Graphical Abstract

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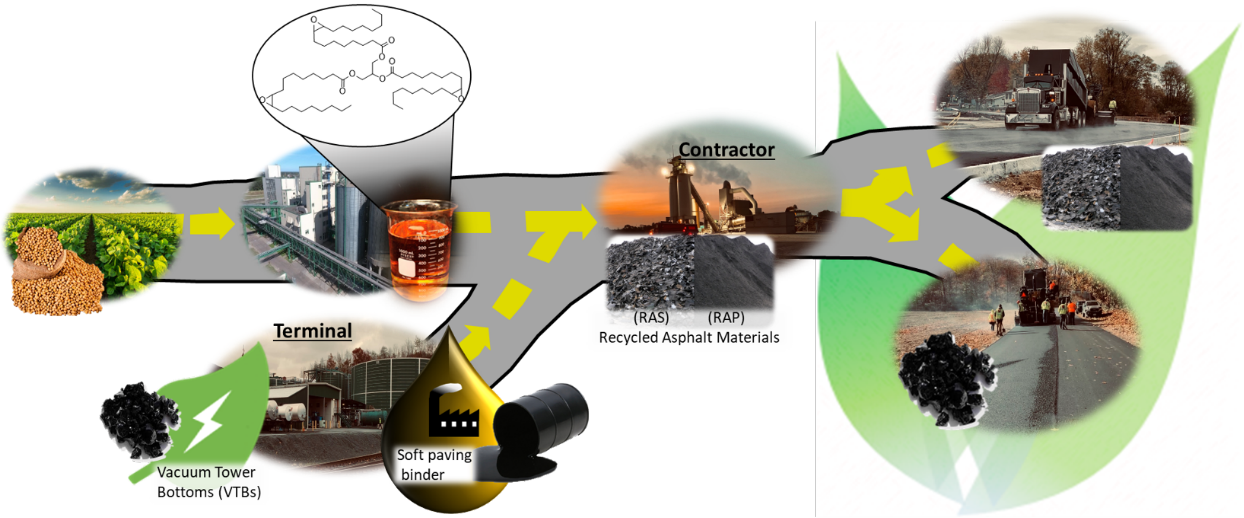

Highlights

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- Sub-epoxidized soybean oil (SESO) reacts with oxidized asphaltenes
- SESO-grafted asphaltenes restore ductility to low quality and recycled asphalts.
- Reactive rejuvenators faciliate reductions in cost, energy, and emissions.

Chemically-mediated asphalt rejuvenation via epoxidized vegetable oil derivatives for sustainable pavements.

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ARTICLE INFO

Keywords:
Rejuvenator
Epoxidized
Oxirane
Cutting agents
Recycled Asphalt Pavement
Low Quality Asphalt
Vacuum Tower Bottoms
Environment

ABSTRACT

Here we report the chemical passivation of agglomerated asphaltenes in low-quality asphalts and reclaimed asphalt pavement via epoxidized vegetable oil derivatives. This facilitates the production of new pavements with 45 wt% recycled content and a 30% reduction in cost, energy, and emissions impact over current best practices. Recycled asphalt pavement and low-quality asphalt both represent materials streams with the potential to drastically reduce the energy and emissions footprint of our transportation infrastructure, provided that their poor performance properties can be ameliorated. We show that epoxidized methyl soyate and sub-epoxidized soybean oil act as chemical rejuvenators that reduce the asphaltene content in binder formulations enabling both low-quality asphalt and recycled asphalt pavement fractions far exceeding common usage. We demonstrate that compared to "fluxes", or inert diluents, these bio-based additives show far superior solvency, rheological characteristics, and resistance to cracking as evidenced by both lab-based binder studies and a full-scale demonstration paving project.

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1. Introduction

The global network of roads is a complex and integrated system, with profound social and economic impacts. Trade and economic activity is directly correlated to the quality of highway access (Duranton et al.). Given the vital role of transportation infrastructure, it is critical to manage the economic and environmental costs of its construction and maintenance. According to the Federal Highway Administration, about 94% of the 2.8 million miles of paved US roads featured an asphalt surface in 2018 (FHWA). While not quite as high as concrete, the production of asphalt pavement is incredibly energy and emissions intensive (Ma et al.; Hu et al.; Ayub et al.). In 2019, US asphalt pavement production was nearly 420 million tons, representing over \$15 billion in economic activity, 21 million tons of CO_2 equivalent emissions, and 80 million barrels of oil equivalent embodied energy (NAPA). Clearly, there are strong incentives to reduce these costs and greenhouse gas emissions. Extending pavement service life, reducing the use of virgin feedstocks, improving the quality of recycled feedstocks, and more efficiently incorporating stiffer refinery outputs are crucial strategies for a more sustainable industry (Chehovits and Galehouse). Such refinery outputs may be broadly classified as Low-Quality Asphalts (LQAs), which are generated from improved crude oil refining process technology. On the other hand, Reclaimed Asphalt Pavement (RAP) is the recycled binder and aggregate from the milling of old roads.

Asphalt, the residue of crude oil refining, historically contained a significant fraction of lighter cuts that imparted softness and rutting-susceptibility in pavement applications. As the efficiency of fuels, monomers, heavy heating oil and lubricant extraction from crude oil has improved, the asphalt residue has become stiffer and more brittle. While these "LQA" binders have little susceptibility to rutting, cracking is far more problematic. Paving-grade binders are now premium products, while lower-cost LQAs proliferate at significant cost savings. Such LQA asphalts include

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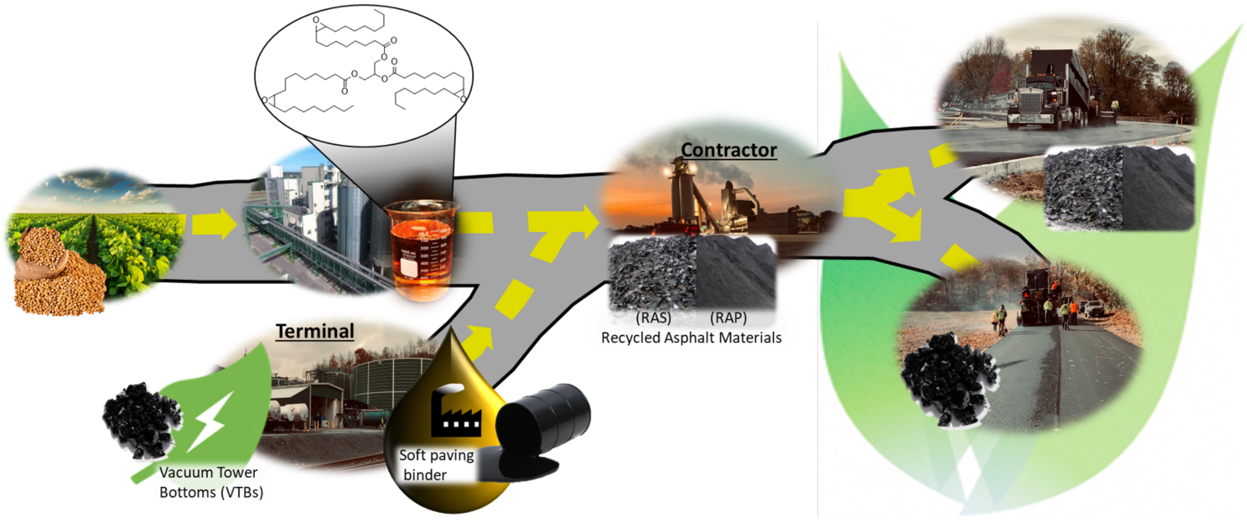

Figure 1 “The road of soy”: chemically activated soy-based rejuvenators reduce waste and life cycle impacts of asphalt pavement by facilitating the use of recycled asphalt pavement (RAP) and low-quality asphalts (LQAs).

Vacuum Tower Bottoms (VTBs), Solvent DeAsphalted (SDA) or Residuum Oil Supercritical Extraction (ROSE) bottoms (Beccari and Romano; Cao et al.; Gu et al.; Jones; Lee et al.; Rana et al.; Shin et al.). These products increase the utility of each barrel of oil, not only by reducing its cost and environmental impact but ensuring that nearly every drop of higher value products, such as fuels, make their way out of the oil. Presently, many producers will blend LQAs with premium grades or even buy back some of those lighter fractions to maintain cracking resistance performance while still allowing lower costs. This is clearly problematic for the paving industry. While asphalt may be a lower value product when compared to the other products that originate from petroleum refining, it is still a critical component of modern society, and thus it is essential to not only use these LQAs, but to also avoid needing to buy back the components that refiners have worked so diligently to extract from the crude.

RAP is produced in the demolition and resurfacing of roadways in which the asphalt pavement is milled to granular form for reuse or landfilling. RAP is composed of both aged asphalt binder and recovered aggregate, representing an enormous store of embodied energy and value. The incorporation of RAP into new hot mix asphalt (HMA) displaces virgin materials with attendant reductions in cost, energy, and emissions. In principle, most plants can produce HMA near 50.0 wt % RAP, with cost and energy savings exceeding 30.0% (Zahoor et al.; Gruber and Hofko, 2023). However, RAP use in 2018 reached only 21.0 wt % nationally, about 90 million tons. Pavement designs featuring higher RAP content are limited by the properties of the stiff oxidized RAP binder. That is, overuse of RAP causes embrittlement and more intensive processing conditions at the HMA plant, potentially offsetting many of the energy and emissions savings (Silva et al.). These factors serve as the rationale for many state DOT RAP use limits, most often ranging from 15 to 25 wt % (Williams et al.).

The use of RAP and LQAs has been considered by the asphalt materials community for over 40 years (Federal Highway Administration, a,b); however, the negative impact on pavement quality, especially crack resistance, introduces a limit to the practice. Asphalt pavements fail predominately through two mechanisms: rutting and cracking: rutting refers to plastic deformation under heavy loads on hot and softened pavement while cracking, on the other hand, represents a host of brittle failure mechanisms due to fatigue and cold weather climates. Since 1993, SuperPave Performance Grade (PG) specifications as outlined in AASHTO M 320 have provided a framework for quantifying the resistance of asphalt binder to these failure mechanisms in terms of minimum and maximum service temperatures, T_L and T_H, respectively (AASHTO). While both T_L and T_H vary continuously depending on binder source, binders sold according to the specification are labeled as PG$T_H^* T_L^*$, where T_H^* and T_L^* fall on a discrete scale of 6°C increments. For example, PG64-22 refers to a binder with $T_H > T_H^* = 64°\mathrm{C}$ and $T_L < T_L^* = -22°\mathrm{C}$. In the US, pavements with $T_L^* > -22°\mathrm{C}$ are rarely used due to crack susceptibility. Further, it has been seen that T_L alone is insufficient as a predictor of cracking performance, newer metrics like $\Delta \mathrm{T}_{L,C}$ are in the process of adoption (Lesueur).

The cleaner production of asphalt pavements can be realized through technologies that facilitate better LQA and

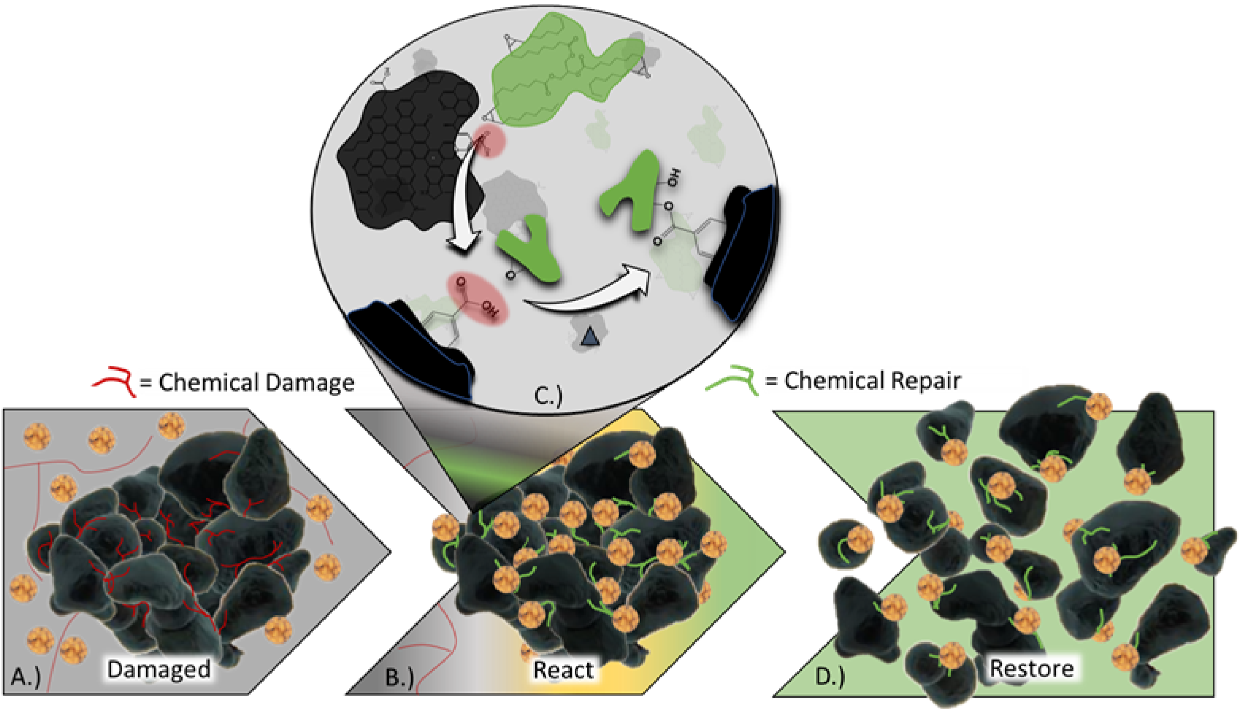

Figure 2 Illustration depicting the action of oxirane-reactive rejuvenators that bind to oxidized asphaltenes. The damaged asphaltenes (oxidized) (A) are shown to agglomerate together. Rejuvenators that react with the oxidized asphaltenes (B & C) by re-peptizing asphaltenes in the SARA matrix, restoring a paving-grade SARA composition (D).

RAP tolerance as envisioned in Figure 1. This can be achieved by counteracting the embrittlement associated with LQA/RAP, which is best understood through the binder composition. Asphalt is a complex mixture of thousands of distinct molecules generally categorized as Saturates, Aromatics, Resins, and Asphaltenes (SARA) (Qu et al., 2018; Wang et al.; Zhang and Greenfield). The binder is a colloidal suspension of polyaromatic asphaltene particles sized ≈ 500–5000 Da in the saturate, aromatic, and resin (SAR) matrix, and are referred to as maltenes. The ratio of SAR and asphaltenes (SARA) controls the properties of the binder: asphaltenes provide elastic modulus and strength while the maltene phase affords viscous dissipation, facilitating flow at high temperature and crack resistance at low temperature. This composition varies widely by crude source, refining technology, and aging. Aging begins with short-term oxidation due to the 150–180°C HMA construction process. This oxidation continues in the pavement through long-term exposure to extreme temperatures, moisture, and UV radiation. During aging, the SARA composition is enriched in asphaltene content due to the fusion of aromatics and resins into asphaltene-like compounds. Additionally, existing asphaltenes agglomerate into larger particles that further stiffen the binder and increase cracking susceptibility (Cannone Falchetto et al.; Gerardu and Hendriks; Shu et al.; Shu Xiang et al.; Zhao et al., a,b), as illustrated in Figure 2A. These physical and chemical processes are largely mediated by oxygen and sulfur based moieties. In addition to hardening, these changes reduce the compatibility with paving-grade binder due to both reduced miscibility and viscosity mismatch. This can result in heterogeneities, *e.g.* non-solvated RAP particles, that further diminish quality and hasten pavement failure (Bowers et al.).

The LQA content added to virgin binder is formulated—and held proprietary—by the supplier. The main tool a contractor employs to mitigate the further embrittlement due to RAP inclusion is through the selected virgin PG. For RAP addition rates in the 15 – 25% range, most follow the "grade-bump" rule-of-thumb that approximates the effect of RAP use as adding 6°C to both the T_L^* and T_H^* values of the virgin binder. For example, a project specifying PG64-22 would require the contractor to purchase a more costly PG58-28 to use RAP. Premium soft grades with $T_L^* = -28$°C or $T_L^* = -34$°C are scarce from the refiner, and suppliers apply a variety of "flux" additives to produce them through artifice. Over the years a host of such agents including recycled motor oil, light maltene fractions, lubricants, vegetable oils, tall oils, fatty acids and fatty esters have been used (Asli et al.; Ma et al.). Fluxes function through the dilution of the maltene phase, attenuating the melt viscosity and viscous modulus such that the desired T_L^* and T_H^* values are attained. Unfortunately this practice fails to mitigate the asphaltene aggregation and enrichment presented in LQA and RAP, and thus improvements to pavement durability are limited.

The industry has noticed these shortcomings and has defined a new class of additives sometimes termed “rejuvenators” or “recycling agent” intended to undo the deleterious effects associated with LQA/RAP use. To earn the moniker of rejuvenator, the material produce pavements with durability akin to those produced from virgin materials. In practice, however, many fluxes have simply been rebranded as such without recognizing the need to address the SARA composition. A functional rejuvenator will facilitate higher incorporation of LQA/RAP by repeptization of colloidal asphaltenes *in addition* to the dilation afforded by fluxes. As shown in Figure 2B, one manner in which this can be achieved is through chemical passivation.

In this work, we hypothesized that the oxygen/sulfur moieties presented by the surface of agglomerated asphaltene sites could be exploited for passivation through the introduction of a rejuvenator species bearing a complementary reactive moiety like oxirane, Figure 2C. By binding with oxidatively and thermally damaged asphaltenes, the chemically restored species should attain a greater degree of dispersion due to enhanced compatibility with SAR phase and a reduced tendency to further agglomerate (Figure 2D). To test this hypothesis, we considered Epoxidized methyl soyate (E) and partially epoxidized soybean oil (S) as biobased rejuvenator candidates. These rejuvenators were compared against Hydrolene 600T-a maltene complex-and corn oil as representative inert fluxes in a series of lab-based binder formulations and a full-scale paving project featuring up to 45 wt % RAP use. In lab-scale binder testing, we applied the SuperPave evaluation criteria to determine the PG dose-response to both fluxes and rejuvenators. Additionally, we determined the $\Delta T_{L,C}$ and Aging Index (AI) parameters, more recently developed as better predictors of cracking. To more directly assess the effects of rejuvenator vs. flux on asphaltene aggregation, we measured the effects of the additives on the SARA composition in both paving-grade and LQA binders. The dissolution kinetics of RAP in each additive were determined as a measure of solvency. Using the binder study results, we designed field tests where both 25 wt % and 45 wt % RAP pavements were installed and tested. Finally, we considered the economic and life cycle impacts associated with the high RAP utilization demonstrated. Our data show that by properly addressing the agglomeration, oxidization, and solvency issues in LQA/RAP, embrittled binders can pave the way to a more sustainable tomorrow.

2. Methods and Materials

2.1. Materials

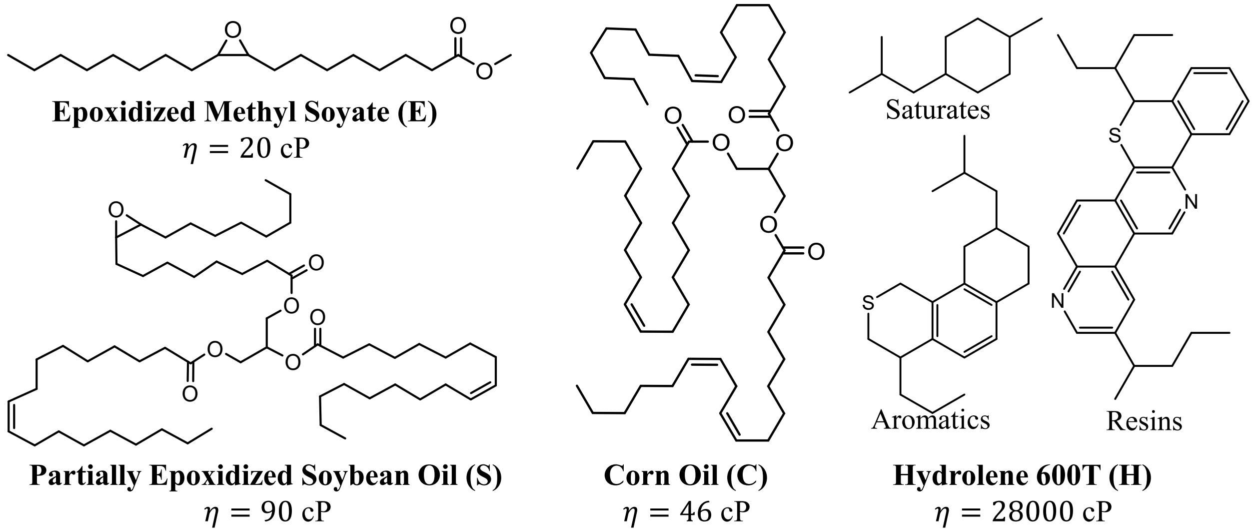

Figure 3 Chemical structures of asphalt flux/rejuvenator additives considered in this study.

Two vacuum tower distillation tower bottoms (VTBs), denoted V1 and V2, were selected as representative LQAs. V1 was obtained from Seneca Petroleum Co., Cresco, IL, and was graded to PG76-10. V2 was obtained from an

Indianapolis, IN area refinery and was graded to PG82-4. RAP was sourced from Des Moines Asphalt, Inc stockpile ABC12-0021 in Johnston, Iowa. RAP binder was passed over a No.4 sieve to create a fine RAP, which contained 5.75 wt % asphalt binder. RAP binder was then extracted using toluene and determined to have a continuous PG grade of 85.5-21.3 (PG 82-16). Rejuvenators used were Epoxidized Methyl Soyate (E) purchased from ACS tehcnical products, partially epoxidized Soybean oil (S) containing 2.5 wt % oxirane purchased from CHS , Corn Oil (C) purchased from Poet, and Hydrolene 600T (HT) purchased from Holly Frontier.

The virgin aggregates used in the Indiana project were sourced from local quarry pits around the Noblesville, IN area. The RAP aggregates were milled from roadways from the local area. The gradation of the mix design is shown in Table S5.

2.2. Additive Viscosity Testing

The additives were tested using a cup and bob system on the Ares G2. Experiments were run at 25 °C and a shear rate of 20 (1/s).

2.3. Asphalt Preparation and Rheological Testing

Blends were prepared by heating to 160 ° C and mixed at 2000 RPM for 2 hours using a Silverson L5M-A and a general purpose mixing head and quart sized samples. E, S, corn oil, or HT was added at several dosages ranging 4–10 wt % by weight of neat binder (bnb). Upon finishing the blend the sample was then removed and allowed to cool to room temperature. The samples are then briefly reheated to around 140 ° to collect samples for subsequent testing.

This study used 5 common rheology based parameters: complex modulus (G^*), phase angle (δ), creep stiffness (S), and relaxation rate (m-value) to determine the property change of rejuvenated asphalt binders. The complex modulus (G^*) and phase angle (δ) were obtained from a dynamic shear rheology test using AASHTO T315 performed on the Anton Parr SmartPave 92. The ratio $G^*/\sin\delta$, was measured at a frequency of $\omega = 10$ rad/s, is predictive of rutting. The unaged, short-term aged, and long-term aged binders were tested according to AASHTO T315-10, including AASHTO T 240–13 and R 28-12. Additionally, the AASHTO standard M320 was followed for mass loss during short term aging of Rolling Thin-Film Oven (RTFO) aging.

The BBR test method was performed on a Cannon model TE-BBR to measure the creep stiffness and relaxation at -6 °C, -12 °C, -18 °C, and -24 °C according to AASHTO T 313-12. Each binder sample was aged using a pressure aging vessel (PAV), formed into beams, and tested in a Bending Beam Rheometer (BBR). The asphalt beams were immersed at the test temperature in a water bath for 60 min and tested with a fixed load applied to the center of the beam. After 60 s, the deflection (creep stiffness) and stress relaxation rate (m-value) were measured and obtained according to AASHTO T313.

Rheology and BBR testing was done in triplicate.

2.4. Rejuvenator RAP Solvency Testing

The ability of each flux/rejuvenator species to solvate oxidized RAP binder was assessed through a solvency test. 250 g of fine RAP millings were mixed with 400 mL of the solvating agent (THF, Corn Oil, E, and S) and mechanically agitated using an IKA W20 mixer equipped with a round bottom paddle impeller at a speed of 400 RPM. 5 mL aliquots were taken at different time intervals up to 48 hours (5, 20, 120, 360, 1440 and 2880 minutes). The aliquots are then allowed to settle, diluted (2-fold dilution of 100 μL solvated asphalt into 3 mL of THF) and analyzed using a Shimadzu UV-Vis/NIR instrument scanning from 400-200 nm. The curves were integrated and normalized on the basis of THF solvent.

2.5. SARA Fractionation

Asphalt binders were fractionated into their SARA components for testing (D04 Committee; Lesueur). Asphaltenes were separated from maltenes by boiling heptane with the asphalt binder and then asphaltenes were collected by passing the mixture over a filter. The filtered material was then dried under reduced pressure to remove solvent. The filtrate was also concentrated under reduced pressure. The asphaltenes and maltenes were weighed to determine ratio of maltenes:asphaltenes before and after rejuvenation.

2.6. Preparation of Asphalt mixture Specimens

The mixtures procured from the Noblesville, IN plant for the demonstration paving project were reheated for gyratory compaction. The specimens were prepared for performing disc-shaped compact tension (DCT) and Hamburg wheel tracking (HWT) testing. The DCT specimens of 150-mm diameters were compacted to a height of ≈50.0 mm for an air void content of 7 ± 0.5%. The DCT specimens were cut and drilled for mounting in the DCT device according to ASTM D7313-13. The same air void content of 7 ± 0.5% was obtained for the HWT specimens. The samples with 150-mm diameters were compacted to a height of ≈60.0 mm, and then cut to obtain flattened faces for performing the HWT testing according to AASHTO T 324-17.

2.7. Characterization of Asphalt Mixtures' Mechanical Performance

The DCT specimens from the Indiana project were conditioned at -12°C, a temperature 10°C higher than the low-temperature grade of the PG 64-22 paving grade binder. Upon conditioning, the specimens underwent tension at a constant rate of 0.017 mm/s. The fracture energy is computed as:

$$G_f = \frac{\int_0^{x_{max}} L \, \mathrm{d}x}{B * (W - a)} \tag{1}$$

where G_f is the fracture energy in J/m^2, L is the load (N), x is the crack mouth opening displacement (CMOD, m), x_{max} is the CMOD at failure (m), B is the specimen thickness (m), and $W - a$ is the ligament length (m) according to ASTM D7313-13. The HWT test specimens were submerged in a temperature-controlled water bath set at 50 °C. Upon conditioning, the HWT testing began and continued until reaching either 20,000 passes or a maximum change in length of 12.5 mm was observed in the readings acquired from linear variable displacement transducers. The HWT test was performed based on the guidelines of Iowa Department of Transportation (DOT) as well as according to the AASHTO T 324-17.

3. Results and Discussion

In this study we investigate the action of epoxidized methyl soyate (E), partially epoxidized Soybean oil (S), corn oil (C), and Hydrolene 600T (HT) on LQA binder performance; chemical structures of these additives are shown in Figure 3. Our aim is to differentiate reactive rejuvenators (E, S) from inert fluxes (C, HT) in the mitigation of the detriment of LQA/RAP use in HMA pavements. The cleaner production of transportation infrastructure can be achieved by maximizing pavement recycling and embracing the generation of LQAs resulting from high efficiency petroleum refining. RAP and VTB share many compositional characteristics, both requiring softening and asphaltene stabilization to yield pavement grade binders with a SARA profile that properly balances stiffness and ductility. VTB binder formulations mimic those based on extracted RAP binder, and thus we first conducted a does-response study using VTB binders V1 (PG76-10) and V2 (PG82-4). The results were subsequently used to guide mix design in a high-RAP paving demonstration featuring RAP with PG88-16 extractable binder.

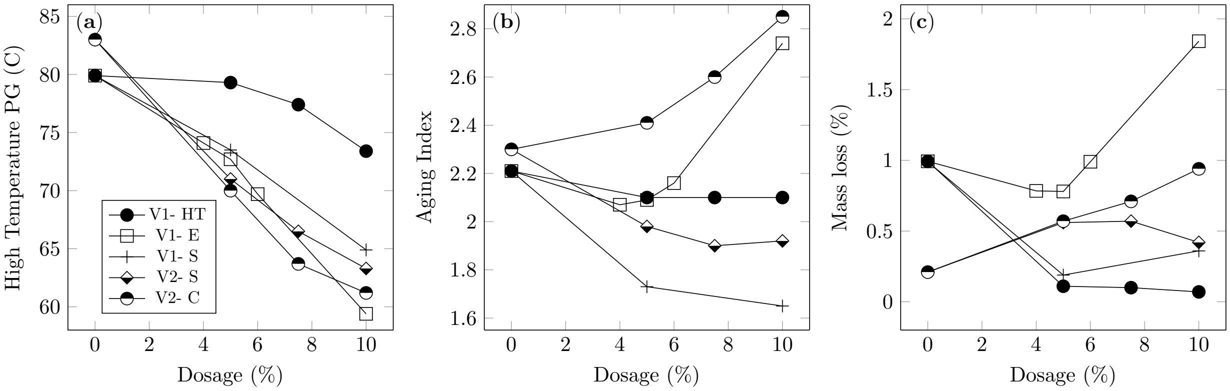

Figure 4 High temperature binder rheology of rejuvenated vacuum tower bottoms to identify how the asphaltene-rejuvenator interaction. This figure compares the (a) T_H, (b) Aging Index and (c) mass loss test data of modified VTBs.

3.1. High Temperature Rheology

Figure 4a summarizes the high temperature rheological characteristics in V1 and V2 with respect to additive dosage and the viscosities of the additive at room temperature are given in 3. The rheological properties of asphalt binders are a critical factor in determining the performance of an asphalt pavement. The high temperature Performance Grade (T_H), described in AASHTO T315 and AASHTO T240, is a frequently used metric that indicates the temperature at which the binder softens and becomes prone to failure via rutting. In general, LQA and RAP have exceptional rutting resistance; however, upon addition of flux/rejuvenator the T_H will be suppressed through a softening effect. While this is largely desirable to improve workability, it also puts an upper limit on the flux/rejuvenator dosage: too high a dosage will cause rutting resistance to plummet to unacceptable levels. Addition of low viscosity materials will reduce both $G^*/\sin\delta$ and T_H, as is demonstrated in Figure 4a. S, E, and C have a pronounced effect on decreasing the T_H, with S having the lowest and C having the highest impact on T_H. Because C has none of the functionality required to react with asphalt, it is unsurprising that it has the most pronounced effect on T_H: it simply acts as a low viscosity diluent. C, S, and E are all long-chain aliphatic molecules, therefore it would be expected that S and E would also have high compatibility with the maltene phase to reduce viscosity through dilution as observed. Interestingly, the effect is somewhat less dramatic in these two compounds when compared to C. This is especially noteworthy due to E having the lowest viscosity amongst the additives considered. This reduced impact on the T_H is due to the ability of E and S to chemically react with many of the moieties present in asphalt. The chemical incorporation into compounds like resins and asphaltenes will reduce the thinning effect due to the aliphatic chains being tied into the stiffer components, thus decreasing chain mobility. Unlike the aliphatic fatty esters/triglycerides, HT is a maltene asphalt-like fraction that has a complex chemical make-up and is higher molecular weight. In contrast to the fatty rejuvenators, HT shows the weakest T_H-suppression. While this may offer some benefits to producing a binder that can survive very high temperatures environments, there are three major draw backs: low temperature performance, lack of $\Delta T_{L,C}$ improvement, and energy intensity associated with producing pavement from this binder.

Effective rejuvenation extends beyond a simple softening of the binder — it must inhibit the aging of the pavement. Premature aging of asphalt pavements is a concern in any binder, but especially so when using RAP or LQA's. Binder aging occurs by either short term aging where the brief extremely elevated temperatures at mix plants can alter the binder chemistry or over time where the elements react and oxidize the pavement. This process can be simulated in the lab and provides critical information on the effect of additives on binder characteristics. The Rolling Thin Film Oven (RTFO) aging process captures the effect rejuvenators have on aged asphalt binders by measuring the modulus and mass change as a result of temperature and simulated time. Aging index (AI), defined by equation 2, is the ratio of the $G^*/\sin\delta$ before and after RTFO treatment and describes the changes in rheological characteristics as a function of simulated short-term aging, giving insight into how the pavement would age in the field. This critical characteristic helps to identify which rejuvenators are reacting to provide long-term stabilization to the SARA network and which only superficially change viscosity. Additives that exhibit no change, level off, or have increased AI can be described simply as flux agents. A decrease in AI suggests permanent chemical repair of damaged sites in the SARA network that stabilize the asphaltene component as illustrated previously in Figure 2. This parameter is critical to a well designed and long lasting pavement. While some of these additives technically bring the pavement to within specifications, they do not provide a long lasting benefit, and thus the pavement often begins to perform as though no additive was used as time progresses. In Table S1 it can be seen that a typical unmodified asphalt binder exhibits an AI value around 2.2–2.7. HT which is comprised of maltenes, has no impact on the AI, as seen in Figure 4b. While C is effective at reducing viscosity, it is negatively impactful on binder aging, raising the AI value to 2.8 at the highest dosage. S, however, demonstrates a lower AI value. The reduction in AI suggests the oxirane molecules located on the S molecule are reacting with oxidized sites that are causing the aggregation of asphaltene particles and stabilizing them to prevent further agglomeration. E, surprisingly, showed an increase in the AI as this material is also reactive with oxidized sites. The change in $G^*/\sin\delta$ is likely due to components breaking down or volatilizing, which can be measured by the mass loss.

$$\mathrm{AI} = \frac{G^*/\sin(\delta)|_{\text{RTFO-aged Binder}}}{G^*/\sin(\delta)|_{\text{Unaged Binder}}} \tag{2}$$

The mass loss calculation examines the change in mass of the material over the the RTFO aging process, with an upper limit of 1% permitted in the AASHTO M320 specification. A change in mass loss would suggest the additive, or part of the additive, is undergoing volatilization. Unsurprisingly, maltene-based additive HT demonstrates no change in mass loss as seen in Figure 4c due to the high molecular weight, and thus negligible vapor pressure, of the additive. S also has low mass loss, which is partially due to the high molecular weight of the triglyceride and partially the epoxy rings reacting with chemical sites within the binder. This is a different result from the C as the mass loss increases according to dosage. The primary difference between S and C is the oxirane groups located on S. The increasing mass loss and AI would suggest that C is not reacting with the oxidized asphaltenes, instead only superficially changing the viscosity and then volatilizing or breaking down during the RTFO process. E shows increasing mass loss with dosage, which is initially surprising due to the functional similarity to S. While E does have these highly reactive oxirane moieties, as a methyl ester it is more susceptible to hydrolysis, transesterification, or other reactions that would cause the release of methanol, which accounts for roughly 10% of the E molecular weight. Thus the 1% increase in mass loss observed at 10% E dosage could be attributed to methanol evolution.

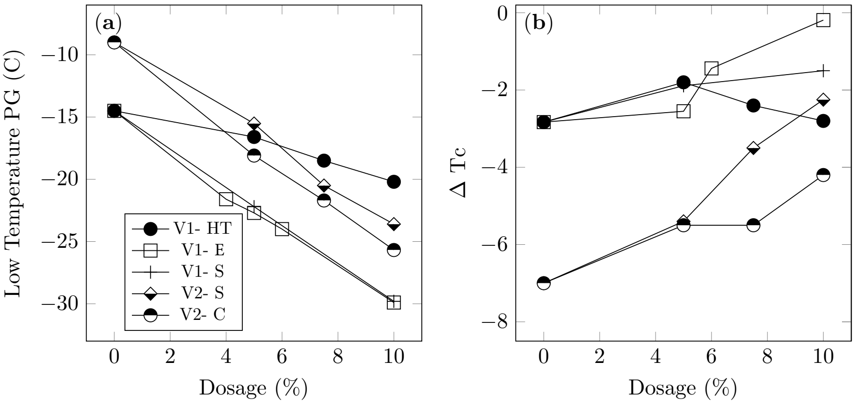

Figure 5 Low Temperature binder rheology of rejuvenated vacuum tower bottoms identify how the asphaltene-rejuvenator interaction. This figure compares the (a) T_L (b) ΔTc test data of modified VTBs.

3.2. Low Temperature Rheology

Where T_H is a surrogate for rutting resistance, low temperature performance grade T_L serves as an indicator for pavement cracking. Rejuvenators that react and restore, as opposed to cutting or diluting, will change how the binder responds to stress at low temperatures. The prevailing theory is that rejuvenators restore the aromatic phase to stabilize the asphaltenes. This SARA rebalancing confers improved ductility and stress dissipation, translating to a less brittle pavement. Mitigating brittleness is critical for any pavement that would be produced using an exceptionally stiff binder such as LQA or RAP. A significant reduction in T_L and increase in $\Delta \mathrm{T}_{L,C}$ would suggest a material is a “quality” rejuvenator for embrittled materials. In Figure 5 E, C, and S demonstrate exceptional reduction of the T_L value, suggesting improved crack resistance according to this metric. Contrarily, the T_L dosage response for HT demonstrates minimal efficacy at modifying cracking resistance. The leveling off response of HT is due to the saturation of the SARA composition with maltene components without modifying the oxidized asphaltenes. This is an excellent, if incomplete, indication that the vegetable oil derived materials have a substantial impact on the low temperature performance. While the T_L is a critical component of a pavement’s ability to resist fracture, it is by no means comprehensive. Many materials, like waste oils, have been shown to reduce T_L but yield low quality pavements in the field.Karki et al. (2019) Binders, and the pavement constructed therefrom, that met the T_L specification were shown to crack in an unacceptably short time. Because of this a more detailed understanding of the cracking resistance is needed. The community has begun to turn towards more fundamental understanding of how materials crack and thus have adapted testing to provide a more complete understand of whether failure is dominated by an elastic or viscous-like behavior.

Low temperature binder rheology failure can be explained by measuring the materials force deflection and the rate of deflection. The force deflection represents the stiffness of the material at the test temperature. The rate of deflection, on the other hand, is an indication of how efficiently the material can dissipate the applied stress. An asphalt specimen can fail the BBR test either through reaching a temperature at which the stiffness becomes too large (denoted as $T_{L,S}$) or reaching a point at which the relaxation rate becomes too small (denoted as $T_{L,m}$). While $T_{L,m}$ is thus more representative of the binder ductility, the original AASHTO M320 specification placed equal weight in the determination of T_L. That is, the T_L value reported for the binder is the largest of $T_{L,S}$ vs. $T_{L,m}$. The $\Delta T_{L,C}$ parameter was introduced to correct this shortcoming (Jóźwiak et al.; Lewandowski and Chorążyczewski) and is defined as:

$$\Delta T_{L,C} = T_{L,S} - T_{L,m} \tag{3}$$

Generally, it is desirable to have $\Delta T_{L,C}$ near zero. Highly negative $\Delta T_{L,C}$ indicates that the pavement is extremely stiff and very susceptible to cracking. In Figure 5b, it can be seen that saturate materials like HT are ineffective at modifying the $\Delta T_{L,C}$ parameter. E and S promote better stress relaxation by stabilizing the asphaltene network. Inert saturate-like rejuvenators, such as C, fail to prevent T_L embrittlement due to the destabilization of the SARA network, allowing asphaltenes to agglomerate into larger particles. Effective rejuvenators will improve the stress relaxation by compatibilizing the saturate and asphaltene molecules in the SARA network thus imparting the ability to resist cracking. As expected, C shows a much lower effect on $\Delta T_{L,C}$ than S due to its lack of asphalt-reactive moieties. Interestingly, Figure 5 shows that despite the mass loss and aging issues associated with E, it is very effective at modifying the T_L and $\Delta T_{L,C}$. This clearly speaks to the fact that while the E is evolving methanol, it is still quite reactive, and that reactivity with the asphalt helps improve interfacial compatibility between the solid-like asphaltene particles and the liquid saturate fractions. The difference in $\Delta T_{L,C}$ modification between E and S is primarily due to the oxirane mass content. E contains close to three times the mass % of oxirane content to S, with E at 7.2 and S at 2.49 mass % per gram. The higher oxirane content in E provides more reactivity and yields a higher degree of stress relaxation in embrittled asphalts.

3.3. SARA Fraction

The direct relationship between structure and mechanical proprieties suggests that reactive rejuvenators, unlike fluxes, will chemically alter the structure of the molecules in the SARA network. The rejuvenator-asphaltene interaction has been largely unexplored. To understand how rejuvenators achieve the rebalancing of the SARA network with the proper ratio of aromatic to saturate-like compounds (Rathore et al.), we conducted SARA fractionation on asphalt binders before and after modification with E and C. The additives were used to modify a PG52-34 binder and an embrittled asphalt binder (RAP extracted binder).

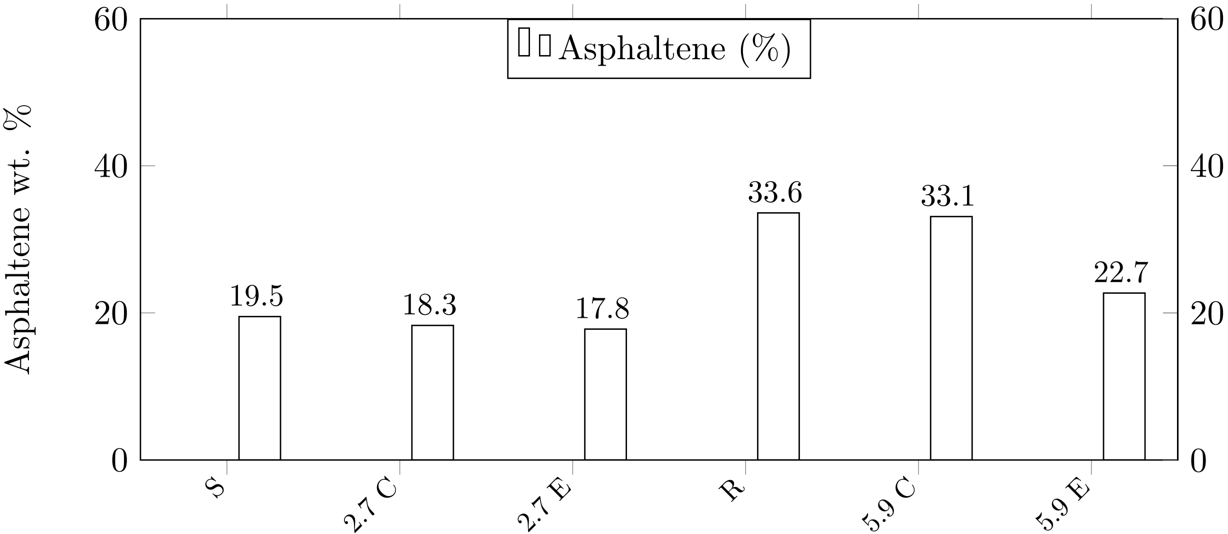

Figure 6: PG52-34 and a RAP-extracted binder were modified with E and C at the dosages of 2.75 and 5.92% by weight of the neat binder. The samples were SARA fractionated to understand the change in asphaltene content.

Figure 6 shows the asphaltene content according to the SARA fractionation procedure for both paving grade PG52-34 and RAP extract PG88-16. The paving-grade PG52-34 represents a binder with a properly balanced SARA network including well-suspended asphaltenes that account for 19.5 wt% of the binder composition. On the other hand, the heavily aged PG88-16 RAP extract clearly shows evidence of asphaltene aggregation with nearly 34 wt % asphaltene content. When additives are introduced to PG52-34, the variation in the asphaltene content is negligible for both E and C. This result illustrates that rejuvenation has little impact on the asphaltene network in a binder whose asphaltenes are already well-distributed. Conversely, the PG88-16 RAP extract shows starkly different responses to additives according to reactivity. The C blend shows negligible change in the asphaltene content, as this is primarily due to C acting as viscosity modifier with no direct asphaltene interaction. On the other hand, the oxirane-baring E blend demonstrates a 30% asphaltene reduction, supporting the hypothesis that the oxiranes react with and repeptize the agglomerated asphaltene particles, rebalancing the SARA network. Materials that act only as inert saturates are detrimental to the SARA network as they destabilize asphaltenes over time leading to hardening of the binder in the long-term. Triglycerides and derivative molecules would largely fall into the saturate category of the SARA, but as demonstrated the oxirane-based rejuvenators play a pivotal role in the deagglomeration of asphaltenes thereby reducing extractable asphaltene content (Rathore et al.; Council; Newcomb et al.). This further demonstrates how the oxirane molecules chemically react to help to reconstitute the oxidized asphaltenes in embrittled binders. Quantitative measurements such as these are important to the demonstration of a "rejuvenation" benefit at a chemical level and acceptance by the asphalt industry of additives presented as such (Jestin and Barré; Savvidis et al.; Storm et al.; Tanaka et al.; Xu et al.).

3.4. Rejuvenator RAP Solvency

High RAP utilization hinges on not only efficacious asphaltene modification, but diffusion between the oxidized RAP binder with virgin binder. This process is constrained due to the limits on time and amount of energy used, which translates into cost and emissions. In the HMA production process, virgin aggregrate is first mixed with virgin binder, followed by the introduction of RAP. Consequently, any additives present in the virgin binder can only directly influence the RAP by the degree to which the RAP binder can mix with virgin binder in a fairly constrained mass transport environment. Overcoming the mass transport issue with RAP utilization is one of the primary issues with high RAP pavements. Rejuvenators need to not only diffuse into the aged binder to restore the RAP binder properties, but also facilitate timely compatibilization of aged binders with virgin binders (Tarsi et al.; Tran et al.; Al-Qadi et al., 2007). There is not an industry standard to quantify the diffusion rate of aged binders. This paper will use rejuvenator solvency of RAP binders to quantify the diffusion rate. This will provide insight on how efficacious rejuvenators are at enabling mass transport between aged and virgin binders (Tarsi et al.; Presti et al.).

Rejuvenator solvency with RAP was quantified by measuring UV absorbance of the asphaltene at various wavelengths over time. Rejuvenators with highest mass diffusion rate and best compatibility will have the highest UV absorbance, suggesting better asphaltene solvency and efficiency at the mix plants. Four materials were tested: tetrahydrofuran (THF), S, C, and E. THF was selected as a "control" solvent due to its excellent compatibility with asphalt binder and rapid dissolution thereof. RAP dissolution as a function of time was quantified by integrating the UV absorbance over wavelengths 215–400 nm and normalizing to that of THF as shown in Figure 7. E has the largest UV absorbance of the materials tested and reaches maximal absorbance most quickly, indicating superior solvency compared to S or C. This suggests that E would provide the most homogeneous asphalt mixtures as produced at mix plants which offer finite mixing times. S, owing to its comparatively higher viscosity, is more sluggish in asphaltene solvation although attains similar solvency given sufficient time. It is clear that speed of dissolution does not have a major impact on the grading performance, but may become an issue at at the mix plant. S has vastly superior performance to C and thus it is important to understand if the slower dissolution would limit the practicality of this additive. This concern was put to rest in Noblesville, Indiana at an Indiana Soybean Association parking lot.

3.5. Rejuvenator Implementation at Mix Plant Production

Based on the binder studies conducted above, we selected S as the most practical rejuvenator to carry forward for a full-scale field trial. A 500 mix ton parking lot construction project was arranged at the Indiana Soybean Alliance (ISA) headquarters in Indianapolis, IN (Figure S2). The parking lot test sections featured high RAP utilization with both control and S-modified test sections. The purpose of this project was to enable high RAP usage, improving the low temperature cracking performance, and maintain a high rutting resistance. The binder (before and after modification), extracted binder (from the commercially produced mix), and asphalt mix of the section were all tested to understand S efficacy, as shown in Table 1. A PG64-22 binder was selected as the base binder. The rejuvenated section included S at a dosage of 5.7% by weight of the neat binder. The extracted binders of the control mix and S sample mix were also tested, denoted as 25R for 25.0% and 40R for 40.0% RAP in Table 1. Prior to the addition of RAP, S reduced T_L by about 8 °C, increased $\Delta T_{L,C}$ to 0.42 °C, and reduced AI from 2.73 to 1.91. Compared to the the S section (H-

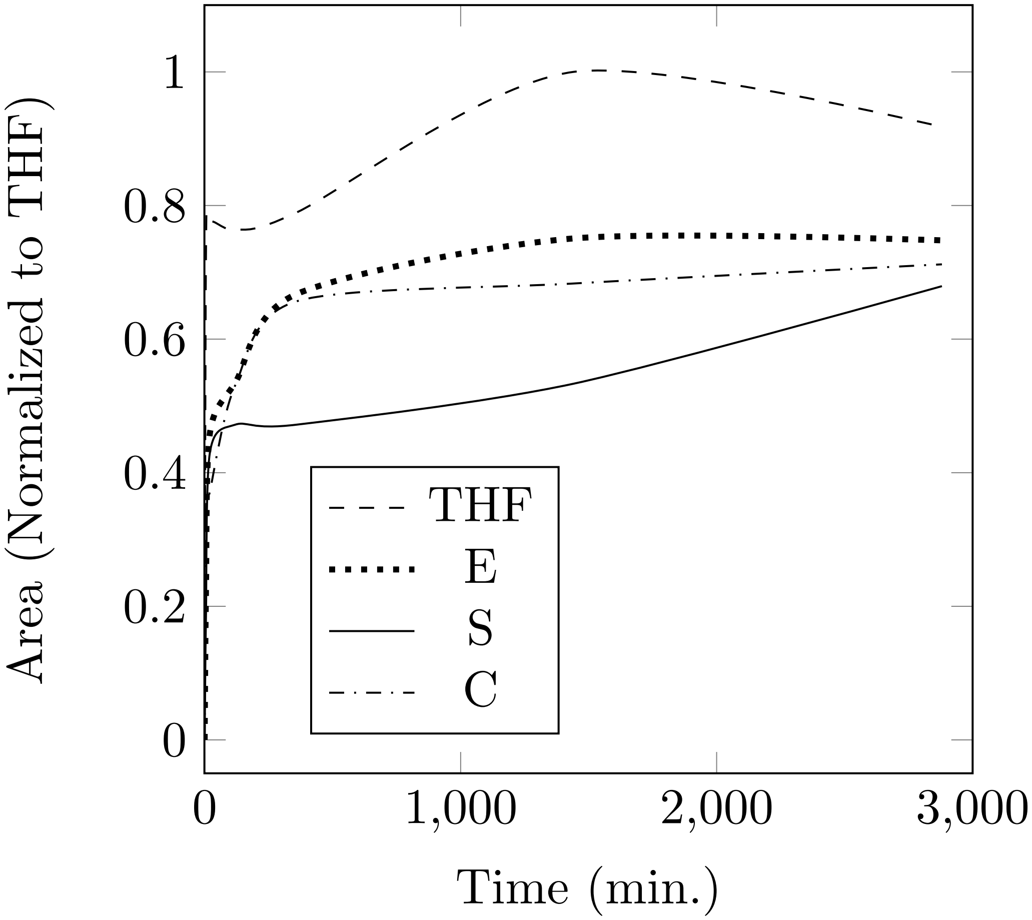

Figure 7: Comparison of RAP solvency performance of various asphalt fluxes and rejuvenators using the area of the UV from wavelengths 215 nm-400 nm. Area is normalized to the highest THF absorbance.

40R-5.7S), the control section (H-25R) showed a significantly higher T_H/T_L values and a more negative $\Delta T_{L,C}$ value. These results indicate that the control section, in spite of its lower RAP content, is more likely to suffer cracking damage than the S-rejuvenated section. The S section extracted binder graded to PG64-28, whereas the control section was PG64-22. This result would suggesting the presence of S improved the crack resistance, while reducing rut resistance. This conclusion is confirmed by the increase in rut depth in the HWT testing from 2.6mm to 6.7mm and the improved fracture energy from 376 J/m^2 to 506.7 J/m^2. This field data compliments the previous laboratory binder data in Figure S1 and 5 which demonstrate the use of a chemically reactive rejuvenators are effective at producing a high quality binders made from highly recycled asphalt content or low quality asphalt sources.

3.6. Energy and Environmental Considerations

The energy consumption and GHG estimation for asphalt binder production includes crude oil extraction, transport, and refining, yielding an estimated energy consumption of 5.810 GJ/ton and GHG emissions of 627lbs CO_2/ton (US EPA; Davis and Boundy; Gable and Gable). Use of RAP and LQA will undoubtedly have an impact on energy consumption and carbon emissions, and in Table 2 we show how RAP use could benefit these parameters. Up to a 33% reduction of energy consumption and up to a 25% reduction in CO2 emissions is possible using this technology.

4. Conclusions

Asphalt rejuvenators are additives primarily used to restore low quality or aged asphalt pavement to a material resembling virgin binder. This restoration has been linked to changes in SARA composition and/or due to an rear-

Table 1
A Noblesville, IN demonstration project in the Indiana soybean Association Parking lot using a 64-22S. The project possess two sections: a control section with 25% RAP and a S section with 40% RAP.

Sample Code	H	H - 5.7S	H 25 %RAP	H 40 %RAP 5.7S
High PG	65	56	74	66
Low PG	-25	-33	-23	-30
Contineous	91	89	97	96
Tc	-0.6	-0.2	-3.6	0.2
Aging Index	2.7	1.9	-	-
HWT- Rut depth (mm)	-	-	2.6	6.7
DCT (-12°C) - Fracture Energy (J/m^2)	-	-	376.0	506.7

			Energy Consumption (MJ/t of Material)								**Emissions (lb. CO^2/t)**					
RAP Content :			*0%*	*15%*	*21%*	*30%*	*45%*	*60%*			*0%*	*15%*	*21%*	*30%*	*45%*	*60%*
Rejuvenator Content :			*0.0%*	*2.3%*	*3.0%*	*4.0%*	*5.2%*	*5.8%*			*0.0%*	*2.3%*	*3.0%*	*4.0%*	*5.2%*	*5.8%*
Binder Content:						6.0%								6.0%		
Raw Materials:		Estimates								Estimates						
Aggregates	Marceau et al., 2007	54.0	50.8	43.1	40.1	35.5	27.9	20.3	Chappat et al. 2003	22.0	20.7	17.6	16.3	14.5	11.4	8.3
Rejuvenator	Pradhan etal. 2011	41.0	0.0	0.9	1.2	1.5	2.0	2.2	Patthanaissaranukool et al. 2016	880.0	0.0	1.2	1.6	2.1	2.7	3.1
Manufacturing:																
Production of bitumen	Yang et al., 2016	5810.0	348.6	296.3	275.4	244.0	191.7	139.4	Chappat et al. 2003	627.0	37.6	32.0	29.7	26.3	20.7	15.0
Storage of bitumen	Zapata et al. 2005	543.0	32.6	27.7	25.7	22.8	17.9	13.0								
Asphalt Mixing and Drying of Aggerates/ RAP	Ang et al. 1993	362.0	340.3	340.3	340.3	340.3	340.3	340.3	Chappat et al. 2003	48.4	45.5	45.5	45.5	45.5	45.5	45.5
Reclaimed Asphalt Pavement (RAP)	Zaumanis et al. (2014a)	16.5	0.0	0.4	0.5	0.7	0.9	1.0	Chappat et al. 2003	8.8	0.0	1.3	1.8	2.6	4.0	5.3
Construction:																
Asphalt pavement	Zapata et al. 2005	13.4	13.4	13.4	13.4	13.4	13.4	13.4	Chappat et al. 2003	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total:			785.6	722.1	696.6	658.2	594.1	529.6			105.2	99.0	96.4	92.5	85.7	78.6
Ratio:			1.00	0.92	0.89	0.84	0.76	0.67			1.00	0.94	0.92	0.88	0.81	0.75

Table 2 The energy consumption and greenhouse emissions from the raw materials, production and paving of asphalt pavement. The sources are located to the left of the estimated numbers.The projected energy consumption and GHG emissions of CO^2 based on RAP binder content usage are shown.

rangement of the resin-asphaltene fractions (Shen et al.). Elevated levels of resins and asphaltenes in LQA and RAP materials result in a high susceptibility to fatigue and cracking. These qualities make RAP and LQA use in Hot Mix Asphalt (HMA) undesirable; however, this reluctance to use RAP and LQA can be overcome by showing cost, emissions, and performance advantages with use of the correct additive. Use of bio-based rejuvenators can provide these much sought-after advantages due to their ability to diffuse in the asphalt, chemically reconstitute the asphaltenes into smaller molecules, and enhance the viscoelastic properties of the binder that then further enhance HMA designs (Zaumanis et al.; Zaumanis and Mallick).

The term "rejuvenator" has been used for a wide range of products that claim to have increased performance with solvency and critical low temperature grade. Unfortunately, a majority of these products fail to substantiate their claims with other critical asphalt properties, such as change in asphaltene concentration and $\Delta T_{L,C}$. Rejuvenators can affect properties from the overall continuous grade range, to mass loss, to the viscoelastic properties. This study provides evidence that oxirane content has a direct influence on asphaltene modification. Asphaltene restoration affects the low temperature performance of LQA and RAP mixes. In VTBs, it was shown that partially epoxidized soybean oil with 2.5 % oxirane content has superior performance in overall continuous performance grade, $\Delta T_{L,C}$, mass loss, and AI compared to epoxidized methyl soyate, corn oil, and Hydrolene-600T. This was further validated by the Indiana paving project which demonstrated SESO's efficacy in the field as a reactive rejuvenator. This enabled a 40% RAP pavement design with superior performance compared to a 25 % RAP control. The Indiana project achieved a PG64-28 extracted binder grade with a $\Delta T_{L,C}$ increase of 3.8 °C to 0.2°C, far outperforming the target grade of 64-22S. The HWT and DCT performance data suggest the project can be reformulated to either reduce rejuvenator or increase RAP dosage. Based on the binder performance of H-5.7S and H-40R 5.7S, RAP content could increase to 60% with acceptable performance. This would achieve a ratio reduction of 0.33 for energy consumption and emissions. This project and others like it only further establish the effectiveness of oxirane additives with aged or embrittled asphalts. SESO has clearly demonstrated its proper designation as an asphalt rejuvenator, positively impacting the chemical makeup of the binder and thus improving both lab and field performance. It is no secret that the demand for the higher value components of petroleum refining such as fuels, lubricates, and monomers are often stretched thin, and these bio-asphalt additives offer a tremendous opportunity by providing an economic, environmentally friendly way to use both lower quality as well as recycled asphalt while leaving the higher value components of the crude refining process available for high value applications thus reducing carbon emissions while also allowing the finite reserve of petroleum to stretch further into the future.

5. Acknowledgments

This work was internally funded. No funding source to declare.

6. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. References

References

AASHTO, . AASHTO M 320: Standard specification for performance-graded asphalt binder. Technical Report. American Association of State Highway and Transportation Officials. URL: `https://store.transportation.org/Item/PublicationDetail?ID=4594`.

Al-Qadi, I.L., Elseifi, M.A., Carpenter, S.H., 2007. Reclaimed Asphalt Pavement – A Literature Review. Technical Report. Illinois Department of Transportation. URL: `https://www.ideals.illinois.edu/handle/2142/46007`.

Asli, H., Ahmadinia, E., Zargar, M., Karim, M.R., . Investigation on physical properties of waste cooking oil – rejuvenated bitumen binder. Construction and Building Materials 37, 398–405. URL: `http://www.sciencedirect.com/science/article/pii/S0950061812005120`, doi:`10.1016/j.conbuildmat.2012.07.042`.

Ayub, A., Sheikh, N., Tariq, R., Khan, M., Invernizzi, C., . Exergetic optimization and comparison of combined gas turbine supercritical CO2 power cycles. Journal of Renewable and Sustainable Energy 10, 044703, 1–23. doi:`10.1063/1.5038333`.

Beccari, M., Romano, U., . Encyclopaedia of hydrocarbons. [Vol. II, [Vol. II,. ENI : Istituto della Enciclopedia italiana. OCLC: 835718466.

Bowers, B.F., Huang, B., Shu, X., Miller, B.C., . Investigation of reclaimed asphalt pavement blending efficiency through GPC and FTIR. Construction and Building Materials 50, 517–523. URL: `http://www.sciencedirect.com/science/article/pii/S0950061813009069`, doi:`10.1016/j.conbuildmat.2013.10.003`.

Cannone Falchetto, A., Alisov, A., Goeke, M., Wistuba, M.P., . Identification of structural changes in bitumen due to aging and fatigue. Czech Technical University in Prague. URL: `http://guarant.topinfo.cz/ee2016/download/proceedings/data/c196.html`, doi:`10.14311/EE.2016.196`.

Cao, F., Jiang, D., Li, W., Du, P., Yang, G., Ying, W., . Process analysis of the extract unit of vacuum residue through mixed c4 solvent for deasphalting. Chemical Engineering and Processing: Process Intensification 49, 91–96. URL: `http://www.sciencedirect.com/science/article/pii/S0255270109002475`, doi:`10.1016/j.cep.2009.11.013`.

Chehovits, J., Galehouse, L., . Energy usage and greenhouse gas emissions of pavement preservation processes for asphalt concrete pavements, in: Compendium of Papers from the First International Conference on Pavement Preservation, pp. 27–42. URL: `https://trid.trb.org/view.aspx?id=919015`.

Council, N.R. (Ed.), . Asphalt concrete mix materials. Number 1436 in Transportation research record, National Academy Press. OCLC: 31692494.

D04 Committee, . Test Method for Separation of Asphalt into Four Fractions. Technical Report. ASTM International. URL: `http://www.astm.org/cgi-bin/resolver.cgi?D4124-09R18`, doi:`10.1520/D4124-09R18`.

Davis, S.C., Boundy, R.G., . Alternative Fuels Data Center: Maps and Data - Fuel Economy at Various Driving Speeds. URL: `https://afdc.energy.gov/data/10312`, doi:`10.1039/D0GC01831G`.

Duranton, G., Morrow, P., Turner, M., . Roads and trade: Evidence from the US | the review of economic studies | oxford academic. The Review of Economic Studies 81, 681–724,. URL: `https://academic.oup.com/restud/article/81/2/681/1519232`, doi:`https://doi.org/10.1093/restud/rdt039`.

Federal Highway Administration, a. Demonstration Project 39 – Asphalt Recycling. Technical Report. Federal Highway Administration. URL: `https://www.fhwa.dot.gov/publications/research/infrastructure/recycling/index.cfm`.

Federal Highway Administration, 1995b. Pavement recycling. Executive summary and report. Technical Report. Federal Highway Administration, Washington, DC (United States). URL: `https://www.osti.gov/biblio/529849`.

FHWA, . Table HM-12 - Highway Statistics 2017 - Policy | Federal Highway Administration. Technical Report. Federal Highway Administration. URL: `https://www.fhwa.dot.gov/policyinformation/statistics/2017/hm12.cfm`.

Gable, C., Gable, S., . How can gasoline gallon equivalents help gauge alternative fuels? URL: `https://www.treehugger.com/fuel-energy-comparisons-85636`.

Gerardu, J.J.A., Hendriks, C.F., . Recycling of road pavement materials in the netherlands. Rijkswaterstaat communications nr 38 URL: `http://resolver.tudelft.nl/uuid:d06e9dd5-0558-48fe-a665-ccedf987970e`.

Gruber, M.R., Hofko, B., 2023. Life cycle assessment of greenhouse gas emissions from recycled asphalt pavement production. Sustainability 15, 4629.

Gu, W., Huang, Y., Wang, K., Zhang, B., Chen, Q., Hui, C.W., . Comparative analysis and evaluation of three crude oil vacuum distillation processes for process selection. Energy 76, 559–571. URL: `http://www.sciencedirect.com/science/article/pii/S036054421400989X`, doi:`10.1016/j.energy.2014.08.053`.

Hu, W., Shu, X., Huang, B., . Sustainability innovations in transportation infrastructure: An overview of the special volume on sustainable road paving. Journal of Cleaner Production 235, 369–377. URL: `https://www.sciencedirect.com/science/article/pii/S0959652619322231`, doi:`10.1016/j.jclepro.2019.06.258`.

Jestin, J., Barré, L., . Application of NMR solvent relaxation and SAXS to asphaltenes solutions characterization. Journal of Dispersion Science and Technology 25, 341–347. URL: `https://doi.org/10.1081/DIS-120037682`, doi:`10.1081/DIS-120037682`.

Jones, D.S.J., . Atmospheric and vacuum crude distillation units in petroleum refineries, in: Treese, S.A., Pujadó, P.R., Jones, D.S.J. (Eds.), Handbook of Petroleum Processing. Springer International Publishing, pp. 125–198. URL: `https://doi.org/10.1007/978-3-319-14529-7_25`, doi:`10.1007/978-3-319-14529-7_25`.

Jóźwiak, B., Orczykowska, M., Dziubiński, M., . Fractional generalizations of maxwell and kelvin-voigt models for biopolymer characterization. PLOS ONE 10, e0143090. URL: `https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0143090`, doi:`10.1371/journal.pone.0143090`. publisher: Public Library of Science.

Karki, P., Meng, L., Im, S., Estakhri, C., Zhou, J., 2019. Re-refined Engine Oil Bottom: Detection and Upper Limits in Asphalt Binders and Seal Coat Binders. Technical Report FHWA/TX-18/0-6881-R1. Texas Department of TransportationResearch and Technology Implementation Office. Texas A&M Transportation Institute. URL: `chrome-extension://oemmndcbldboiebfnladdacbdfmadadm/https://static.tti.tamu.edu/tti.tamu.edu/documents/0-6881-R1.pdf`.

Lee, J., Shin, S., Ahn, S., Chun, J., Lee, K., Mun, S., Jeon, S., Na, J., Nho, N., . Separation of solvent and deasphalted oil for solvent deasphalting process. Fuel Processing Technology 119, 204–210. doi:`10.1016/j.fuproc.2013.11.014`.

Lesueur, D., . The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. Advances in Colloid and Interface Science 145, 42–82. URL: `http://www.sciencedirect.com/science/article/pii/S0001868608001413`, doi:`10.1016/j.cis.2008.08.011`.

Lewandowski, R., Chorążyczewski, B., . Identification of the parameters of the kelvin–voigt and the maxwell fractional models, used to modeling of viscoelastic dampers. Computers & Structures 88, 1–17. URL: `https://www.sciencedirect.com/science/article/pii/S0045794909002314`, doi:`10.1016/j.compstruc.2009.09.001`.

Ma, Y., Hu, W., Polaczyk, P.A., Han, B., Xiao, R., Zhang, M., Huang, B., . Rheological and aging characteristics of the recycled asphalt binders with different rejuvenator incorporation methods. Journal of Cleaner Production 262, 121249. URL: `https://www.sciencedirect.com/science/article/pii/S0959652620312968`, doi:`10.1016/j.jclepro.2020.121249`.

NAPA, . National Asphalt Pavement Association: Market Facts. Technical Report. National Asphalt Pavement Association. URL: `https://www.asphaltpavement.org/index.php?option=com_content&view=article&id=891&Itemid=1068`.

Newcomb, D.E., Nusser, B.J., Kiggundu, B.M., Zallen, D.M., . LABORATORY STUDY OF THE EFFECTS OF RECYCLING MODIFIERS ON AGED ASPHALT CEMENT. Transportation Research Record URL: `https://trid.trb.org/view/216830`. ISBN: 9780309037501.

Presti, D.L., Vasconcelos, K., Orešković, M., Pires, G.M., Bressi, S., . On the degree of binder activity of reclaimed asphalt and degree of blending with recycling agents. Road Materials and Pavement Design URL: `https://www.tandfonline.com/doi/abs/10.1080/14680629.2019.1607537`. publisher: Taylor & Francis.

Qu, X., Wang, D., Wang, L., Huang, Y., Hou, Y., Oeser, M., 2018. The state-of-the-art review on molecular dynamics simulation of asphalt binder. Advances in Civil Engineering , 1–14URL: `https://www.hindawi.com/journals/ace/2018/4546191/`, doi:`https://doi.org/10.1155/2018/4546191`. ISSN: 1687-8086 Library Catalog: www.hindawi.com Pages: e4546191 Publisher: Hindawi Volume: 2018.

Rana, M.S., Sámano, V., Ancheyta, J., Diaz, J.A.I., . A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel 86, 1216–1231. URL: `http://www.sciencedirect.com/science/article/pii/S001623610600295X`, doi:`10.1016/j.fuel.2006.08.004`.

Rathore, M., Zaumanis, M., Haritonovs, V., . Asphalt recycling technologies: A review on limitations and benefits. IOP Conference Series: Materials Science and Engineering 660, 012046. URL: `https://iopscience.iop.org/article/10.1088/1757-899X/660/1/012046/meta`, doi:`10.1088/1757-899X/660/1/012046`. publisher: IOP Publishing.

Savvidis, T.G., Fenistein, D., Barré, L., Béhar, E., . Aggregated structure of flocculated asphaltenes. AIChE Journal 47, 206–211. URL: `https://onlinelibrary.wiley.com/doi/abs/10.1002/aic.690470120`, doi:`10.1002/aic.690470120`.

Shen, J., Amirkhanian, S., Tang, B., . Effects of rejuvenator on performance-based properties of rejuvenated asphalt binder and mixtures. Construction and Building Materials 21, 958–964. URL: `http://www.sciencedirect.com/science/article/pii/S095006180600050X`, doi:`10.1016/j.conbuildmat.2006.03.006`.

Shin, S., Lee, J.M., Hwang, J.W., Jung, H.W., Nho, N.S., Lee, K.B., . Physical and rheological properties of deasphalted oil produced from solvent deasphalting. Chemical Engineering Journal 257, 242–247. URL: `http://www.sciencedirect.com/science/article/pii/S1385894714009279`, doi:`10.1016/j.cej.2014.07.037`.

Shu, X., Huang, B., Vukosavljevic, D., . Laboratory evaluation of fatigue characteristics of recycled asphalt mixture. Construction and Building Materials 22, 1323–1330. URL: `http://www.sciencedirect.com/science/article/pii/S0950061807001225`, doi:`10.1016/j.conbuildmat.2007.04.019`.

Shu Xiang, Liu Jenny, Huang Baoshan, . Special issue on innovation on paving materials. Journal of Materials in Civil Engineering 29, D2017001. URL: `https://ascelibrary.org/doi/10.1061/%28ASCE%29MT.1943-5533.0001911`, doi:`10.1061/(ASCE)MT.1943-5533.0001911`.

Silva, H.M.R.D., Oliveira, J.R.M., Jesus, C.M.G., . Are totally recycled hot mix asphalts a sustainable alternative for road paving? Resources, Conservation and Recycling 60, 38–48. URL: `http://www.sciencedirect.com/science/article/pii/S0921344911002485`, doi:`10.1016/j.resconrec.2011.11.013`.

Storm, D.A., Sheu, E.Y., DeTar, M.M., . Macrostructure of asphaltenes in vacuum residue by small-angle x-ray scattering. Fuel 72, 977–981. URL: `https://linkinghub.elsevier.com/retrieve/pii/001623619390295D`, doi:`10.1016/0016-2361(93)90295-D`.

Tanaka, R., Sato, E., Hunt, J.E., Winans, R.E., Sato, S., Takanohashi, T., . Characterization of asphaltene aggregates using x-ray diffraction and small-angle x-ray scattering. Energy & Fuels 18, 1118–1125. URL: `https://pubs.acs.org/doi/10.1021/ef034082z`, doi:`10.1021/ef034082z`.

Tarsi, G., Tataranni, P., Sangiorgi, C., . The challenges of using reclaimed asphalt pavement for new asphalt mixtures: A review. Materials 13. URL: `https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7560297/`, doi:`10.3390/ma13184052`.

Tran, N., Taylor, A., Willis, R., . Effect of rejuvenator on performance properties of HMA mixtures with high RAP and RAS contents URL: `https://trid.trb.org/view/1250368`. number: 12-05.

US EPA, O., . Greenhouse gas emissions from a typical passenger vehicle. URL: `https://www.epa.gov/greenvehicles/greenhouse-gas-emissions-typical-passenger-vehicle`.

Wang, Y., Sun, L., Qin, Y., . Aging mechanism of SBS modified asphalt based on chemical reaction kinetics. Construction and Building Materials 91, 47–56. URL: `http://www.sciencedirect.com/science/article/pii/S0950061815005115`, doi:`10.1016/j.conbuildmat.2015.05.014`.

Williams, B.A., Copeland, A., Ross, T.C., . Asphalt Pavement Industry Survey on Recycled Materials and Warm-Mix Asphalt Usage: 2017. Technical Report. National Asphalt Pavement Association. URL: `https://trid.trb.org/view/1526267`. number: IS 138 (8e).

Xu, Y., Koga, Y., Strausz, O.P., . Characterization of athabasca asphaltenes by small-angle x-ray scattering. Fuel 74, 960–964. URL: `http://linkinghub.elsevier.com/retrieve/pii/0016236195000332`, doi:`10.1016/0016-2361(95)00033-2`.

Zahoor, M., Nizamuddin, S., Madapusi, S., Giustozzi, F., . Sustainable asphalt rejuvenation using waste cooking oil: A comprehensive review. Journal of Cleaner Production 278, 123304. URL: `https://www.sciencedirect.com/science/article/pii/S0959652620333497`, doi:`10.1016/j.jclepro.2020.123304`.

Zaumanis, M., Mallick, R.B., . Review of very high-content reclaimed asphalt use in plant-produced pavements: state of the art. International Journal of Pavement Engineering URL: `https://www.tandfonline.com/doi/abs/10.1080/10298436.2014.893331`. publisher: Taylor & Francis.

Zaumanis, M., Mallick, R.B., Poulikakos, L., Frank, R., . Influence of six rejuvenators on the performance properties of reclaimed asphalt pavement (RAP) binder and 100% recycled asphalt mixtures. Construction and Building Materials 71, 538–550. URL: `http://www.sciencedirect.com/science/article/pii/S0950061814009854`, doi:`10.1016/j.conbuildmat.2014.08.073`.

Zhang, L., Greenfield, M.L., . Analyzing properties of model asphalts using molecular simulation. Energy & Fuels 21, 1712–1716. URL: `https://doi.org/10.1021/ef060658j`, doi:`10.1021/ef060658j`. publisher: American Chemical Society.

Zhao, S., Huang, B., Shu, X., Jia, X., Woods, M., a. Laboratory performance evaluation of warm-mix asphalt containing high percentages of reclaimed asphalt pavement. Transportation Research Record 2294, 98–105. URL: `https://doi.org/10.3141/2294-11`, doi:`10.3141/2294-11`.

Zhao, S., Huang, B., Shu, X., Woods, M., b. Comparative evaluation of warm mix asphalt containing high percentages of reclaimed asphalt pavement. Construction and Building Materials 44, 92–100. URL: `http://www.sciencedirect.com/science/article/pii/S0950061813002134`, doi:`10.1016/j.conbuildmat.2013.03.010`.

Fuel

Material	Data source	Energy Consumption (J/t of Material)	Data Source	Emissions (lb CO^2/t)
Raw Materials:				
Aggerates	Marceau et al.,2007	5.40E+07	Chappat et al. 2003	22.0
Manufacturing:				
Production of Bitumen	Yan et al.,2016	5.81E+09	Chappat et al. 2003	627.0
Storage of Bitumen	Zapata et al. 2005	5.43E+08	Chappat et al. 2003	48.4
Mixing & Drying of Aggerates	Ang et al. 1993	3.62E+08		
Reclaimed Asphalt Pavement	Zaumanis et al. (2014a)	1.65E+07	Chappat et al. 2003	8.8
Placement:				
Asphalt Pavement	Zapata et al.2005	1.34E+07	Chappat et al. 2003	1.5

Figure S1 The Energy consumption and greenhouse emissions used with the corresponding sources.

Supplemental Information

Table S1 Binder rheology of rejuvenators in various asphalt binders understand how rejuvenators influence the binders mechanical properties. This table compares the critical performance grade (PG), ΔTc, Aging Index and mass loss of modified VTBs. A 64-22 and 58-28 AC were selected as a comparison with the rejuvenated VTBs.

Sample Code	V1	V1-5HT	V1-7.5HT	V1-10HT	V1-4.0E	V1-5.0E	V1-6.0E	V1-10.0E	V1-5.0S	V1-10.0S	V2	V2-5.0C	V2-7.5C	V2-10.0C	V2-5.0S	V2-7.5S	V2-10.0S	M	H
High PG	80	79	77	73	74	73	70	59	74	65	83	73	67	63	75	70	67	60	65
Low PG	-15	-17	-19	-20	-22	-23	-24	-30	-22	-30	-9	-18	-21	-25	-15	-20	-22	-29	-25
Continuous	94	96	96	94	96	95	94	89	96	95	92	90	88	89	90	90	90	89	91
Tc	-2.8	-1.8	-2.4	-2.8	-5.3	-2.6	-1.4	-0.2	-1.9	-1.5	-7.0	-5.5	-5.5	-4.2	-5.4	-3.5	-2.3	-0.3	-0.6
Aging Index	2.2	2.1	2.1	2.1	2.1	2.1	2.2	2.7	1.7	1.7	2.3	2.5	2.6	2.9	2.1	2.0	2.1	2.2	2.7
Mass Loss %	1.0	0.1	0.1	0.1	0.8	0.8	1.0	1.8	0.2	0.4	0.2	0.6	0.7	1.0	0.6	0.6	0.3	0.1	-

Table S2 The oil energy consumption required for asphalt pavement. Energy consumption uses the estimated value is 785 MJ/ ton of asphalt mix.

Oil Conversion to Asphalt Mix		
Amount of Oil	3.0	Qt.
Energy from Oil	4586.25	Mj.
Amount of Asphalt mix produced	5.83	tons
Volume of Asphalt	81.50	ft^3
Number of Parking stalls (9ft x 18ft x 3in)	≈ 2	

Table S3 Disk compact tenstion testing of the control sample and SESO sample from the Noblesville, IN project.

Sample Code	Fracture Energy(J/m^2)		Peak Load (kN)	
	Avg.	SE	Avg.	SE
H 25% RAP	376.0	28.9	N/A	N/A
H 40% RAP 5.7S	506.7	31.7	N/A	N/A

Table S4 The equivalent energy consumption and emissions generated per ton of asphalt binder.

Fuel economy Mid-size Sedan at 55 mpg		
Emissions	0.43	lb. CO^2/mile
Energy	3.71	MJ/mile
Distance	1550.00	mile
Emissions generated	683.44	lb. CO^2
Energy Consumption	5757.14	MJ

Table S5 The sieve size for the mix design used at the Indiana demonstration project for the control and SESO sections.

Sieve Size (mm)	*Percent passing for each Section*	
	Control 25% RAP	SESO 40% RAP
12.5 mm	100.00	100.00
9.5 mm	95.30	94.00
4.75 mm	65.60	67.70
2.36 mm	41.50	44.20
1.18 mm	27.00	29.20
600 µm	18.20	19.40
300 µm	11.10	11.70
150 µm	7.20	7.30
75 µm	5.50	5.60

Figure S2: Images of the mix and the location of the demonstration project where S was used.