EVALUATION OF THE ASPHALT APPLICATION POTENTIAL OF AN EASTERN US SHALE OIL

K. Mahboub[1], S. D. Carter[3], R.E. Robertson[4], P.M. Harnsberger[4], P. K. Oduroh[2], A. L. Simpson[2], and D. N. Taulbee*[3]

[1]Kentucky Transportation Center
[2]Dept. Civil Engineering
[3]Center for Applied Energy Research
University of Kentucky, Lexington
and
[4]Western Research Institute, Laramie, Wy.

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Abstract. A 3" fluidized bed retort was used to generate oil samples from a Devonian oil shale from Fleming County, Kentucky. Following distillation, samples of heavy end materials were subjected to a battery of tests aimed at evaluating their potential utilization as an asphalt cement, additive, or recycling agent. Due to the unusually rapid aging characteristics of the shale oil, emphasis was placed on the latter applications. Preliminary tests of the asphalt recycling potential were generally favorable, indicating that the eastern shale oil exhibits good dispersant and rejuvenation properties.

Introduction. This manuscript describes the results of a scoping study directed at evaluating the potential road paving applications for oils derived from the eastern U.S. oil shale deposits, more specifically, for eastern shale oils (ESO) produced in a KENTORT II prototype reactor.[1,2] The KENTORT concept comprises a series of three fluidized bed reactors,i.e., pyrolyzer, gasifier, and combustor, that fully utilize the available carbon during oil shale processing. This process has been under continuing development at the CAER since about 1984 and has demonstrated that significant enhancements over Fischer Assay oil yield can be obtained using proven technology without resorting to high H_2 partial pressures. Further, this process was designed to mitigate many of the environmental concerns often associated with related technologies. However, in the present era of plentiful and reasonably priced petroleum, commercial production of motor fuels from oil shale is viewed as a high risk venture by those capable of lending financial support. Thus, the prospects for a near term commercial oil shale development is not promising.

Coincidental to the advances in oil shale technology of the past decade has been a continuing decline in both the quality and availability of road asphalts. The decline in availability has led to the recycling of road asphalts (milling and reapplication) in many areas of the country. The decline in quality, attributed primarily to advanced processing (e.g., fluid-cat crackers) used to recover more heating or motor fuel per barrel, has resulted in asphalts which do not have the desirable properties or longevity as asphalts from 3-4 decades past. Though this is bad news for motorists, this situation has created a potential niche market for shale oils,[3,4] particulary since these materials often exhibit physical/chemical properties that suggest they may be a viable alternative to petroleum derived asphalts. Accordingly, a test program was implemented to evaluate KENTORT oils in three different paving applications; i.e., as an asphalt cement, an asphalt modifier, and an asphalt recycling agent. The study included a series of binder and mixture characterization procedures for evaluation of both short- and long-term performance potential.

Details of the test methods along with preliminary results are described elsewhere[5,6] and so only a brief description of test methods is given here. The conclusion from this earlier work was that unmodified ESO showed an unacceptable rate of 'aging' or hardening which would ultimately lead to pavement failure if used directly as an asphalt cement. However, the potential for use as an asphalt modifier and particularly, as an asphalt recycling agent showed more promise. Accordingly, these latter applications are the focus of this report.

Methods and Results. Study samples. Two oil streams, produced in a 5 lb/hr KENTORT prototype unit, were selected for study. The first was a highly viscous material (3440 P @60^o C) recovered in an electro-static precipitator and is referred to as the 'hard' ESO. The second, referenced as the 'soft' ESO (8 P @60^o C), was derived from a composite of the total oil product that was subjected to a vacuum distillation prior to testing. These two oils were deliberately selected for study since it is believed they represent the types of material that would be readily available and most likely to be utilized for asphalt production in a commercial operation. Both samples were derived from the Cleveland Member of the Ohio shale acquired from a freshly exposed outcrop in Rowan County, Ky. A detailed description of the oil shale sample and retort operation is given elsewhere.[1,2]

Binder Characterization. If eastern shale oil is to be useful as an asphalt modifier, then the blend of asphalt and ESO must exhibit aging characteristics and rheological properties that are superior to the unmodified asphalt. Likewise, if ESO is to find application as an asphalt recycling agent, it must exhibit properties that are equivalent to or better than conventional agents. In an effort to determine if ESO could meet these criteria, the research was divided into two parts. The first part focused on evaluation of the 'hard' ESO as an asphalt additive and the second on evaluation of the 'soft' ESO as a softening agent for aged asphalt and aged asphalt mix (pavement recycling).

Evaluation as an asphalt additive involved determining the rheological properties of an AC-20 asphalt, a 7 wt. % blend of "hard" ESO and AC-20 asphalt, and neat "hard" ESO. The rheological properties of the three samples were also determined after they were subjected to an accelerated aging procedure. Evaluation of ESO as an asphalt recycling agent entailed measuring the viscosity of an asphalt extracted from a laboratory-aged pavement mixture, the "soft" ESO, and an AC-5 asphalt (representative of a commercial recycling agent). Two "recycle" blends, with a target viscosity of 10,000 poise at 60°C, were prepared by blending the laboratory-aged asphalt with 1) the "soft" ESO and 2) with the AC-5 asphalt. Rheological properties of the two blends were then examined.

Dynamic viscosity measurement were made on a Rheometrics RMS-605 mechanical spectrometer using a shear frequency range of 0.1 to 100 rad/sec at 25, 45, and 60°C from which the two components of shear modulus, G' and G", were determined. The storage modulus or the elastic component (G') quantifies the elastic rebound capability of the material. The loss modulus or viscous component, G", is a measure of damping capacity. Higher G' values indicate good resistance to permanent deformation (rutting) but greater susceptibility to cracking failure. Higher G" values indicate the reverse behavior. Since there is always a trade-off between rutting performance and cracking performance, the term Tan Delta (ratio of G"/G') is used as a measure of the balance between damping and elastic properties. For a fresh asphalt, a Tan Delta value higher than 3 indicates better than average resistance to cracking but less than average resistance to rutting.[7] Values less than 3 indicate the opposite.

Aged Asphalt Binder Rejuvenation. The 60°C viscosities of the laboratory-aged asphalt, the soft eastern shale oil, and the AC-5 asphalt as described above were determined to be 5.98 x 10^6, 15, and 515 poise, respectively. Three trial blends each of the laboratory-aged asphalt/soft ESO and the aged asphalt/AC-5 were prepared in an effort to produce samples whose viscosity would bracket the 10,000 poise target value (see Fig. 1 and 2). Unfortunately, the trial blends did not bracket the target viscosity for either blend series. Nonetheless, from the trial blends data, the mixing ratios required to produce 10,000 P blends were estimated to be 66% aged asphalt/34% soft ESO and 42% aged asphalt/58% AC-5 asphalt. The measured viscosity of the test blends prepared at these ratios are shown by the unfilled square symbols in Figures 1 and 2. The amount of soft ESO needed to achieve the target viscosity is considerably less than for the AC-5 due to the lower viscosity of the ESO.

Nearly identical viscosity-temperature relationships are shown for the test blends in Figure 3. Likewise, tan delta values were similar at all three temperatures with the AC-5/aged asphalt blend being slightly lower at 60°C and slightly higher at 25 and 45°C (Table 1). These results are favorable indicating good asphalt rejuvenation potential for the soft ESO both in terms of adequate dispersal of the aged asphalt and the ability to provide an equivalent viscosity as the AC-5 with less sample.

Mixture Characterization. The term mixture refers to a combination of asphalt and road aggregate. The mixture characterization program was designed so that the potential pavement performance of ESO modified asphalts could be related to that of an asphalt modified with a more conventional material with known field performance. This was accomplished by on-site sampling of ~40 Kg of hot mix (containing no modifier) during construction of an asphalt overlay research project during September 1990 (Pulaski County, Ky.). For this project, several test strips were constructed from a single asphalt blended with different commercial modifier agents. The test strips were placed on a long term monitoring schedule and samples of each asphalt/modifier blend were returned to the laboratory for testing. So, by blending the ESO with the same hot mix and subjecting this asphalt/ESO blend to the same lab tests as the field samples, a more realistic assessment of pavement performance could be obtained.

The field sampled hot mix was divided into two portions. The first portion was mixed with the "hard" ESO at the same proportions as the polymer modified mixtures. This was to compare the behavior of the hard ESO modified asphalt to the asphalts modified with commercial agents. The second portion was aged in a forced draft oven at 80°C for two weeks prior to mixing with the "soft" ESO. This was in order to test the soft ESO as a pavement recycling agent. An additional 4 Kg of the aged mixture was set aside for extraction and binder characterization. Mixture characterization included a series of mechanical response tests on compacted specimens (Marshall procedure; ASTM 1559) directed at evaluating the performance potential of the "hard" ESO modified asphalt mixture relative to the conventional polymer modified asphalts (brands "A" through "D"). All statistical comparisons were conducted at 95% level of confidence.

Tensile Strength Characterization. Fatigue and durability of asphalt pavements are believed to be related to tensile strength. It is customary to characterize tensile strength of pavement materials indirectly in accordance with ASTM-4123. Figure 4 shows the 'hard' ESO blend has tensile strength properties that are superior to the control mixture (unmodified, aged hot-mix) and are on par with two of the high tensile strength polymer modified asphalts. Taken alone, these results indicate desirable fatigue and durability performance potential for the "hard" blend ESO. However, previously reported results suggest that the aging characteristics of a 'hard' ESO blend that has not been subjected to some sort of pre-aging treatment may lead to early pavement failure.[5,6]

Moisture Damage Characterization. Asphalt binder stripping from aggregate is a moisture induced effect. The potential for this type of damage is often characterized in the laboratory in accordance with the Root-Tunnicliff test[8]. The mean tensile strength data shown in Figure 4, along with statistical analyses of the data, indicates that the 'hard' ESO moisture damage susceptibility compares favorably with the control mixture and was not significantly different than at least two of the polymer modified mixtures. Nonetheless, the data show that 'hard' ESO modified asphalt is somewhat susceptible to binder stripping.

Freeze-Thaw Damage Characterization. The potential susceptibility to freeze-thaw damage was characterized, again using tensile strength as an index parameter. Mixtures were subjected to 100 cycles of freeze and thaw (3 hours at -18°C, followed by 3 hours at +4°C). Cross comparisons (Figure 4), along with statistical data analyses, revealed no statistically significant change in tensile strength after 100 cycles of freeze-thaw. Evidently, more freeze-thaw cycles would be necessary in order to induce significant mixture differences.

Rejuvenated Mixture Characterization. Asphalt aging/oxidation severely reduces the tensile strength properties of an asphalt-aggregate mixture as demonstrated by the substantial decline in tensile strength of the aged control sample plotted in Figure 5. Addition of "soft" ESO to the aged mixture resulted in a notable increase in tensile strength, comparable to that from adding AC-5 asphalt. However, ESO addition did not restore the tensile strength to the level prior to aging. This phenomenon in not untypical and has led to a common practice of adding fresh hot mix to the recycled mixture along with the rejuvenating agent. Nonetheless, the mixture rejuvenation analysis shows the "soft" ESO to have potential asphalt recycling applications and merits further examination.

Summary. Two samples of eastern shale oil (ESO), one a hard ESO and the other a soft ESO, produced in the Kentort II process, were evaluated for potential use with paving asphalts. The hard ESO material was evaluated as an asphalt additive and the soft ESO was evaluated as an asphalt recycling agent to soften both an aged asphalt and an aged asphalt-aggregate mix.

The 'hard' ESO added at 7 wt. % to an AC-20 asphalt showed unfavorable susceptibility to moisture damage. An improvement in tensile properties of the aged asphalt mixture was achieved through addition of the hard ESO, however, this effect is likely to diminish rapidly with time due to previously reported aging characteristics.[5,6]

Both soft ESO and AC-5 asphalt were used to soften a hardened asphalt extracted from a laboratory-aged pavement mixture. The rheological properties of the aged asphalt/soft ESO blend were essentially the same as those of the aged asphalt/AC-5 blend. This finding was verified by mixture rejuvenation analysis. The amount of ESO required to soften the aged asphalt was less than the amount of AC-5 due mostly to the lower viscosity of the soft ESO. However, the large negative deviation of the ESO blending curve suggests that even at equal viscosity, the soft ESO would exhibit more softening per unit weight. Overall, the soft ESO appears to have potential application as an asphalt rejuvenating agent.

Recommendations. Previously reported results indicate that the 'hard' ESO was unstable or reactive for some time following preparation. Measurement and control of this phenomenon is an important step that must be addressed prior to further testing since a chemically and thermally stable material is necessary for paving applications. Further mixture studies are needed to fully characterize both short-term and long-term performance potential of ESO modified/rejuvenated asphalts. Field trial projects are recommended for verification of laboratory test results.

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Table 1. Rheological Properties of Aged Asphalt Blended With Soft ESO and AC-5 Asphalt.

Binder	Dynamic Viscosity, 60°C, Poise	Tan Delta
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	1.244×10^4	6.112
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.376×10^4	5.973
Binder	**Dynamic Viscosity, 45°C, Poise**	**Tan Delta**
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	1.576×10^5	2.513
42 wt.% Recovered Asphalt/58 wt.% AC-5	1.627×10^5	2.721
Binder	**Dynamic Viscosity, 25°C, Poise**	**Tan Delta**
66 wt.% Recovered Asphalt/34 wt.% Soft ESO	5.077×10^6	1.582
42 wt.% Recovered Asphalt/58 wt.% AC-5	6.187×10^6	1.738

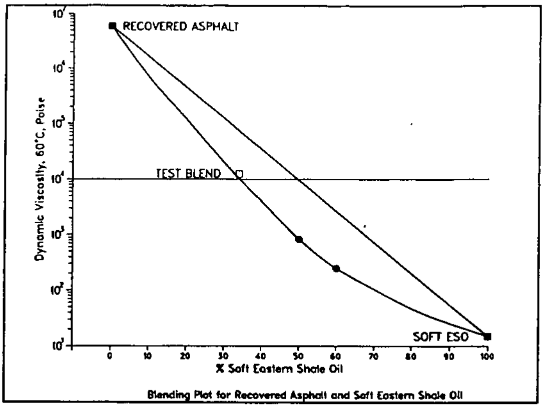

Figure 1. Viscosity of blends from aged asphalt/soft ESO blends.
●-trial blends; □-blend used for mechanical testing.

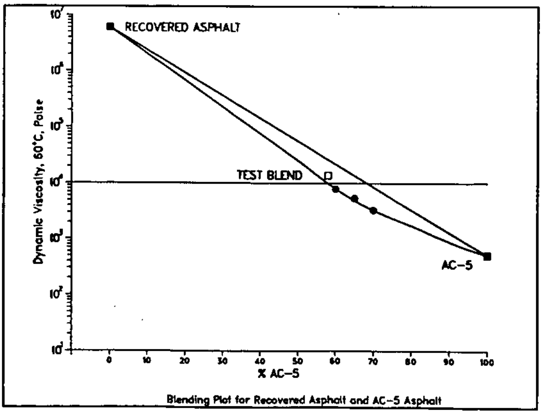

Figure 2. Viscosity of blends from aged asphalt/AC-5 blends.
●-trial blends; □-blend used for mechanical testing.

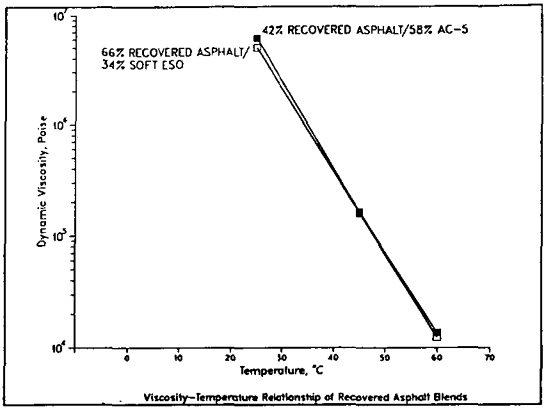

Figure 3. Viscosity-Temperature plots. □-soft ESO/aged asphalt (34%/66%); ■-AC-5/aged asphalt (58%/42%).

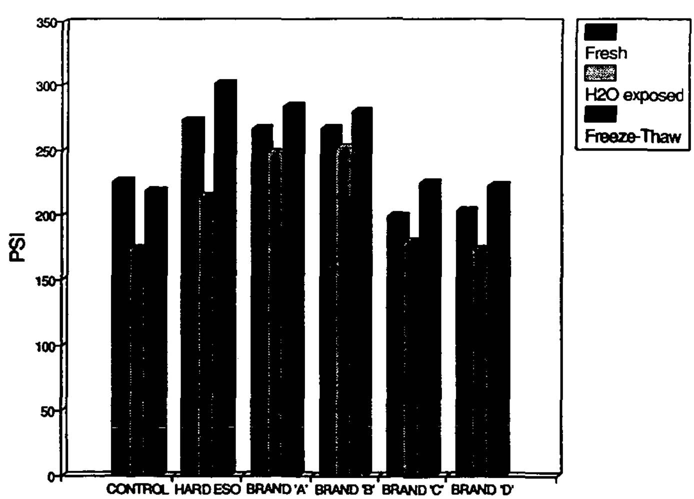

Figure 4. Tensile strength data for series of modified pavement mixtures. Samples were tested following preparation, moisture susceptibility analysis, and 100 freeze-thaw cycles. Control is pavement mixture without added modifier.

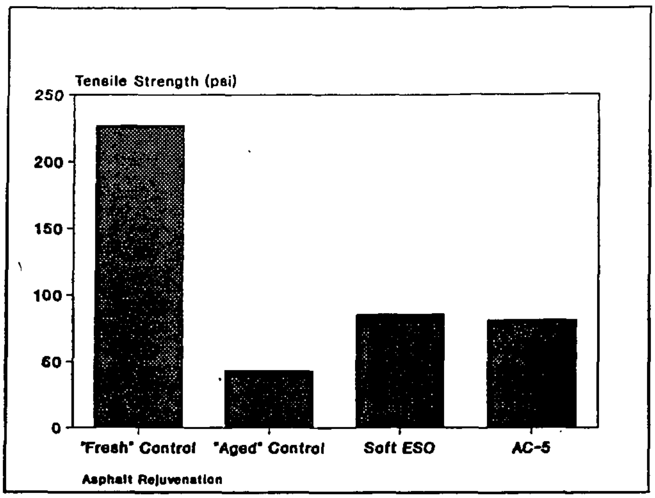

Figure 5. Tensile strength test series for fresh pavement mix, aged mix, and mix rejuvenated with either soft ESO or AC-5.