At the 9% level, the viscosities differed only by 3.7%.

Performance testing of asphalt/lignin blends showed consistent trends with all four binders. In general, the addition of lignin slightly stiffened the asphalt. Figure 1 illustrates consistent trends with binders AAD-1 and the local polymer modified binder (LPMB). Both graphs show $G^*/\sin(\delta)$ values tested at 64°C on the y-axis with the means represented as solid bars. A larger $G^*/\sin(\delta)$ value

represents a stiffer binder, while a smaller $G^*/\sin(\delta)$ value represents a more viscous, flowing binder. It is easily seen that the further addition of lignin continues to stiffen the binder. In the case binder AAD-1, lignin B produces a significantly stiffer blend than lignin A or C based upon a 95% level of confidence. Also in the case of AAD-1, the addition of all three lignins at the 9.0 and 12.0% level increase the high-temperature performance grade from a PG 58 to a PG 64. For the LPMB, the performance grade remained a PG 64 for all blends.

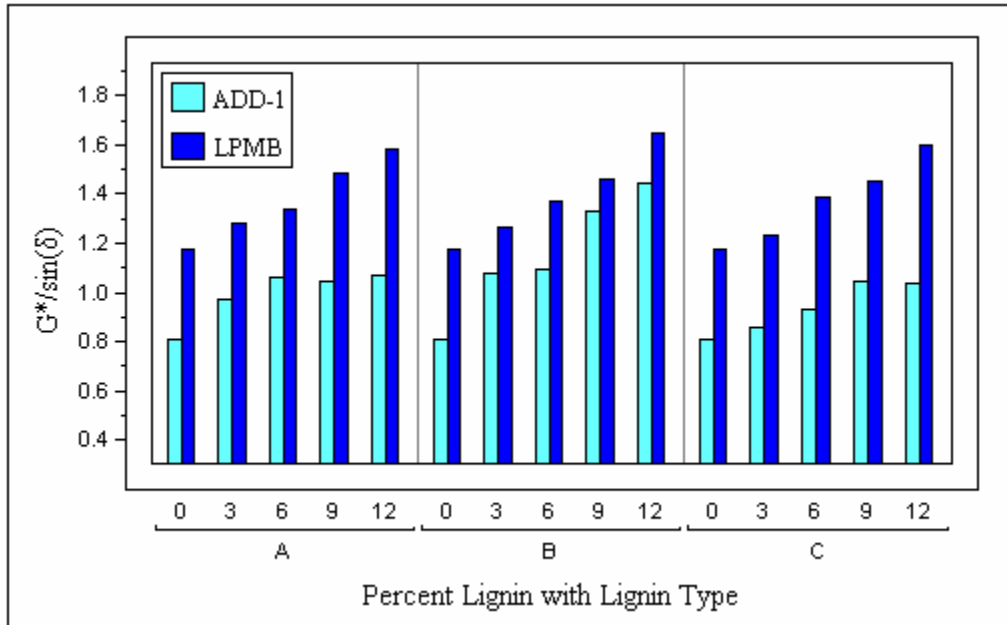


Figure 1. Unaged AAD-1 and LPMB Data at 64°C

After being RTFO aged, the same trends appear. Figure 2 illustrates the effects of the same two previous binders. It is seen from the LPMB that once the addition of lignin reaches the 12.0% level, the stiffness dramatically increases while AAD-1 has a more gradual stiffening effect. The presence of polymer in LPMB indicates some possible interaction effects because of this sharp increase. Since both binders pass at 64°C, the results of the unaged DSR test determine the actual performance grade. Therefore, AAD-1 increased from a PG 58 to a PG 64 with the addition of 9.0 and 12.0% of any of the three lignins. This is a positive effect that adds potential benefit in areas of a warmer climate.

Of most interest is the results of the PAV aged blends. In a PAV, 50.0 gram samples were subjected to high pressures (2.1 MPa) and high temperature (100°C) for 20 hours. After aging, the asphalt loses much of its viscous component and becomes much stiffer than the RTFO aged residue. The goal of this project is to evaluate the antioxidant potential of the lignin. If the lignin acts as an antioxidant, then the PAV aged samples with lignin present should see less age hardening than the samples without lignin. The PAV residue was tested for both intermediate-temperature properties with the DSR and low-temperature properties with the BBR.

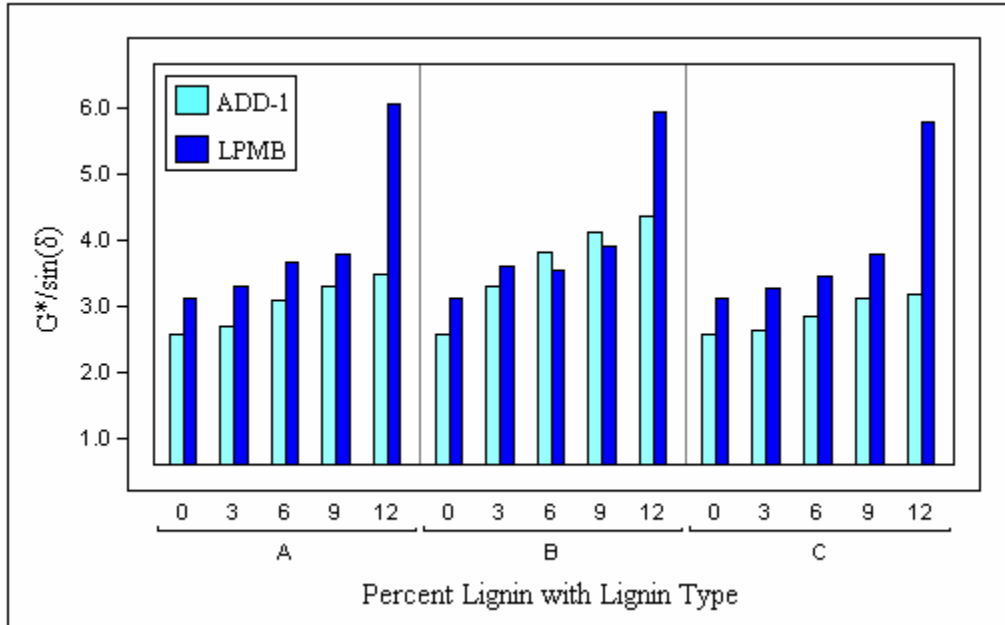


Figure 2. RTFO Aged AAD-1 and LPMB Data at 64°C

The DSR results of the PAV residue show the same pattern as the high-temperature tests. As more lignin was added, the stiffness of the binder generally increased. The intermediate critical temperature does not determine the performance grade, but rather gives an estimation of how the pavement will behave in average operating temperatures. Figure 3 shows the results of ADD-1 and LPMB at 19°C and 25°C, respectively. Both binders show a general increase in stiffness with the further addition of lignin. With the addition of 9.0 and 12.0% lignin B to AAD-1, the binder actually fails at 19°C by having a $G^*\sin(\delta)$ greater than 5,000 kPa. The same happens to the LPMB at 22°C with 6.0 and 12.0% lignin B. The data indicates that lignin B stiffens the binders statistically more than lignins A and C at a 95% confidence level. Lignins A and C produce results that are not statistically different. The results suggest that binders with lignin B would be more susceptible to fatigue cracking than lignins A and C. At the 3 and 6% levels, the binder behaves statistically similar to the neat binder (no lignin added) with lignins A and C.

Finally, the binders were tested for their low-temperature properties in a BBR. A BBR measures two key properties, stiffness and change in stiffness (m-value). To pass at a given temperature, a sample needs to have a stiffness less than 300 MPa and a m-value greater than 0.300. An asphalt with greater stiffness has a higher susceptibility to thermal cracking. The m-value is a measure of the rate of stress relaxation of the binder. Binders that can relieve thermal stresses faster have a greater ability to resist cracking. It can be seen from Figure 4 that the addition of lignin increases the stiffness of the binder at low temperatures. However, there are no statistical differences between the different lignins. The binders all passed the failure criterion of having stiffness less than 300 MPa. What caused the binders to fail was the m-value criterion. It can be seen from Figure 5 that the addition of lignin causes the m-value to slightly decrease. This is a negative effect, but the change is small, so the actual performance grade is not changed. All of the blends passed at -12°C for AAD-1 and failed at -18°C. Every blend for the LPMB passed at -6°C and failed at -12°C. It must be noted that there were no statistical differences between the different lignins with the m-value criterion at a 95% confidence level.

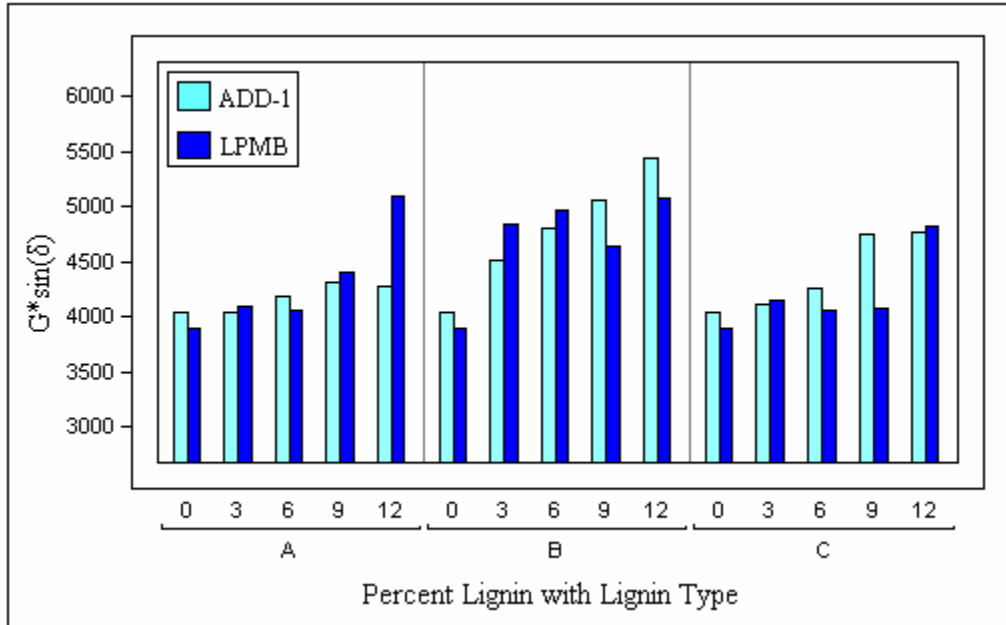


Figure 3. PAV aged AAD-1 and LPMB Data at 19 and 22°C

CONCLUSIONS

The addition of lignin containing co-products to asphalt binders causes a slight stiffening effect depending upon the percentage and type of lignin used. The high-temperature properties were positively affected. At high lignin contents, the high-temperature performance grade was increased. At the intermediate and low temperatures, the increased stiffness had a negative effect, but this effect was small and did not change the actual performance grade. Since the high temperature of the performance grade was increased and the low-temperature grade was not affected, the lignin has an effect of widening the temperature range of the binders. This is opposed to a filler, which would simply shift the temperature range. The lignin provides an overall benefit to the asphalt. Also, there were no negative interactions with the polymer present in the local binder. The LPMB behaved similar to the binders without polymer. The optimum amount of lignin to be added was 6.0 or 9.0%. The 12.0% level was overly susceptible to separation. Lignin B provided the highest increase in the high-temperature properties but also has the greatest susceptibility to fatigue cracking at intermediate temperatures. Therefore, lignins A and C are recommended over lignin B.

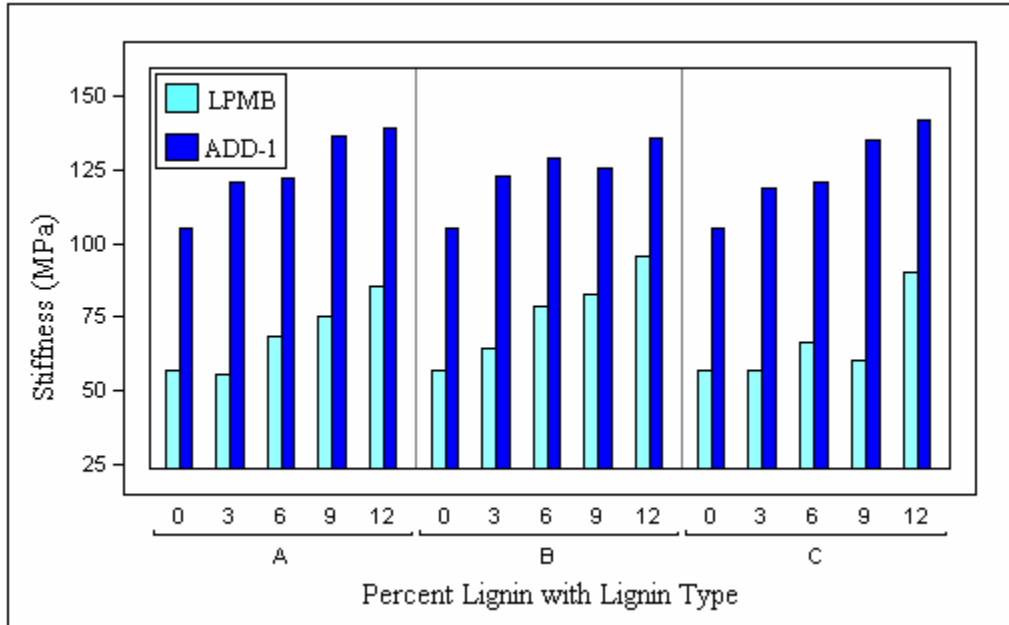


Figure 4. BBR Stiffness for AAD-1 and LPMB data at -12 and -6°C

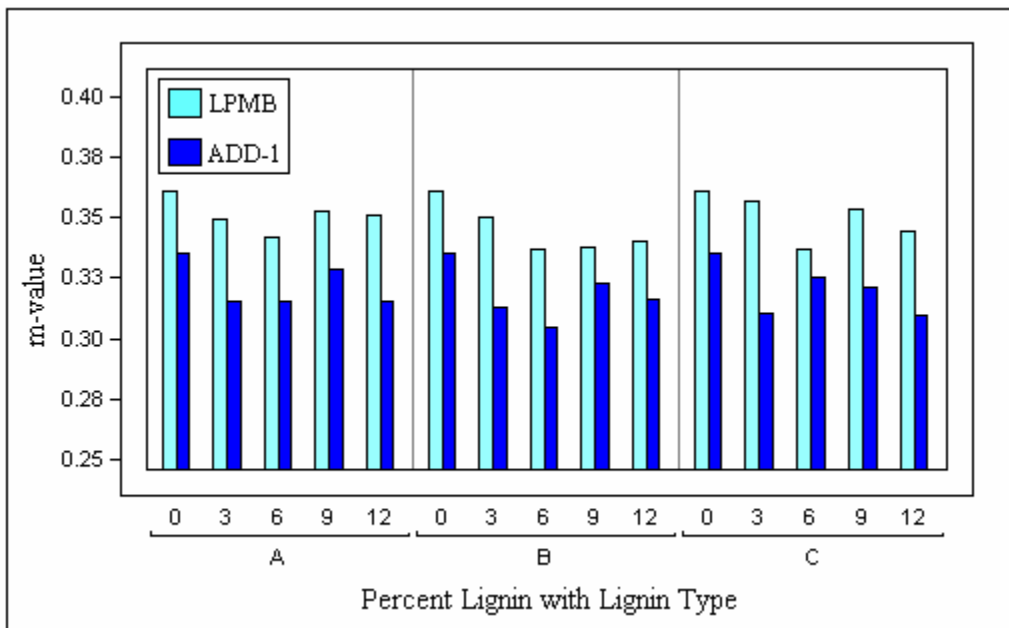


Figure 5. BBR m-value for AAD-1 and LPMB data at -12 and -6°C

ACKNOWLEDGEMENTS

Thanks to the Iowa Department of Transportation and Iowa Highway Research Board for funding this project. Also, thanks to Grain Processing Corporation for providing the lignin-containing co-products for this study. Finally, special thanks to Sheng Tang, Alison Soderberg, and Jinwei Huang for their hard work.

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