

Delft University of Technology

### Proceedings 2nd workshop KPE-CEAB 2022

### KPE-CEAB Characterization and Evaluation of Asphalt Binder Properties (CEAB)

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### KPE-CEAB CHARACTERIZATION AND EVALUATION OF ASPHALT BINDER PROPERTIES (CEAB)

Rijkswaterstaat Ministry of Infrastructure and Water Mongaement



8<sup>th</sup> December, 2022 Delft, the Netherlands

### **Editors:**

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#### 1. Preface

The Dutch bitumen market is currently experiencing changes influenced by geopolitical events, sustainability initiatives, and quality considerations. The evolving refinery landscape, driven by economic and regulatory factors, has raised concerns regarding the quality and consistency of bitumen. Recent geopolitical events have caused disruptions in global oil prices and supply chains, indirectly affecting the availability and pricing of bitumen in Europe. Additionally, the blending of crude oils, refining processes, and additive treatments have become common practices, leading to a diverse range of compositions for asphalt binder. Whereas, existing specifications are inadequate in accurately predicting the performance of complex bituminous binders.

Besides, sustainability initiatives have prompted a shift towards using higher quantity of reclaimed asphalt pavement (RAP), necessitating higher demand for additives to revitalize the old binder from RAP and improve workability during production. The increasing use of additives i.e. rejuvenators, has led to the emergence of complex bituminous binders. These developments highlight the significant influence of binder properties on asphalt performance in road engineering. To address recycling challenges and environmental requirements, there is a need to enhance understanding of how different sources and processes of binders affect asphalt performance properties.

The 'Characterization and Evaluation of Asphalt Binder Properties (CEAB)' project, part of the KPE program, aims to evaluate bitumen properties in response to current trends and changes in the bitumen market. Its goal is to gain a better understanding of how these changes impact the properties of asphalt binder.

To achieve this, as a continuation of previously organized workshop, TNO and TU Delft organized the 2nd International workshop-CEAB on December 8, 2022 in Delft. The workshop focused on discussing the changes in bitumen properties and exploring a set of characterization tools that can accurately predict asphalt binder properties. By bringing together academia, research organizations, industries, and road authorities, the workshop provided a platform to address the challenges associated with asphalt binder properties.

The workshop featured six presentations involving a wide range of stakeholders. Here is a brief overview of the presentations.

Dr. Sandra Erkens, Dr. Xueyan Liu and Dr. Sayeda Nahar addressed the welcome note and presented some highlights of the 1st international workshop from the previous year.

The first speaker, Jeroen Besamusca presented a recent study focusing on performance related issue of the binder during a road construction in the Netherlands. Investigations revealed that the problem stemmed from the presence of non-bituminous component in the binder without the knowledge of the contractors. This was identified as a broader problem by the road authorities, which necessitates more research. Further investigations highlighted similarities to issues reported in the US in 2014. The presentation explores the differences and similarities between the Dutch and US investigations. Dr. Sayeda Nahar and Dr. Peng Lin have presented the progress of CEAB project highlighting the set-of chemical and physical characterization tools used to identify and fingerprint bitumen and additives, leading to some rheological and chemical indices to distinguish performance properties of bitumen.

The study presented by Dr. Hassan Tabatabaee focused on assessing the compatibility of complex bitumen compositions, which are increasingly used in asphalt applications. Next to conventional methods of evaluating compatibility: i.e. rheological parameters and solvent-extracted fractional ratios, the study proposed a new approach based on the number of glass transition occurrences in

bitumen/ blends. By analyzing the modulated differential scanning calorimetry (MDSC) response, a quantification method was developed. The analysis of different types of bitumen demonstrated the potential of the proposed parameters and analysis framework to serve as an analytical measure for assessing compatibility of bituminous binders.

The presentation of Dr. Jeramie Adams highlighted the changes of bitumen production since the SHRP Superpave studies due to economic, technical, and environmental factors. He introduced different programs in the US such as 'the Asphalt Industry Research Consortium' (AIRC) and the NCHRP 9-60 addressing these issues sharing scopes with CEAB. He discussed insights gained from studying a large number of binders using various techniques such as rheology, black Space analysis, SAR-ADTM, ABCD, DSC, Waxphaltene Determinator, FTIR, and GPC/SEC. These methods of characterization highlight their potential for diagnosing different binder compositions, modifiers, and assess potential failure i.e. cracking characteristics.

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### Workshop participants

Name	Affiliation	Role
Jeroen Besamusca	Kuwait Petroleum Research	Speaker
	and Technology B.V	
Sayeda Nahar	TNO	Speaker
Peng Lin	TU Delft	Speaker
Shisong Ren	TU Delft	Speaker
Hassan Tabatabaee	Cargill Asphalt Solutions	Speaker
Jeramie Adams	Western Research Institute	
	(WRI)	
Xueyan Liu	TU Delft	Organizer/Chair/Speaker
Laurent Porot	Kraton Polymer B.V.	Speaker
Sandra Erkens	TU Delft	Organizer/Chair
Eli I. Assaf	TU Delft	Participant
		Participant

### 4 Workshop Program

13:00-13:30	Walk in & coffee					
14:00 - 14:15	Welcome					
14.00 - 14.15	Sayeda Nahar-TNO, Sandra Erkens & Xueyan Liu-TU Delft					
	Session 1					
	moderator: Xueyan Liu-TU Delft					
14:15-14:45	Quality problems in Dutch Roads (Online)					
1 110 1 110	Jeroen Besamusca, Kuwait Petroleum Research and Technology B.V					
	Project- KPE-CEAB Characterization and Evaluation of Asphalt Binder					
14:45 – 15:15	properties: approach and preliminary results					
	Dr. Sayeda Nahar, TNO					
15:15 – 15:30	Break					
	Session 2					
	moderator: Sayeda Nahar-TNO					
	Multi-scale research of rejuvenation mechanism towards the challenge of					
15:30 - 16:00	changing bitumen properties					
	Dr. Peng Lin & Shisong Ren, TU Delft					
	Glass Transition Deconvolution Method for Assessing Bitumen					
16:00 - 16:30	Incompatibilities Initially and upon Aging					
	Dr. Hassan Tabatabaee, Cargill Asphalt Solutions					
16:30 - 17:00	Asphalt Industry Research Consortium (AIRC): An Innovative Approach for					
	Binder Understanding					
	Dr. Jeramie Adams, Western Research Institute (WRI)					
17:00-17:30	Closure & drinks					

#### 5. Workshop discussion

## Quality Problems in Dutch Roads (Online) Jeroen Besamusca – Kuwait Petroleum Research and Technology B.V.

**KEYWORDS - REOB:** Re-refined Engine Oil Bottom, additive used in asphalt binders. **XRF:** Xray fluorescence,  $\Delta T_c$ : A binder parameter that characterizes relaxation properties in relation to aging and additives. **KPE:** Knowledge-based Pavement Engineering project from TU Delft. **Tc:** Performance parameter.

**SAYEDA NAHAR** – What I was curious about what you said in your comments that *REOB is* one side of the problem. There are also bitumen that are produced from different processing techniques or sources, which shows challenging properties; which doesn't contain REOB. Do you think  $\Delta T_c$  parameter can be also a useful tool to characterize and distinguish the performance of these binders as well?

**JEROEN BESAMUSCA** – Good question, I hope so. At this moment if we look at the results actually what I try to say is that I don't think we should aim at one specific test method, I think we should at least have several indications if a bitumen is well performing or not, and one of the things we have to be very careful about, modified binders are actually the most important products, but modified binders are nothing else than a Pen-Grade binder with a modification, but if the Pen-Grade is not of the proper material, then you actually lose anything when you put in anything in the modification so to my understanding we should aim to have as good as possible specification around the PEN grade binder to make sure that if you put in a modification, you at least start with something that is good, and if we can find a test that can discriminate [to find something that fits certain criteria]. The problem with this is that from previous experience, we see that some people claiming to have found an additive that boosts that specific test but performs poorly in others. My whole point is that we should establish several tests (2 or 3) to have different discriminators to obtain a better idea of what is good or bad.

**SAYEDA NAHAR** –Yes great, I think my presentation in later parts of this conference show some additional tools that could be potentially be used to characterize and assess bitumen.

**LAURENT POROT (31:44):** One question, you stress that there are many problems between the policies in the European Union and the use of REOBs in asphalt pavements. Do you think that banning the use of REOB would be a solution? Or creating a set of rules for the use of REOB is a good idea? Introducing the categorization of REOB-modified binders using a CAS number could be useful, given that in Europe REOB-modified bitumens have no additional labelling requirements? **JEROEN BESAMUSCA** – To control *REOB* in the asphalt industry, yes, a CAS number could be enough, but also in my presentation I highlight that the use of *REOB* is not the only problem. So, at this moment, we should focus on the discriminating tests that dictate performance of the binders instead of looking back and trying to withhold *REOB* from being used. However, I do agree that a CAS number can absolutely help, and I think that for contractors it would be very good know if somebody put REOB in their material which they buy [at this moment, they do not know].

### Characterization and Evaluation of Asphalt Binder Properties: Approach and Preliminary Results Dr. Sayeda Nahar – KPE-CEAB Project, TNO

KEYWORDS - REOB: Re-refined Engine Oil Bottom, additive used in asphalt binders. DSR: Dynamic Shear Rheometer. KPE: Knowledge-based Pavement Engineering project from TU Delft. JOHAN (TIME 55:04) - You started one of the last part, in the info, you said that the environmental part is very important, that we are all concerned about the world, so I wonder... it's very important to know what we are dealing with, but I think we are missing something we are looking at performance, we are looking into all kinds of mechanisms, but one important factor is what are we going to do with these in the future? We know that there is going to be a shortage of bitumen in the future, and that we will be shifting into other types of 'greener' binders... so in this research we should also implement the measurement of the impact of these new alternative binders (and materials used) in the health and environment because we are all focused in something problems of the present and not actually measuring whether the new materials may have a detrimental impact in the future. What we see now is that bitumen is being mixed with all sorts of things, and bitumen is becoming a material with dangerous pollutants without us noticing. We keep on mentioning its recyclable, it is a clean material, but what we are doing now is making something now that could be detrimental in the future, because we aren't measuring the impact of these materials now. We should create a standard that measures the impact of the newly used materials.

**SAYEDA NAHAR** – Thank you for this important message. Let me go a bit back, while I was trying to collect bitumen samples, I actually had trouble finding a so called 'bad binder', which poorly performs and also creates concerns in emissions which is a threat to health and safety. But no supplier was volunteered to provide a 'bad' binder. It was a difficult topic to discuss even, but the thing is, what you said, people are not registering/ recording these possible detrimental characteristics/ issues in a structural manner because there is no consensus on this topic to reporting possible flaws in the bitumen characteristics. The market itself and the people should be more open and bring this forward. The idea is that when there is a deviation in bitumen performance property, then this information can be made public.

**JOHAN** – The problem also lies in how the government sets objectives. They put emphasis in how we should become a circular, greener society, with zero carbon emissions, but if we don't have the technology yet to achieve that, then the only way to do it is to modify our mindset, which, is a good start, but I think we should focus on being more open so that we can attain the necessary skills faster. **MARTIN VAN DE VEN (TIME 1:00:26)** – I want to react on what was just said, of course you are right, but we are also very busy. Yes, sure, we can label the product [bitumen] with what are the possible 'environmental loads' of using it, but we don't have the time to properly achieve it. However, we are on the right track already, maybe not as desired, but we are all concerned with the environmental impact, and doing our best to manage and use alternative material which are known to cause the least impact to the best of our abilities.

**SAYEDA NAHAR** – Indeed Martin, we did not include a Health and Safety mark into this project but it's a dynamic process after all, so we can shift our approach and progress to address the relevance of these points.

**JIAN QIU (1:02:27)** – I have two questions. The first: You shared a lot of information, is this presentation (and all of its data) to be shared or not?

SAYEDA NAHAR – Yes, the content will be made public as a published proceedings.

JIAN QIU - And the second is related to the practice. It's good that you test bitumen obtained from

their source and age them all from the same degree, but what happens when recyclable binders start making themselves into the labs and aged materials are going to be considered 'fresh' again? How are you going to tackle this issue, and perform the tests so that all bitumen tests are standardized?

**SAYEDA NAHAR** – The *KPE CEAB* project is divided into two sections actually, one that focuses on testing of bitumens that are obtained directly from crude oil sources, and one that focuses on the characterization of bitumen samples that come from recycled asphalt mixtures. Maybe next year we will start implement a way to combine these results and obtain a consistent way to test these materials.

**GEORGIOS PIPINTAKOS (1:04:40)** – Hi, my name is Georgios Pipintakos, from Universiteit Antwerpen, the presentation is quite nice, especially how it presents different values... I was just wondering if you are trying to come up with another metric, no just one that is based on human interpretation, like one that processes the image from the samples as a whole. This comes because many studies report an increase or decrease in different factors (in microscopy) but they are all subject to interpretation. Maybe there is a more sophisticated technique, let's say a image processing technique, to back the claims made before?

**SAYEDA NAHAR** – Indeed, one point is that when capturing micrographs, we are talking about an area of a few microns in size, which forces us to capture micrographs at several locations of the single to provide an overview of the binder morphology and less room for interpretation. But indeed, these could benefit from more sophisticated imaging post-processing techniques, whereas it is good to keep in mind that AFM is a local characterization technique.

**GEORGIOS PIPINTAKOS (1:06:00)** – Yeah, one of the cool features of the Optical Laser Scanning Microscopes is that it allows us to cover much larger areas by taking several pictures... it can cover squares of side length equal to 50 or even 100 microns, and therefore see a very diverse representation of the bitumen sample. This technique could reduce this (local) issue and help us reach more objective interpretation of these images because we are looking at a much larger picture that can somehow tell us the story of the whole sample.

**MILLIYON WOLDEKIDAN (1:07:19)** – I have one question, in one of your slides you show us two AFM pictures, from different years, of the sample bitumen, right?

**SAYEDA NAHAR** – Not the same bitumen exactly...the same provider. Two batches delivered, but not exactly from the same batch of bitumen. The grade was different as well.

**MILLIYON WOLDEKIDAN** - I was just curious maybe, if you have seen some difference in the mechanical properties, like when testing with a *DSR*?

**SAYEDA NAHAR** – I have to check, now, the *DSR* tests I didn't show the data, but with two different batches the rheological properties could also show some differences

### Multi-scale Research of Rejuvenation Mechanism Towards the Challenge of Changing Bitumen Properties Dr. Peng Lin & Shisong Ren – KPE-CEAB Project, TU Delft

**KEYWORDS - RAP:** Recycled Asphalt Pavement. **SARA:** Saturates, Aromatics, Resins, and Asphaltenes. **FTIR:** Fourier-Transform Infrared. **REOB:** Re-refined Engine Oil Bottom. **MD:** Molecular Dynamics. **PAV:** Pressure Aging Vessel. **KPE:** Knowledge-based Pavement Engineering project from TU Delft.

**SAYEDA NAHAR** – Thank you very much Peng, you nicely shown how Molecular Dynamics can be a very useful tool in to look rejuvenation mechanisms, material compatibility, bitumen behavior and detailed mechanisms, and some other important aspects that cannot be obtained using conventional methods. Now, we are open for questions.

**GEORGIOS PIPINTAKOS** - Thank you Peng for your presentation, maybe I missed it, the binders were aged in the Lab or were they from actual real samples?

**PENG LIN** – In this research, we aged our samples in the laboratory, and then we collected some RAP to validate our results, because we all know that aging varies slightly from Lab-induced techniques to what is found in reality.

**GEORGIOS PIPINTAKOS** - I ask my question because for example, I love what you did with the solubility parameters, and maybe these parameters will be completely different for *RAP* binders, so how do we differentiate between fresh binders and those that have been made using *RAP*?

**PENG LIN (1:49:20)** – I think this is a great question and a great suggestion, first in the lab aging, we used the Hans Parameter and the Solubility Parameters, and we saw that it is consistent with the experimental results, but as you said, if we use the field samples, maybe the results will be substantially different, so we have to take these into account. Thank you very much.

**MARTIN VAN DE VEN (1:49:20)** – In order to run these simulations, we often start with the Greenfield 12-component model... did you change the model? Did you really, for the different binders, change the chemical composition of the molecules that are originally established by Greenfield?

**PENG LIN** – Thank you for the question, maybe the time was limited during my presentation, and I did not cover it very clearly, but actually, the models were indeed built using the 12-component model from Greenfield, but we revised the molecule's functional groups and molecule number ratios for them to fit the chemical characterization results that we obtained for each bitumen sample. These characterization techniques include the elemental analysis, *SARA* solubility analysis, and also a functionals group analysis given by an *FTIR* run. The ratio of the *SARA* fractions is modified so that it fits the *SARA* results, so the 12-component model is still there, but the ratio and some functional groups are different. Different aging degrees also incur a change in the *SARA* fraction, so the *SARA* ratio and functional groups are also changed as aging degrees change. Bitumen, for an example, undergo oxidation during aging, so with an increasing aging degree we increase the functional groups: sulfoxide and carbonyl accordingly. This is done cautiously, taking care about the thermodynamics and the kinetics so that the molecules we form are indeed plausible and realistic in nature. All these changes are corroborated against other characterization tests to make sure that the changes are correct and fit experimental information. That's the process.

**JIAN QIU (1:51:40)** – Thank you for the presentation, I think I have a question. You talk about different types of rejuvenators, one of them is Engine Oil, and another one is *REOB*. How exactly is their composition different from one another? And how are *REOBs* studied given that their consistency and composition vary immensely from sample to sample? How is this controlled in your

research project?

**PENG LIN** – Thank you for your question. Indeed, in our project, we have selected five different rejuvenator ingredients, and indeed, we are still working on how to check the influence of the different types of *REOBs* and how to treat them as one (or more) materials. Our idea is to differentiate between the engine oil samples received and a reference sample we have in the lab. We would slowly be measuring their difference and measure their influence in the *MD* simulations. After a while, we would obtain a model on which factors (present in *REOBs*) affect their performance and it would tell us how to categorize them properly, but right now we are just starting and still devising a plan to tackle these. It's important to do so (and not just ignore them) because *REOBs* have become cheap and widely available. We will keep on working on this for the time being. Thank you for the remark and suggestion.

**JAN STRUIK (1:53:30)** - Thank you for the presentation, it has really nice slides. What about considering 'aging' on the rejuvenator samples collected? Have you modelled these as well?

**PENG LIN** – Thank you, and that is a good suggestion. We haven't tested aging on the rejuvenator ingredients themselves. However, we have tested on Vegetable Oil, and we have found out that its viscosity increases *PAV* aging, and it has helped us understand why the rejuvenation effect of Vegetable Oil decreases so much after a while. We are still working on this, and we are going to establish a plan on how to take rejuvenator ingredients into account (so that their aging degrees are all the same) and do not affect the results when combined with binders. Thanks a lot for your suggestion.

**SAYEDA NAHAR** – I am curious if someone from our online audience has any question? Please feel free to ask.

**JIAN QIU** – First, I would like to give you a compliment for such a nice presentation. I have several questions. First, how long did it take you to do this? Moreover, in regard to the quality of bitumen, what is the impact of aging in bitumen samples that have been previously rejuvenated? Did you consider this point in your research...my second question is...you present a very nice bitumen model for measuring the diffusion of rejuvenator into different layers of bitumen, what were the dimensions of this layer-profile column? Was it 160 mm. in depth, right? And how did you grab the column, and sliced it into several layers in order for you to study the diffusion coefficient and compatibility of the bitumen and the additive?

**PENG LIN (1:57:24)** – For the first question, the durability of the rejuvenator is one of the most important questions that we should answer. In my presentation, I showed that the *KPE-CEAB* project is divided into 5 tasks. As of now, we are in Task 2, but evaluating the durability and performance of the rejuvenators in bitumen is expected to be studied in Task 3. This Task will involve two sections, the first studies the durability in regard to aging, and the second evaluates the damage caused by moisture and ultraviolet light.... you also asked how long did this take us...actually, this is distributed among a team of researchers. Each member of the team is expected to dedicate 2 or 3 years to culminate their corresponding part.

For the second question, in order to measure the mechanical and rheological properties is, once the rejuvenator has diffused into the bitumen sample, we insert the column into the fridge at -20 °C, wait until its fully frozen, and then use a very hot, thin knife in order to slice it. The slices are then put into separate containers, are heated back up until liquid, and mixed thoroughly again. This is to make sure that the composition of the diffused component is even throughout the slice sample...we need to make sur it is homogeneously mixed. Afterwards, the samples are then subjected to chemical

and rheological characterization tests.

**SAYEDA NAHAR (2:00:00)** – Thank you very much Peng, we have got one question from Jeramie Adams, from our US (online) audience.

**JERAMIE ADAMS (2:00:06)** – Did you check the oxidation of the rejuvenators themselves; we have seen that after performing PAV conditioning in the lab, the chemical and rheological properties of some rejuvenators drastically change... what has been done to tackle this?

**PENG LIN (2:00:27)** – Thanks a lot of the question. We met at the Petersen Conference and it's really nice to see you here again. For the question, we have already partially seen this problem happening, as we saw how Vegetable Oil's viscosity increases eight-fold, and its solubility in bitumen decreases. But the full evaluation of this question will be tackled in Task 3 of the *KPE-CEAB* project.

**SAYEDA NAHAR (2:01:26)** – Thank you a lot for the questions. Our next presenter will be Dr. Hassan A. Tabatabaee.

**YVONG HUNG (2022-12-08 4:30 PM)** - Hi Peng! Nice talk! do you investigate the consequence of rejuvenator/aged bitumen interaction in terms of molecule polydispersity and motion continuum as we know that one of major ageing impact lead to non-equilibrium state of bitumen matrix.

**PENG LIN** - Hi Yvong, thank you very much for your question! I have not done analysis in terms of molecule polydispersity and motion continuum. But I think you point out a very promising direction for us and we will try to understand this topic from this perspective. Thank you again for your question and suggestion!

Glass Transition Deconvolution Method for Assessing Bitumen Incompatibilities Initially and Upon Aging Dr. Hassan A. TABATABAEE– Global Technical Manager, Cargill, United States.

**KEYWORDS - Tg:** Glass Transition Temperature. **Tc:** Performance factor. **Excel Solver:** Excel's default built-in function to find solutions to tabled values subject to a number of constraints.

**HASSAN TABATABAEE** – With that, I would certainly be happy to answer any questions, here is my contact information < anova-asphalt@cargill.com > and also the contact information of my colleagues in Europe, that you folks may want to reach out to.

**MOHAMAD MOHAJERI (2:30:51)** – How can we use these tools to differentiate between the functionality and the quality of different rejuvenators?

**HASSAN TABATABAEE** – That's a great question. Actually if you look back at this slide here <slide 11>, there are indications that there's differences between different types of additives in terms of the impact that we see on the glass transition temperatures, and I think it's important to look at how does this further evolves as you continue to age these samples...so, I think instead of looking at one or two points in time (in regard to primary, secondary, and tertiary transition points), we need to look at several points during aging to see how the importance of these peaks evolve over time. This is especially powerful when looking back into the neat (or fresh) bitumen evolution and using additives to modify how these peaks evolve over time.

SAYEDA NAHAR (2:32:45) – Okay thank you, now for a second question.

**LIZ MENSINK** – Thank you for your nice presentation, I have a question that is related to the results you showed... I see that there is a great difference between the Tc's <not to be confused with Tg (slopes, magnitudes, positions in the plot). Is this purely incidental, or has it been correlated to the quality and compatibility between the substances? Could Tc be used as a metric to measure what you are trying to do, or what you show is merely coincidental?

**HASSAN TABATABAEE** - That is absolutely true, they are not incidental. Maybe I did not show properly during my presentation but there is a ton of corresponding rheological data that go hand in hand with the expected evolution of the values of *Tc*. In general, Relaxation related parameters are the ones that show the biggest correlation (m-values or crossover parameters) to the ratio of the primary and secondary glass transition temperatures, so there is definitely some correlation between those parameters. What we are seeing is that no all of the parameters seem to be moving in the same direction with all the binders, and these correlations are not always equal, so maybe the first step would be to evaluate which one of these parameters remains consistent among several bitumen samples, to make this technique a more robust way to evaluate compatibility and impact of additives in bitumen...moreover, the delta *Tc* factor seems to be influence by other factors as well, some of that is well known, but generally speaking there is a very clear correlation between these relaxation parameters and black-space related parameters with delta *Tc*, so work will be done to improve this differentiation and make it a formal method for future studies.

**SAYEDA NAHAR (2:35:18)** – Thank you very much, we should really move on. Thank you everyone for being in.

**JERAMIE ADAMS (2022-12-08 5:05 PM)** - Hi Hassan, do you see a larger spread between Tg(H) (half-height) and Tg(I) (inflection) consistent with growth of the secondary peak in the derivative curve, either due to source of bitumen or oxidation?

**HASSAN TABATABAEE** - Hi Jeramie. This is a great question. the amount difference between the half height Tg and the inflection point reflects the strength of secondary Tgs. The stronger the secondary Tgs are, the more different the inflection point Tg will be from the half height, as the shape of the overall Tg curve becomes less symmetrical.

SADAF KHALIGI (2022-12-08 5:06 PM) - Hi Hassan, what software you have used for this study? HASSAN TABATABAEE - Hi Sadaf. We created our own analysis spreadsheet using *Excel Solver*. SADAF KHALIGI (2022-12-08 5:10 PM) - So it means that you found peaks for initial guess manually?

**HASSAN TABATABAEE-** Essentially yes. It needed an initial solution estimate to further fit. However, in order to make this less prone to subjective we always used the unaged neat binder's fitted results as the starting point for the next condition (e.g., further aging or modification).

### Asphalt Industry Research Consortium (AIRC): Innovative Approach for Binder

### Understanding Dr. Jeramie Adams – Western Research Institute, United States.

SAYEDA NAHAR – Due to the presentation being well over, any questions that you may have must be directed through the chat and the answers will be included in the written transcript of the questions <this one>.

### <ONLINE / WRITTEN QUESTIONS>

<Due to time limitations, no questions were asked>.

### <END OF TRANSCRIPT>

Meeting ended at 2022-12-08 8:02 PM after 6h 25m 52s.

### 6. Presentations

6.1 Jeroen Besamusca, Quality problems in Dutch Roads













### ReOB in Europe sold as Flux oil



For years this is forbidden in "Bunker Fuel". ISO 8217, Petroleum Products – Fuels (class F) - Specification for marine fuels, clearly state: free of Used Lubricating Oil:

Category ISO-F-								1000						
Characteristic Unit	Unit	Limit	RMA	RMB	RMD	RME	RMG				RMK			Test method reference
		10*	30	80	180	180	389	500	700	380	500	700		
Aluminium plus silicon	mg/kg	ITLBX.	25	40	40	50		6	0				60	see 7.9 IP 501. IP 470 or ISO 10478
Used lubiticating oils (ULO): calcium and zine; or calcium and phosphorus	mg/kg	-	The fuel shall be free from ULO. A fuel shall be considered to contain ULO when either one of the following conditions is met: calcium > 30 and ptopshorus > 15 calcium > 30 and ptopshorus > 15						see 7.10 IP 501 or IP 470 IP 500					
This category is based on a j  Trem <sup>2</sup> Is = 1cSt.  The purificient shall defee the  Due to maxom stated in Anne  See Annex M.	mesittum sul	fur conte	nt in acc	ordance	with role	rvani sta	lutory lie	etations.	See 0.3	and Are	neta C.			
	tia pour point		1.1.1.		1.1		S			C	100			

7

## Asphalt Institute, IS-235 - 2016



This document is careful to define REOB/VTAE as the non-distillable residuum from a vacuum tower in a used oil re-refinery. Other re-refined products derived from used oil not meeting this definition are not addressed herein, and the extent of their use in asphalt is unknown. REOB/VTAE has been used as a blending agent to soften binders. The demand for softer binder grades has grown due to higher levels of RAP and RAS being used in mixtures. The use of higher concentrations of hard oxidized binder from RAP and RAS require a softer virgin binder to meet the combined blend requirements. This factor has led to a heightened use of softening agents, which include non-asphalt blending stocks such as REOB/VTAE.

Some research indicates REOB/VTAE has an adverse effect on the aging characteristics of the asphalt binder and in turn the cracking resistance of in-service pavements. Other research indicates REOB/ VTAE blended asphalt has equivalent or better asphalt mixture performance relative to mixtures

with neat asphalts of similar stiffness. The literature is largely inconsistent; with various authors suggesting that REOB/VTAE may be innocuous while others suggest its usage may be detrimental to performance. Further, there is date indicating that the performance of biodurs and mixtures

containing REOB/VTAE is dependent on the REOB/VTAE dosage, the REOB/VTAE source and the binder source.

### Quality measurement, $\Delta Tc$ (IS-240) 2019





Delta  $T_{\epsilon} (\Delta T_{\epsilon})$  is a derived asphalt binder property that has been gaining attention for the last decade. It has become a topic of focus to both researchers in the asphalt binder technical community and user agencies seeking physical property parameters that will improve hat mix asphalt parement performance. It is generally accepted that  $\Delta T_{\epsilon}$  targets cracking behavior that is affected by asphalt binder durability related to aging of the binder in an asphalt mixture. More specifically,  $\Delta T_{\epsilon}$  provides insight into the relaxation properties of a binder that can contribute to non-load related cracking or other age-related embrittlement distresses in an asphalt parameter. It is accented, asphalt asingles or samples recovered from pavements. At the time this decument was developed (mid-2010), ten user agencies have or soon will implement  $\Delta T_{\epsilon}$  as part of their purchase specification, with two more expecting to do so in the near future. In addition, several national level research project led by the Asphalt institute.

According to the original purpose of this study, an in-place asphalt sample could be extracted and evaluated for  $\Delta T_c$ . If that sample indicated a  $\Delta T_c$  of about 2.5°C, then it is likely that the pavement would need a preventive maintenance treatment because cracking would be imminent. Likewise, if the sample indicated a  $\Delta T_c$  of 5°C or greater, then the pavement was likely already exhibiting cracking and thus, a maintenance treatment more targeted to this condition would be necessary.

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6.2 Sayeda Nahar, Project- KPE-CEAB Characterization and Evaluation of Asphalt Binder properties: approach and preliminary results



THO for life

### SOURCES OF CHANGE IN BITUMEN INDUSTRY INSERT SECOND TITLE HERE

- ) General trend: upgrading of refineries
- ) Closure of bitumen production in some refineries
- ) 3rd party blenders: blending outside the refinery
- ) A wide variety in crude cocktails
- ) Change in legislation, policy: IMO 2020

THO minovacion for life

### IMPACT OF CHANGE IN BITUMEN PROPERTIES BITUMEN/POLYMER MODIFIED BITUMEN

- > Viscosity and workability
- ) Temperature sensitivity
- ) Adhesive, cohesive strength
- ) Moisture resistance
- Durability
- ) Low temperature properties
- ) Phase behavior and stability
- ) Storage stability (PmB)
- Recycling of bitumen
- ) Health and safety aspects

TNO introductor

### **OBJECTIVES**

### INSERT SECOND TITLE HERE

) To develop an evaluation methodology by introducing a set of characterization tools to reliably assess bitumen properties and durability for asphalt applications.

) To relate bitumen properties to potential damage mechanisms i.e. raveling in porous asphalt.

TNO for life

### SELECTION OF BITUMEN INSERT SECOND TITLE HERE

#### Composition:

- ) Bitumen produced from different nature/ origin of crudes or crude cocktails
- ) Bitumen having different sulfur content
- REOB containing bitumen

Production process: Bitumen produced and obtained from different refining processes

- Straight-run
- ) Cracking, Vis-breaker
  ) Solvent de-asphaltene unit.

#### Biturnen grades:

) PEN: 40/60, 70/100, 20/30, 160,220 ) PmB

### **OVERVIEW OF THE BITUMEN SAMPLES**

Bitumen suppliers	Remark
Vitol Group - 2 grades	Straight run process
NordBit- 3 grades	PDA unit
TOTAL energies- 1 grade	PDA unit
ADNOC Refining – 2 grades (Abu Dhabi National Oil Company)	-
RILEM TC-PIM- 2 grades	To provide two samples from RILEM- TC PIM-TG- for fingerprinting purpose and discussion. o Bitumen PEN 35/50 o Bitumen PEN 35/50+ 8% REOB blend
Nynas- Antwerp (old)- 3 grades	Straight run process
Federal Highway Administration (FHWA)- 2 grades	Bitumen containing 3% REOB  PmB

### PERFORMANCE PROPERTIES CHARACTERIZATION TOOLS





TNO for life

### VISCO-ELASTIC PROPERTIES OF BITUMEN MASTER CURVES



- ) The frequency sweeps were performed at different temperatures i.e. -10, 0, 10, 20, 30, 40, 50 and 60  $^\circ C.$
- ) reference temperature of 20°C

TNO mesoverior

### BLACK SPACE DIAGRAM CROSS-OVER MODULUS CROSS-OVER MODULUS & AGEING INDEX



- > The susceptibility to ageing is studied from the viscoelastic response of the bitumen.
- As ageing progresses, black space curves shift towards lower phase angles; suggesting more hardening.
- ) The curvature is reduced with ageing towards a more straight line.
- )  $\rm Al_{CM}$  , ageing index of crossover modulus will be calculated  $\rm AI_{CM}=\frac{CM_{Fresh}}{CM_{Aged}}$

Here,  $\text{CM}_{\text{Fresh}}$  and  $\text{CM}_{\text{Aged}}$  are the crossover modulus of fresh and aged bitumen, respectively

) Al<sub>cm</sub> ageing index increases with ageing

TNO introvenion

# A TOOL TO ANALYSE TRACE ELEMENTS IN BITUMINOUS MATERIALS

- REOB is an oily black residue that is liquid at room temperature. It contains the remains of the additives such as- polymers, zinc dialkyldithiophosphates, calcium phenate, and molybdenum disulfide that are originally present in the source engine-oil.
- Characteristic elements in these additives—calcium, copper, zinc, and molybdenum—can be used as indicators for REOB identification.
- ICP-OES technique can be applied to characterize trace elements and to evaluate presence of any secondary streams (i.e. REOB) in bitumen.
- ICP-OES has low detection limits and can characterize multiple elements with limited spectral interferences. It has good stability and low matrix effects.



Avio 200 ICP-OES

TNO for life

### ELEMENTAL ANALYSIS OF REOB CONTAINING BITUMEN FINGERPRINTING REOB

Trace elements of interest in bituminous materials to be characterized by ICP-OES

Elements	Chemical	Origin of the
	symbol	elements
Calcium	Ca	REOB
Phosphorous	P	REOB
Copper	Cu	REOB
Molybdenum	Mo	REOB
Zinc	Zn	REOB
Potassium	K	REOB
Sulphur	S	REOB & Bitumen
Vanadium	V	Bitumen
Iron	Fe	Bitumen
Nickel	Ni	Bitumen

- ) Elemental analysis on CEAB samples
- Characteristic REOB elements can be identified with ICP-OES and are highlighted in the table below:

Elements	MP1029-A	MP1029-B				
	(ppm)	MP1029-A+ 8%				
		REOB				
		(ppm)				
Ni	112.30	966.8				
Ca	0.02	344.2				
P	0.47	12.91				
Cu	0.00	31.91				
Mo	0.00	1296.83				
Zn	8.72	105.33				
К	4.63	24.3				
Fe	25.00	25.0				
V	848.02	698.9				



- reference group.
- ) C=0 and sulfoxide S=0 peaks increases with progressing oxidative ageing.

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### **ELEMENTAL ANALYSIS**



> Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen (ISO 16948)

> Bio-based products- Determination of the oxygen content using an elemental analyser (EN 17351)

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### **PHASE BEHAVIOUR: AFM STUDY**

### MP 1029-G: NEAT


#### PHASE BEHAVIOUR

### MP 1029-G: TFOT+ 20H PAV













 Mw - weight average molecular weight: correlates with properties such as melt viscosity

- With increasing Mw brittleness, viscosity increases
- > Mn number average molecular weight

TNO introversion for life



6.3 Peng Lin & Shisong Ren, Multi-scale research of rejuvenation mechanism towards the challenge of changing bitumen properties







# BACKGROUND CHALLENGES IN MOLECULAR DYNAMIC SIMULATION





























**T**UDelft

## STEP 2: ESTABLISH THE MOLECULAR MODEL 04 ELEMENTAL ANALYSIS

#### Table 2

Elemental compositions in various rejuvenators.

Rejuvenators	N%	C%	H%	S%	<b>O%</b>	H/C	O/C
Bio-oil	0.15	76.47	11.96	0.06	11.36	1.88	0.1114
Engine-oil	0.23	85.16	14.36	0.13	0.12	2.02	0.0011
Naphthenic-oil	0.12	86.24	13.62	0.1	0.1	1.90	0.0009
Aromatic-oil	0.55	88.01	10.56	0.48	0.4	1.44	0.0034

**T**UDelft





### STEP 3: BETWEEN BITUMEN AND REJUVENATOR MD SIMULATION OF DIFFUSION



Fig Mass density profile of rejuvenators in bi-layers system





## STEP 3: DIFFUSION BETWEEN BITUMEN AND REJUVENATOR EXPERIMENT VALIDATION OF DIFFUSION COEFFICIENT









Molecule Model of Rejuvenated Bitumen

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## STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR SIMULATION OF COMPATIBILITY BETWEEN BITUMEN AND REJ



Binding energy Ebinding values of various rejuvenated bitumen

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Characterize the compatibility of rejuvenated bitumen based difference in rheological properties.









6.4 Hassan Tabatabaee, Glass Transition Deconvolution Method for Assessing Bitumen Incompatibilities Initially and upon Aging



Glass Transition Deconvolution Method for Assessing Bitumen Incompatibilities Initially and upon Aging

Presented by: Hassan A. Tabatabaee, Ph.D. Global Technical Manager

Co-authors: Tony Sylvester, Professional Chemist Cristian Calcanas, Associate Chemist

Main Reference:

Tabatabaee H.A., Sylvester T., Calcanas, C.; "Phase-compatibility of Bitumen defined through Deconvolution of Modulated Differential Scanning Calorimetry Response," Proceedings of the 2021 EATA Conference, Vienna, June 2021. Cargill 📰







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- Miscible blends show a single combined  $\underline{T}_{g}$ . The more clearly defined  $\underline{T}_{g}$ , the less miscible.
- The Derivative of DSC heat flow (<sup>dH</sup>/<sub>dT</sub>) or heat capacity is often used to detect underlying T<sub>gS</sub>
- Quantification of the impact of various factors on formation of multiple T<sub>es</sub> remains a gap.
- Deconvoluting the derivative of DSC response is a great way to analyze miscibility!



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# <sup>*dH*</sup>/<sub>*dT*</sub>: AC#1 Progression of Aging … and Rejuvenation

Bitumen aging increases intensity of secondary T<sub>a</sub>s (e.g. T<sub>a</sub>β)

- Increased area fraction of T<sub>g</sub>β (and <u>decreases % area of T<sub>g</sub>α</u>)
- Broadens overall transition width a multiple Tgs become more resolved
- · Proper rejuvenation reverses these trends.



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# $^{dH}/_{dT}$ : AC#2 Progression of Aging ... and Rejuvenation

- Bitumen aging increases intensity of secondary T<sub>as</sub>(e.g. T<sub>a</sub>β) Increased area fraction of T<sub>µ</sub>β (and <u>decreases % area of T<sub>µ</sub>α</u>)
  - Broadens overall transition width a multiple Tgs become more resolved
- · Proper rejuvenation reverses these trends.



## <sup>dH</sup>/<sub>dT</sub>: RAS Glass Transition Analysis...

- Bitumen aging increases intensity of secondary  $\underline{T}_{g\underline{S}}(e.g.\;\underline{T}_{g}\beta)$ 
  - Increased area fraction of T<sub>α</sub>β (and <u>decreases % area of T<sub>α</sub>α</u>)
  - Broadens overall transition width a multiple Tgs become more resolved



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6.5 Jeramie Adams, Asphalt Industry Research Consortium (AIRC): An Innovative Approach for Binder Understanding

# Asphalt Industry Research Consortium (AIRC): Innovative approach for binder understanding

Jeramie Adams, Jean-Pascal (JP) Planche, Yogesh Kumbargeri, Joe Rovani

TNO/TU Delft - Workshop- Characterization and Evaluation of Asphalt Binder properties, Dec 8, 2022

# WesternResearch

#### WesternResearch

#### Context - "360" Industry Changes

#### Drivers: economics, geopolitics, societal, regulatory

- Changes in crude oils & processes
- World of additives & modifiers
   New chemistries, more biomass origins...
- Changes to product specifications
   Asphalts and heavy fuels (IMO 2020)
- Market changes
  - WMA, RAP, RAS, PMA, GTR, Plastics...
- Environmental footprint of asphalts
   EPD's, LCA, LCCA
- IARC classification asphalt fumes
- Product Regulation for Importing Chemicals







VesternResearch	WRI Partnerships		
	Inception-		
Tools and knowledge (with FHWA)	2007-		
<ul> <li>"Fingerprint" project : Proof of concept – Initial Trials Eurovia)</li> </ul>	(with 2013-		
Validation – Industrial Perspective (Asphalt Industry Responses) Consortium #1)	<sup>earch</sup> 2015-		
Proposed Specifications & Formulation Guidelines (N 60 – Agencies' Perspective)	CHRP 9- 2016-		
Further Validation & Applications (AIRC #2)	2018-		
Proposed Specifications Framework validation (NCHR	2022-		
Evolutions: PMA/ Recycling /Alternative binders (AIR	C #3)		
Others	1		









#### WesternResearch

Exp: Testing Program

	AIRC	9-60	
Elemental Analysis	<ul> <li>Image: A second s</li></ul>		
Saturates, Aromatics, Resins, and Asphaltene	<ul> <li>Image: A second s</li></ul>	<ul> <li>✓</li> </ul>	
Determinator (SAR-AD <sup>™</sup> )			
Waxphaltene Determinator (WD™)	×	1	
Infrared Spectroscopy (FT-IR)	×	1	
Size Exclusion Chromatography/Gel Permeation	1		
Chromatography (SEC/GPC)			
Differential Scanning Calorimetry Results (DSC)	<ul> <li>✓</li> </ul>	<ul> <li>✓</li> </ul>	
SuperPave Performance Grade	×	×	
Black Space Diagram	×	×	
□Rheological LVE Parameters (∆T <sub>c</sub> & GR)	×	×	
□Multiple Stress Creep and Recovery Test (MSCR)	1	1	
Asphalt Binder Cracking Device	<ul> <li>Image: A second s</li></ul>	×	
Machine Learning/Regression	<ul> <li>✓</li> </ul>	×	10



# WesternResearch



HC from various origins / processes







## Asphalt structure and properties

Western Research









# •VALIDATION •Examples







From petroleum or non-petroleum origins (biomass, coal, wastes...)
 For various applications – paving and roofing new frontiers
 Will increase changes in production and application processes

22

Failure (NCHRP 9-60 outcomes) and other properties

>Machine learning to understand relationships

New approaches

> STAY TUNED!





60th Petersen Asphalt Research Conference Online/Onsite

July 17-20, 2023 Laramie, Wyoming

Thank You! - Questions?

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WesternResearch