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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 Management



2nd Workshop:
KPE-CEAB
8 Dec 2022

DR. X. LIU
DR. S.N. NAHAR
DR. P. LIN
IR. S. REN
IR. E. ASSAF

**Knowledge-based
Pavement
Engineering
2020-2024**

TNO 

8th December, 2022
Delft, the Netherlands

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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.

2 Content

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3 Workshop participants

Name	Affiliation	Role
Jeroen Besamusca	Kuwait Petroleum Research and Technology B.V	Speaker
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
		Participant
		Participant
		Participant
		Participant

4 Workshop Program

13:00-13:30	Walk in & coffee
14:00 – 14:15	Welcome <i>Sayeda Nahar-TNO, Sandra Erkens & Xueyan Liu-TU Delft</i>
	Session 1 moderator: Xueyan Liu-TU Delft
14:15-14:45	Quality problems in Dutch Roads (Online) <i>Jeroen Besamusca, Kuwait Petroleum Research and Technology B.V</i>
14:45 – 15:15	Project- KPE-CEAB Characterization and Evaluation of Asphalt Binder properties: approach and preliminary results <i>Dr. Sayeda Nahar, TNO</i>
15:15 – 15:30	Break
	Session 2 moderator: Sayeda Nahar-TNO
15:30 - 16:00	Multi-scale research of rejuvenation mechanism towards the challenge of changing bitumen properties <i>Dr. Peng Lin & Shisong Ren, TU Delft</i>
16:00 – 16:30	Glass Transition Deconvolution Method for Assessing Bitumen Incompatibilities Initially and upon Aging <i>Dr. Hassan Tabatabaee, Cargill Asphalt Solutions</i>
16:30 – 17:00	Asphalt Industry Research Consortium (AIRC): An Innovative Approach for Binder Understanding <i>Dr. Jeramie Adams, Western Research Institute (WRI)</i>
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:** X-ray fluorescence, ΔT_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 ΔT_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 - **T_g**: Glass Transition Temperature. **T_c**: 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 T_c 's <not to be confused with T_g (slopes, magnitudes, positions in the plot). Is this purely incidental, or has it been correlated to the quality and compatibility between the substances? Could T_c 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 T_c . 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 T_c 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 T_c , 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 $T_g(H)$ (half-height) and $T_g(I)$ (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 T_g and the inflection point reflects the strength of secondary T_g s. The stronger the

secondary T_g s are, the more different the inflection point T_g will be from the half height, as the shape of the overall T_g 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*



Quality problems in Dutch roads

TNO/TU Delft -WORKSHOP
CHARACTERISATION & EVALUATION
ASPHALT BINDER PROPERTIES

8 December 2022
Jeroen Besamusca
Kuwait Petroleum Research & Technology




"If you want to reduce your carbon footprint, you'll have to get rid of the fire and invent a smaller wheel!"

1




Asphalt issues Dutch highway, 2019



Unworkable asphalt mix with PmB binder



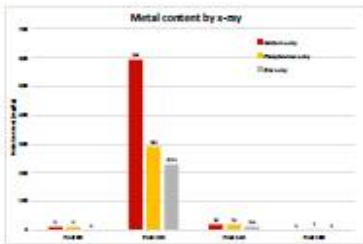
Asphalt with poor adhesion with PmB binder



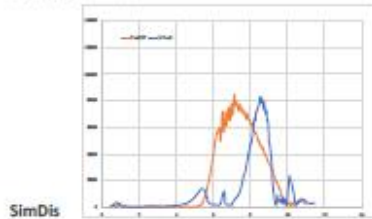
Fume during asphalt laying

2

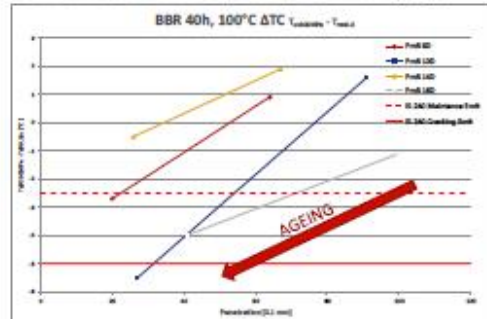
Un-expected additives in bitumen, 2019



Elements - Ca, Zn, P, - content



Delta Tc vs Penetration 25°C, before/after 2x PAV ageing



Start of project Leerruimte

3

Common Wealth Magazine, Fall 2014

THE RISE OF REOB

Asphalt is produced by refining crude oil. For the most part, it is a byproduct of oil refining rather than the intent. With the cost of oil skyrocketing in recent decades, asphalt producers are constantly looking for ways to reduce costs. One area where they've had some success is with the binders used to stabilize the product. Worn-out rubber tires, reclaimed asphalt, and old roofing shingles are just some of the materials that have been used as binders to keep costs down.

About 30 years ago, refiners began experimenting with adding recycled engine oil to asphalt, but its use was limited and confined to warmer climates. The binder, labeled Recycled Engine Oil Bottoms, or REOB, by industrial officials, is what sinks to the bottom when waste engine oil is re-refined. The lighter oil at the top can be used for other products, including engine oil. But there wasn't much use for REOB until it was added to asphalt as a cheaper alternative to existing binders.

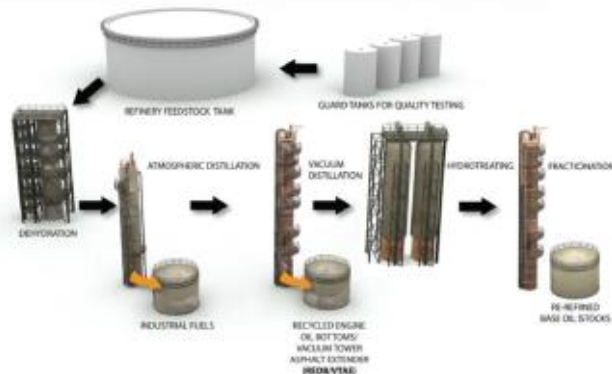
More hard "additives" in asphalt requested softer bitumen grades.

REOB/VTAE in the US: 1985
REOB in Europe: 1970



4

ReOB/VTAE, simplified production process



USA: registered CAS number 12893_17_0
Europe: "Bitumen"

- History
 - Initial Technology from Europe
 - Established in North America in the 1980's
 - VTAE used in asphalt at 1.7 MM tons since 1990
- Paving
- Roofing
- Industrial

Asphalt Institute IS-235, The use of ReOB/VTAE in asphalt, 2016

Rocky Mountain user/Producer group, Idaho Oct 2014

5

ReOB/VTAE, US and Europe



Capacity \approx 2 Mton Oil (\approx 400 kton ReOB)
GEIR website

Capacity \approx 1.5 Mton Oil (\approx 300 kton ReOB)
North American Used Oil Facilities



Rocky Mountain user/Producer group, Idaho Oct 2014

6

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:**

Table 2 (continued)

Characteristic	Unit	Limit	Category ISO-F-										Test method reference
			RMA	RMB	RMD	RME	RMG				RMK		
			10 ^a	30	60	180	180	360	500	700	380	500	
Aluminium plus silicon	mg/kg	max.	25	40	40	50	60				60		see 7.9 IP 501, IP 470 or ISO 10478
Used lubricating oils (ULO): calcium and zinc; 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 zinc > 15; or calcium > 30 and phosphorus > 15										see 7.10 IP 501 or IP 470 IP 500

^a This category is based on a previously defined distillate DMC category that was described in ISO 8217:2005, Table 1. ISO 8217:2005 has been withdrawn.

^b 1 mm²/s = 1cSt.

^c The purchaser shall define the maximum sulfur content in accordance with relevant statutory limitations. See 0.3 and Annex C.

^d Due to reasons stated in Annex D, the implementation date for compliance with the limit shall be 1 July 2012. Until such time, the specified value is given for guidance.

^e See Annex H.

^f Purchasers shall ensure that this pour point is suitable for the equipment on board, especially if the ship operates in cold climates.

7

Asphalt Institute, IS-235 - 2016

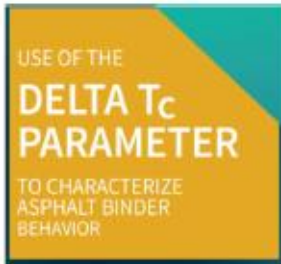


This document is careful to define REOB/VTAE as the non-distillable residuum from a vacuum tower in a used oil re-refinery. Other re-refined products derived from used oil not meeting this definition are not addressed herein, and the extent of their use in asphalt is unknown. REOB/VTAE has been used 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 data indicating that the performance of binders and mixtures containing REOB/VTAE is dependent on the REOB/VTAE dosage, the REOB/VTAE source and the binder source.

8

Quality measurement, ΔT_c (IS-240) 2019



Delta T_c (ΔT_c) 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 hot mix asphalt pavement performance. It is generally accepted that ΔT_c targets cracking behavior that is affected by asphalt binder durability related to aging of the binder in an asphalt mixture. More specifically, ΔT_c 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 pavement. It is a calculated value using the results of the bending beam rheometer test determined on laboratory-aged asphalt samples or samples recovered from pavements. At the time this document was developed (mid-2019), ten user agencies have or soon will implement ΔT_c as part of their purchase specification, with two more expecting to do so in the near future. In addition, several national level research projects are actively considering ΔT_c as part of their studies. In fact, ΔT_c was first hypothesized via a 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 ΔT_c . If that sample indicated a ΔT_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 ΔT_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.

9

ΔT_c in US, IS-240



➤ Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken.

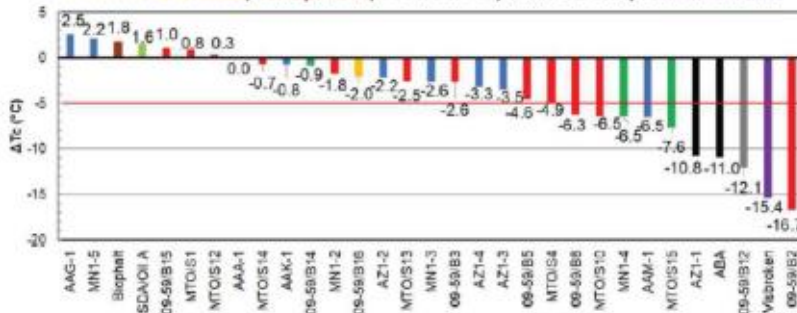
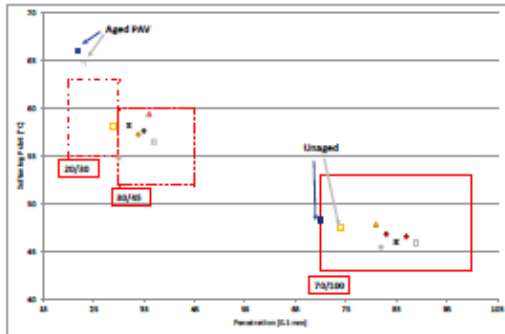


Figure 12. ΔT_c (PAV40) of Various Binders from NCHRP 9-60 Research Project Database (4)

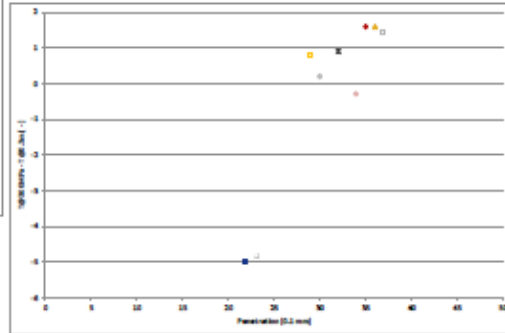
10

Delta Tc the Netherlands, 70/100 bitumen, 2017



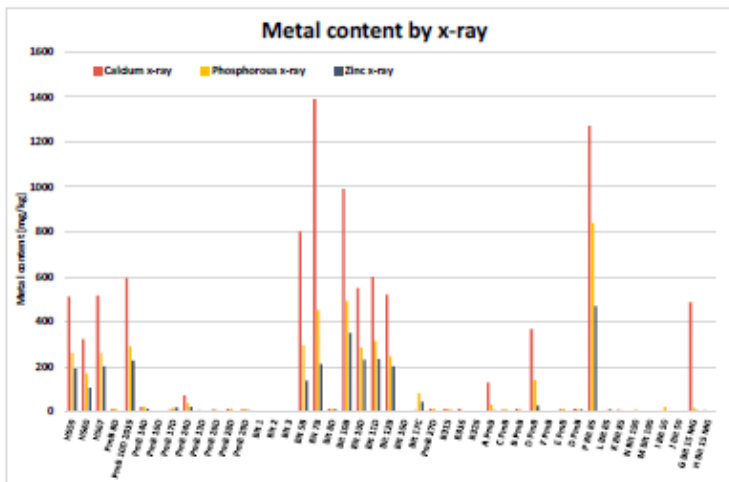
Softening Point vs Penetration 25°C, before and after RTFOT/PAV ageing

Delta Tc vs Penetration 25°C, after RTFOT/PAV ageing



11

VTAE used in the Netherlands, 2020/2021



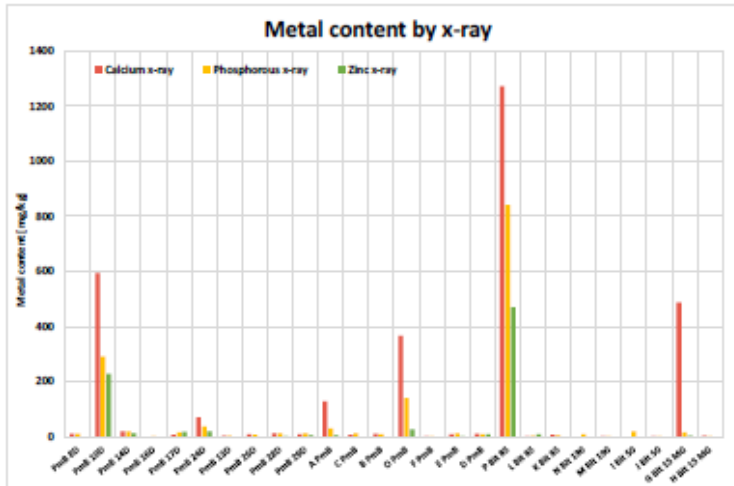
Remember:
ISO 8217 demands
free of ULO.

Ca < 30 ppm
P < 15 ppm
Zn < 15 ppm

Clearly REOB is
used.
But is it a problem?

12

VTAE used in the Netherlands



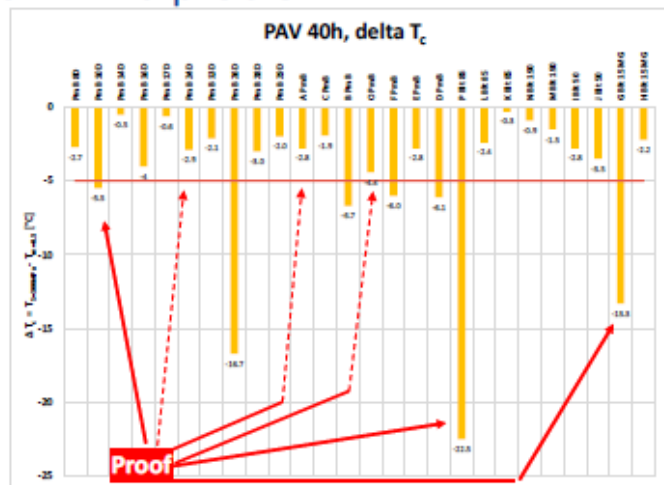
Remember:
ISO 8217 demands
free of ULO.

Ca < 30 ppm
P < 15 ppm
Zn < 15 ppm

6 Binders with high
content of one or all
off the ISO 2017
components.
**PmB 10D; PmB 24D;
A PmB; O PmB; P Bit
85; G Bit 15MG**

13

Is VTAE a problem



Proof of 3 binders:

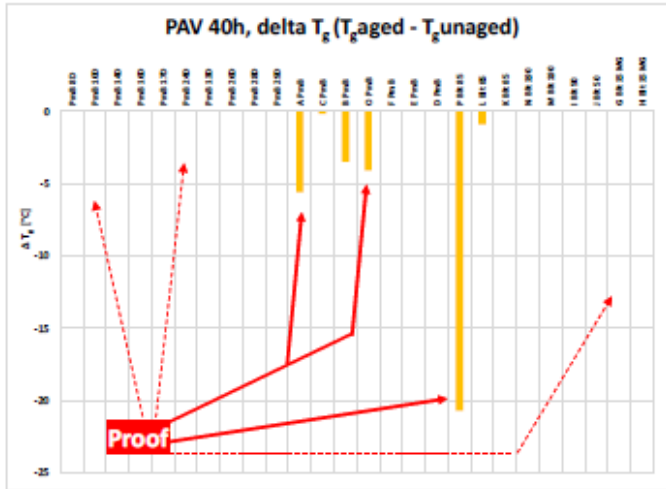
**PmB 10D; PmB 24D; A PmB;
O PmB; P Bit 85; G Bit 15MG**

Delta Tc
DSC – Tg value
Cross-Over Temperature

And the others?
PmB 26D; B PmB; F PmB;
D PmB

14

VTAE used in the Netherlands



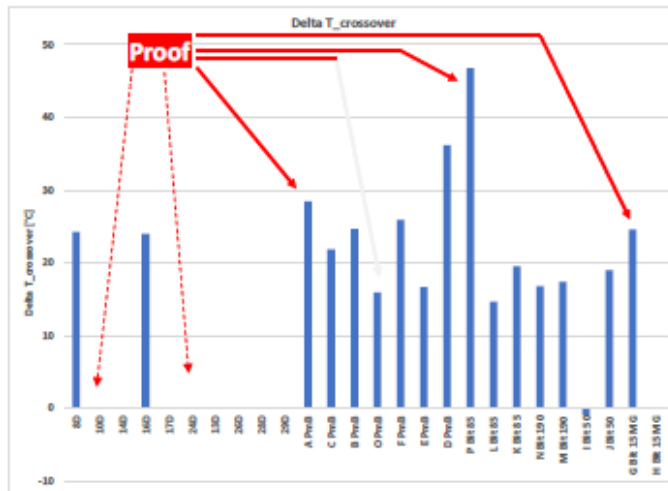
Proof of 6 binders:
Work in progress
 PmB 10D; PmB 24D; A PmB;
 O PmB; P Bit 85; G Bit 15MG

Delta Tc
 DSC – Tg value
 Cross-Over Temperature

And the others?
 PmB 26D; B PmB; F PmB;
 D PmB

15

VTAE used in the Netherlands



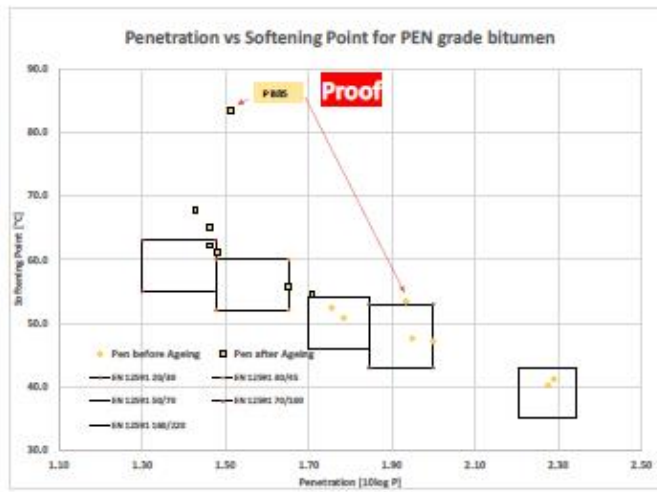
Proof of 6 binders:
Work in progress
 PmB 10D; PmB 24D; A
 PmB; O PmB; P Bit 85; G
 Bit 15MG

Delta Tc
 DSC – Tg value
 Cross-Over Temperature

And the others?
 PmB 26D; B PmB;
 F PmB; D PmB
 Work in progress

16

VTAE used in the Netherlands



Proof of pen binders:

Delta Tc
 DSC – Tg value
 Cross-Over Temperature

Modified binder =
 PEN bitumen + additive

17

Continuation after project Leerruimte

In Canada, they use special stickers to slow cars.



In the Netherlands we use 3D techniques



Grip on asphalt:
 Start in September 2022 till December 2023.

Discussion TC 336 WG1:
 *Ban "used oil" ?
 *Introduce ΔT_c ?

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Thank you for your attention.

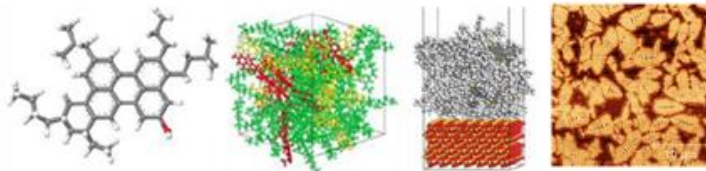


Q8  **Research**

19

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

KPE-CEAB: CHARACTERIZATION AND EVALUATION OF ASPHALT BINDER PROPERTIES: APPROACH AND PRELIMINARY RESULTS



Sayeda Nahar

2nd Workshop- Characterization and Evaluation of Asphalt Binder properties, Dec 8, 2022

TNO 100000000
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



› 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



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.

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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

Bitumen grades:

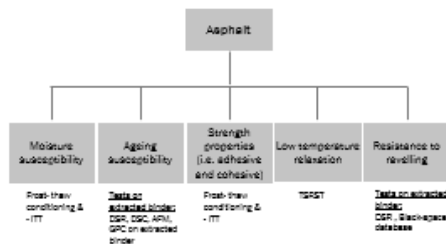
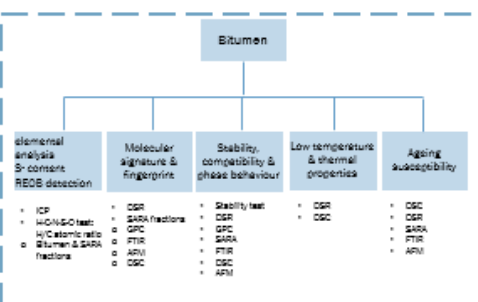
- › PEN: 40/60, 70/100, 20/30, 160,220
- › PmB

TNO 2020/2021
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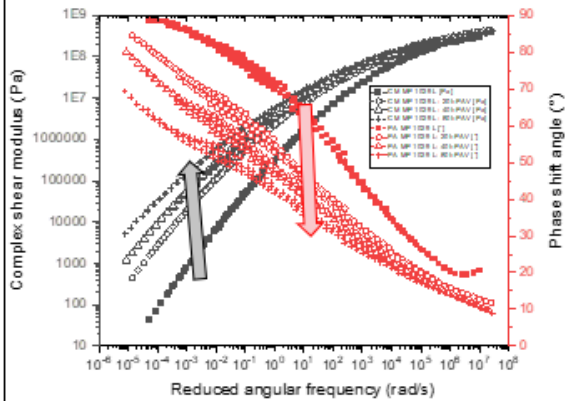
OVERVIEW OF THE BITUMEN SAMPLES

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. <ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> • Bitumen containing 3% REOB • <u>PmB</u>

PERFORMANCE PROPERTIES CHARACTERIZATION TOOLS



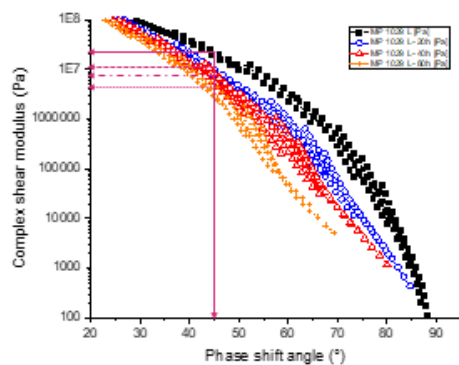
VISCO-ELASTIC PROPERTIES OF BITUMEN MASTER CURVES



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

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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.
- › AI_{CM} , **ageing index of crossover modulus** will be calculated

$$AI_{CM} = \frac{CM_{Fresh}}{CM_{Aged}}$$

Here, CM_{Fresh} and CM_{Aged} are the crossover modulus of fresh and aged bitumen, respectively

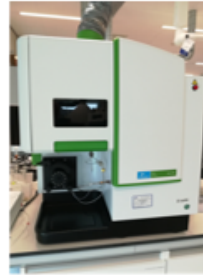
- › AI_{CM} ageing index increases with ageing

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ICP-OES

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

Element	Wavelength (nm)
Ca	317.833
Cu	327.383
Fe	238.204
K	788.480
Mo	202.031
Ni	231.804
P	213.817
Si	251.811
V	292.484
Zn	208.200
Co	228.818
(internal standard)	

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ELEMENTAL ANALYSIS OF REOB CONTAINING BITUMEN FINGERPRINTING REOB

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

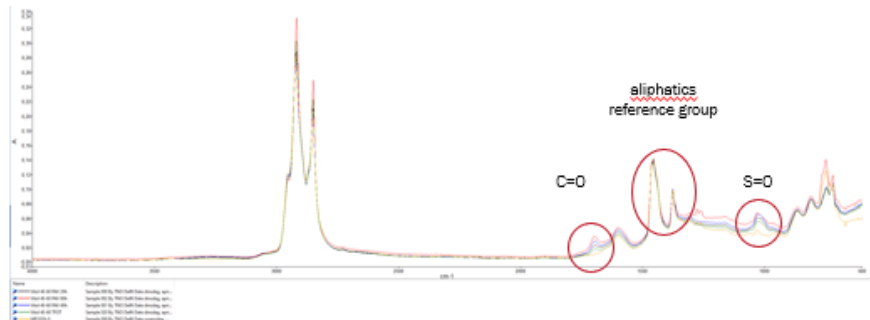
Elements	Chemical symbol	Origin of the elements
Calcium	Ca	REOB
Phosphorous	P	REOB
Copper	Cu	REOB
Molybdenum	Mo	REOB
Zinc	Zn	REOB
Potassium	K	REOB
Sulphur	S	REOB & Bitumen
Vanadium	V	Bitumen
Iron	Fe	Bitumen
Nickel	Ni	Bitumen

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

Elements	MP1029-A (ppm)	MP1029-B 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
K	4.63	24.3
Fe	25.00	25.0
V	848.02	698.9

TNO 1000000001
For life

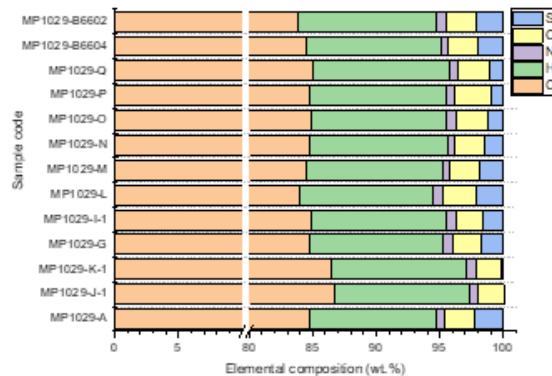
AGEING SUSCEPTIBILITY FTIR RESULTS



- FTIR results on fresh bitumen and after short and long term laboratory ageing
- FTIR results are shown for MP 1029-G bitumen fresh, TFOT, PAV 20h, 40h and 80h.
- Functional groups of interests are carbonyl (C=O) and sulfoxide (S=O),
- Carbonyl (C=O) area is the band around the 1680 cm^{-1} peak, the sulfoxide area is the band around 1030 cm^{-1} .
- The aliphatic group (symmetric and asymmetric bending vibrations around 1460 and 1376 cm^{-1} , respectively) is commonly used as a reference group.
- C=O and sulfoxide S=O peaks increases with progressing oxidative ageing.

TNO 2008000001
For life

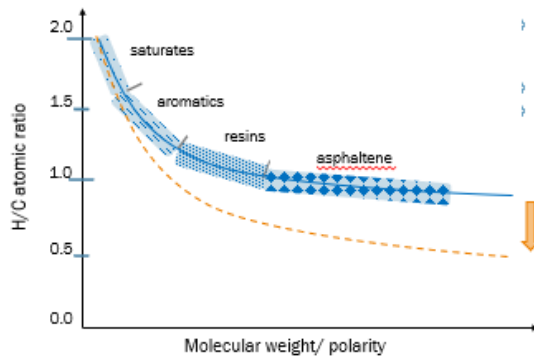
ELEMENTAL ANALYSIS



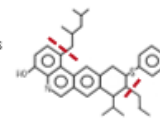
- Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen (ISO 16948)
- Bio-based products- Determination of the oxygen content using an elemental analyser (EN 17351)

TNO 2008000001
For life

REFINERY UPGRADING & INFLUENCE OF SECONDARY STREAMS



- Secondary blend stream (outside refinery) may introduce a new fraction of maltene, i.e. saturates, aromatics of different properties;
- Long term compatibility of the secondary streams;
- Special attention to low and high temperature properties.

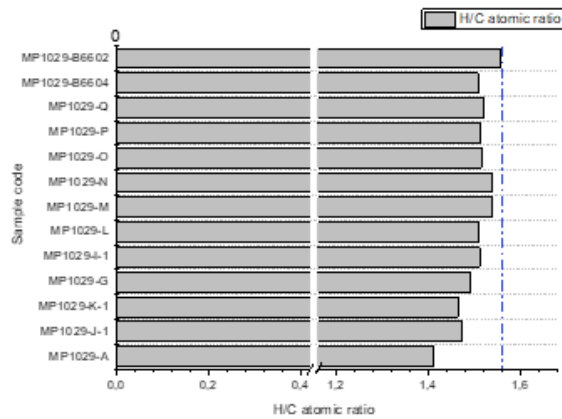


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For life

H/C ATOMIC RATIO

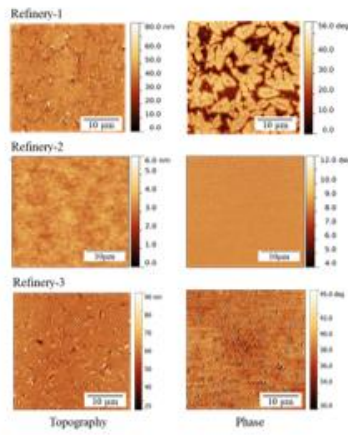
INSERT SECOND TITLE HERE

$$\text{H/C atomic ratio} = \frac{\text{Weight percent hydrogen} \times \text{Atomic weight hydrogen}}{\text{Weight percent carbon} \times \text{Atomic weight carbon}}$$



TNO 2022/0504
For life

PHASE BEHAVIOUR: AFM STUDY
DIFFERENCE IN CRUDE OIL FEEDSTOCK & PROCESS

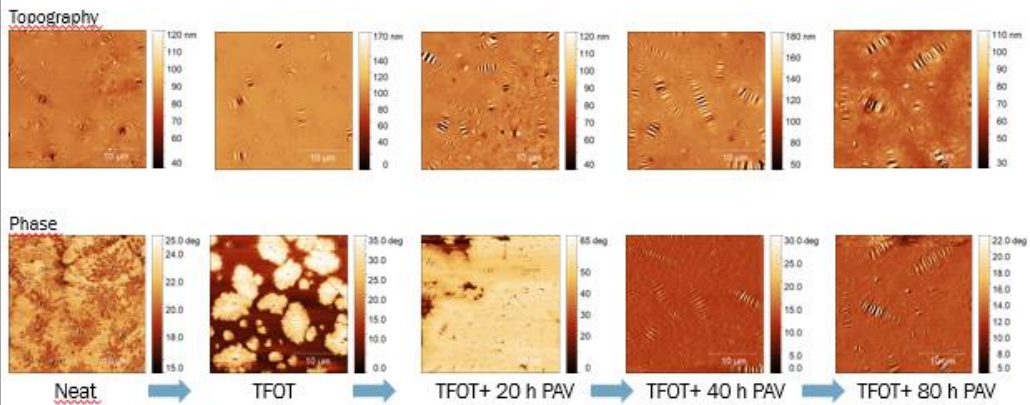


30x30 nm² AFM micrographs of neat bitumens of **PEN 70/100**, obtained from different refineries.

Source: PhD thesis- Sayeda Nahar: "Phase separation characteristics of bitumen and their relation to damage healing"

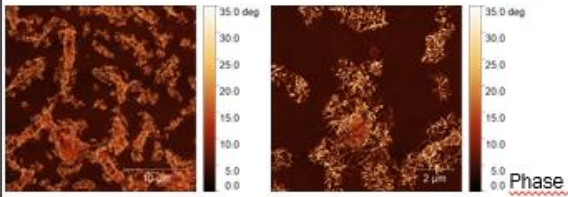
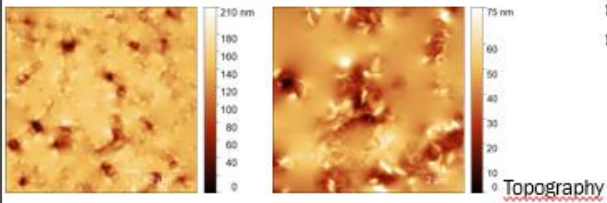


PHASE BEHAVIOUR: AFM STUDY
MP 1029-L



PHASE BEHAVIOUR: AFM STUDY

MP 1029-G: NEAT

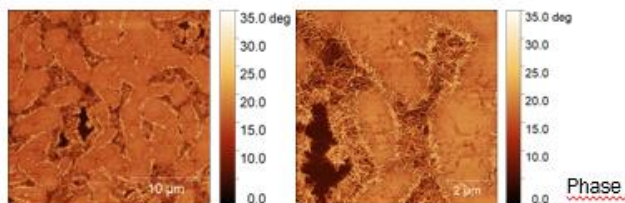
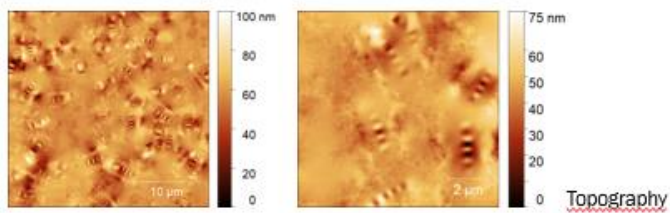


- › One source of bitumen showing unique phase morphology
- › The change of phase behaviour due to oxidative ageing is studied using AFM : ageing conditions were TFOT, PAV 20h, 40h and 80h.

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FOR LIFE

PHASE BEHAVIOUR

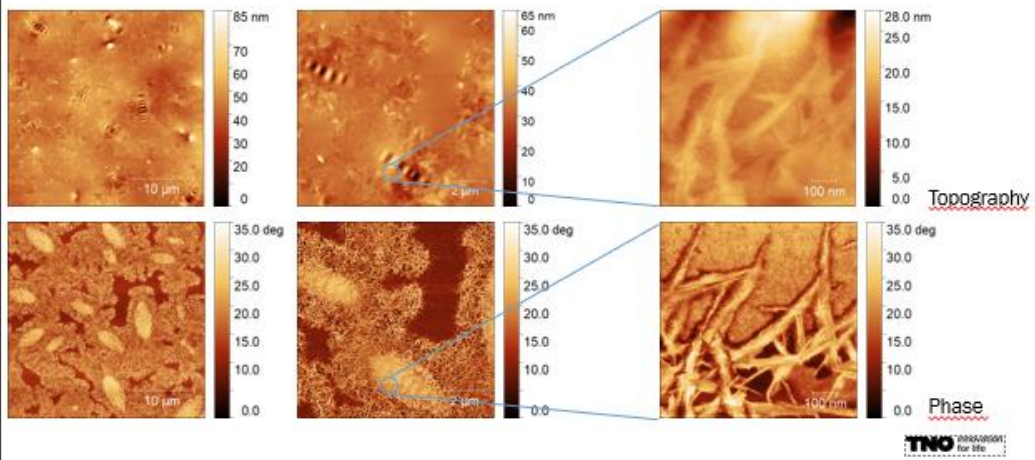
MP 1029-G: TFOT



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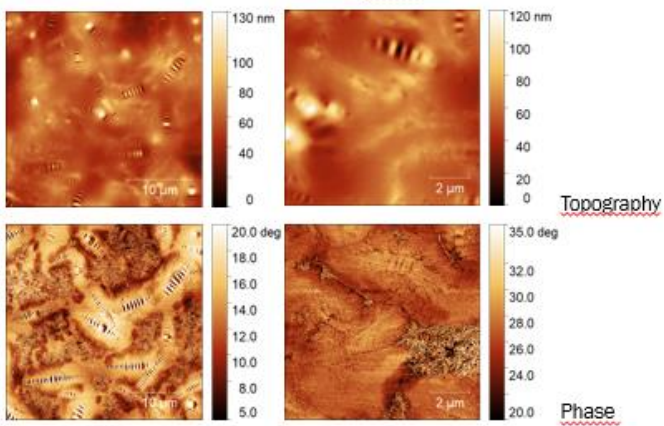
PHASE BEHAVIOUR

MP 1029-G: TFOT+ 20H PAV



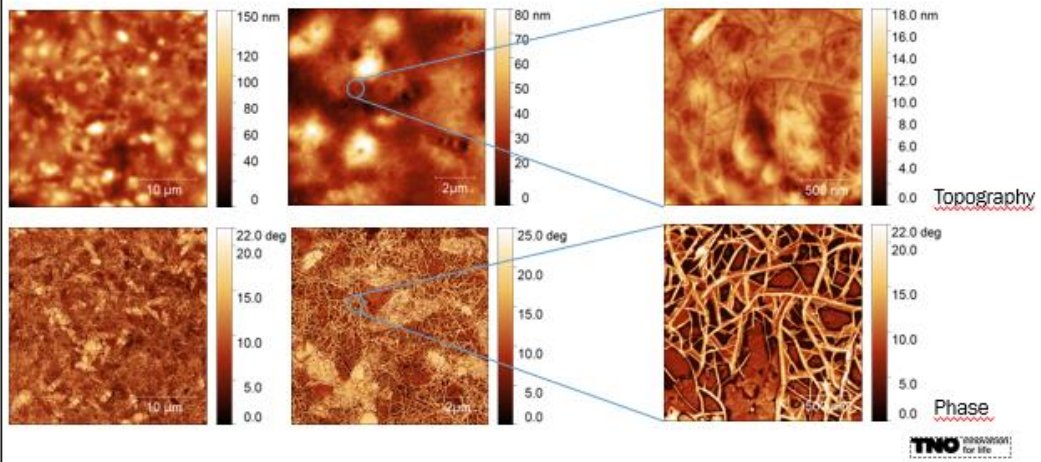
PHASE BEHAVIOUR

MP 1029-G: TFOT+ 40H PAV



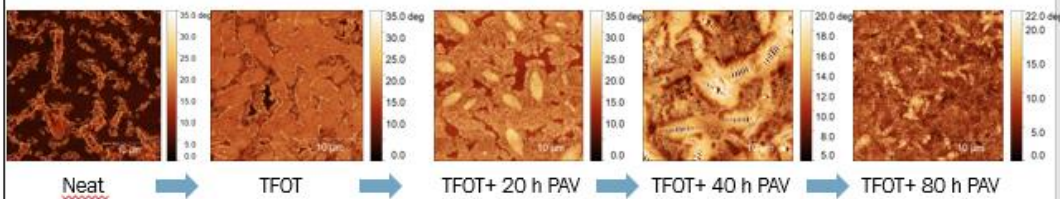
PHASE BEHAVIOUR

MP 1029-G: TFOT+ 80H PAV



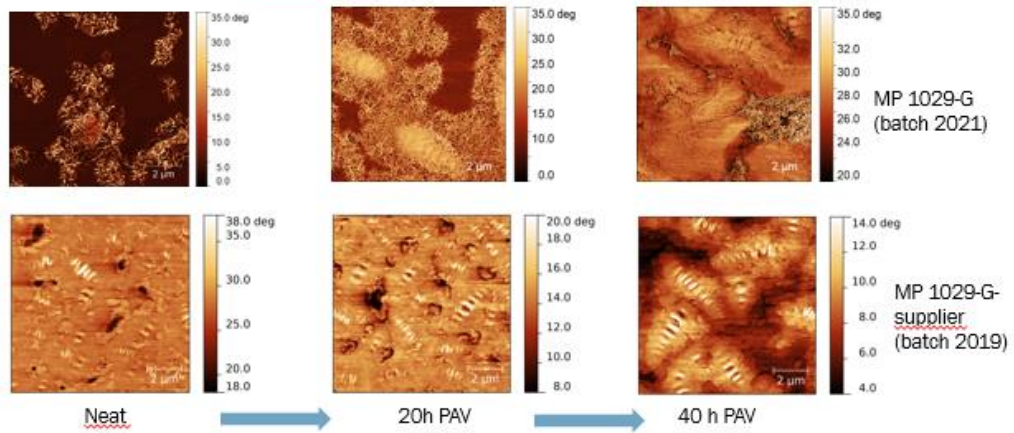
CHANGE OF PHASE BEHAVIOUR DUE TO AGEING

MP 1029-G- AFM PHASE IMAGES



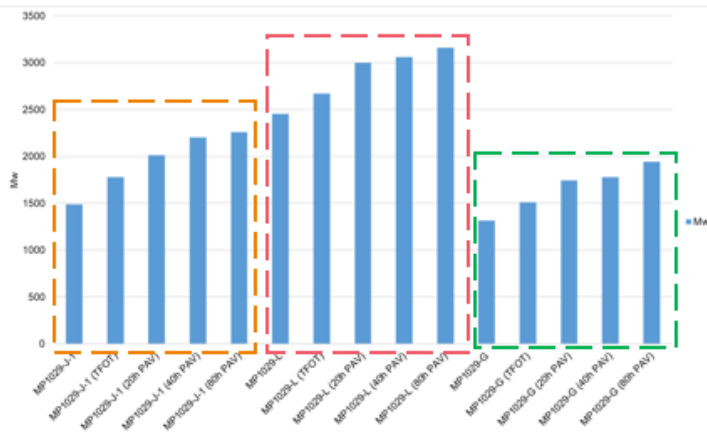
COMPARISON OF PHASE BEHAVIOUR BETWEEN DIFFERENT BATCHES

MP 1029-G- AFM PHASE IMAGES



TNO INNOVATION
for life

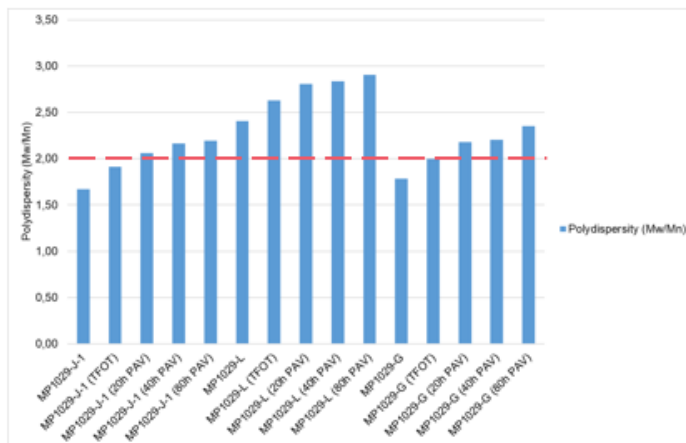
GPC RESULTS PRILIMINARY ANALYSIS



- › **Mw** - weight average molecular weight: correlates with properties such as melt viscosity
- › With increasing Mw brittleness, viscosity increases
- › **Mn** - number average molecular weight

TNO INNOVATION
for life

GPC RESULTS (CONTD)



- › Polydispersity index (GPC): Mw/Mn Polydispersity index characterizes the shape of the distribution
- › 1-2: Moderate distribution
- › > 2: Broad distribution

TNO PROFESSIONAL For life

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

Multi-scale research of rejuvenation mechanism towards the challenge of changing bitumen properties

Rijkswaterstaat
Ministry of Infrastructure
and Water Management

Workshop:
KPE-CEAB
8 Dec 2022

DR. X. LIU
DR. P. LIN
IR. S. Ren
IR. E. Assaf

**Knowledge-based
Pavement
Engineering
2020-2024**

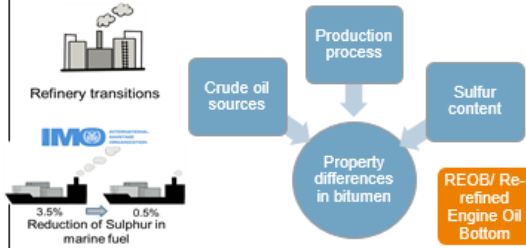
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BACKGROUND

CHANGE OF BITUMEN

Changes in the Bitumen Industry

- Refineries are in transition
- Changes in fuel demand
- Closure of bitumen production in refineries around this region
- Change in legislation: IMO 2020
- Variation in refinery feedstocks



VARIOUS REJUVENATORS

Changes in the Rejuvenation Methodology

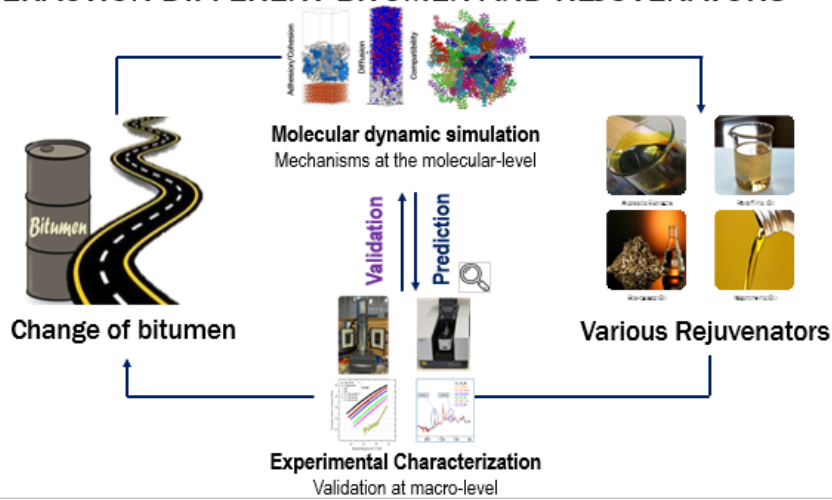
- High RAP content in new asphalt mix
- Changing of recycling methods of RAP
- Evolution of rejuvenator types and application methods
- Use of sustainable/recycled sources of raw materials



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BACKGROUND

INTERACTION DIFFERENT BITUMEN AND REJUVENATORS



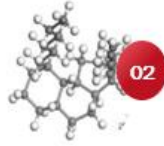
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BACKGROUND CHALLENGES IN MOLECULAR DYNAMIC SIMULATION



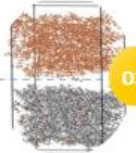
01 No Accurate Bitumen Model

How represent different type of bitumen at different aging level?



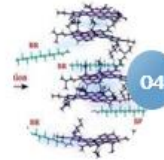
02 No Representative Rejuvenator Model

How to represent rejuvenerator fraction with simple molecular structure?



03 Simulation to Engineering Properties

How to calculate the engineering relative properties based on MD simulation?

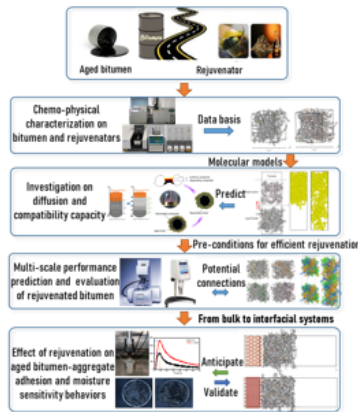


04 Simulation to Rejuvenation Mechanism

How to have better understanding of rejuvenation mechanism from MD simulation?



BACKGROUND RESEARCH SCHEME



Step 1: Select representative bitumen and rejuvenators

Step 2: Establish the molecular model

Step 3: Diffusion between bitumen and rejuvenator

Step 4: Compatibility between bitumen and rejuvenator

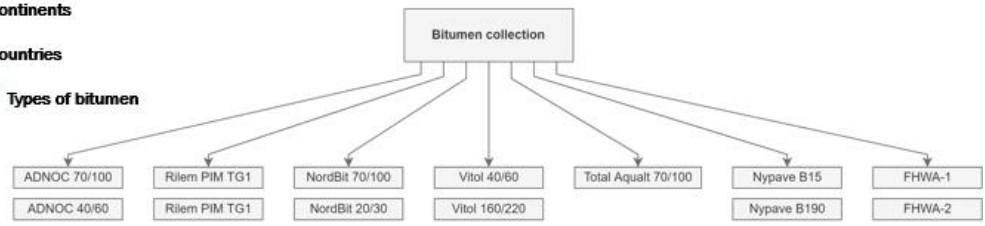
Step 5: Prediction the rejuvenation effect on rheology



STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

SELECTION OF BITUMEN

- 4 Continents
- 7 Countries
- 17 Types of bitumen



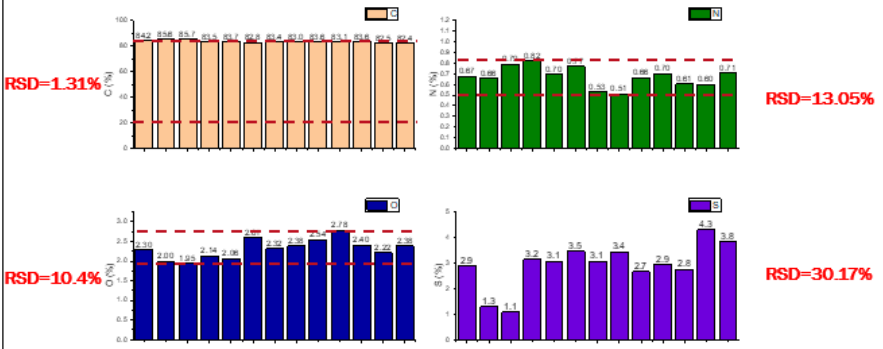
Elemental Analysis



STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

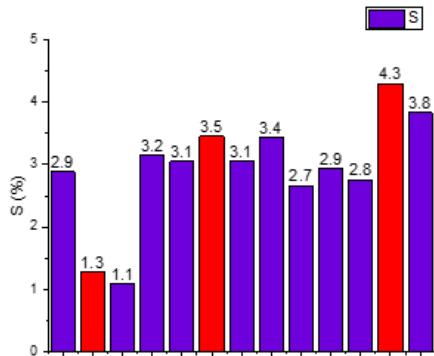
CHARACTERIZATION: ELEMENTAL ANALYSIS

Relative Standard Deviation (RSD)



STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

CHARACTERIZATION: ELEMENTAL ANALYSIS



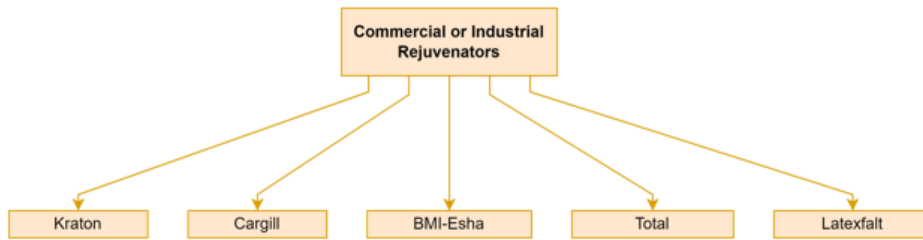
Select three representative bitumen:

- Bitumen 1 (S=1.3%)
- Bitumen 2 (S=3.5%)
- Bitumen 3 (S=4.3%)



STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

SELECTION OF COMMERCIAL REJUVENATOR



- Problem: Commercial rejuvenators are combination of different ingredients.
- Purpose: Understand the rejuvenation mechanism of individual ingredients

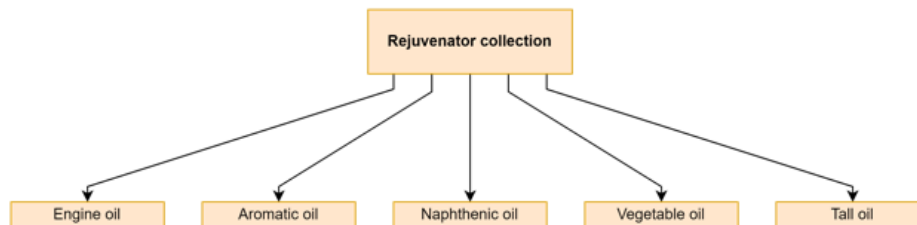


STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

SELECTION OF REJUVENATOR INGREDIENTS

Selection Criteria:

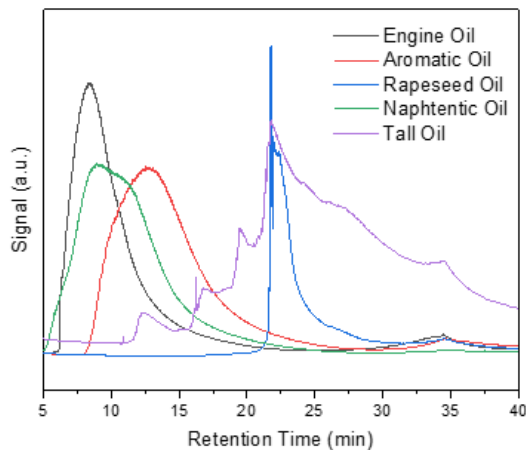
- Raw material that is **widely applied** in commercially available rejuvenators.
- Chemical structures that are **consistent** and **representative**.
- Molecule that shows **different rejuvenation effects**.



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STEP 1: SELECT REPRESENTATIVE BITUMEN AND REJUVENATORS

CHARACTERIZATION: GC-FID

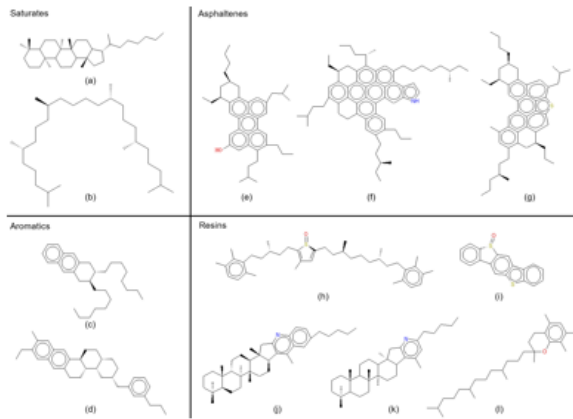


Select five rejuvenator ingredients:

- **Engine oil**
- **Aromatic oil**
- **Vegetable oil**
- **Naphthenic oil**
- **Tall Oil**

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STEP 2: ESTABLISH THE MOLECULAR MODEL
 ESTABLISH BITUMEN MOLECULAR MODEL



Greenfield 12 component model

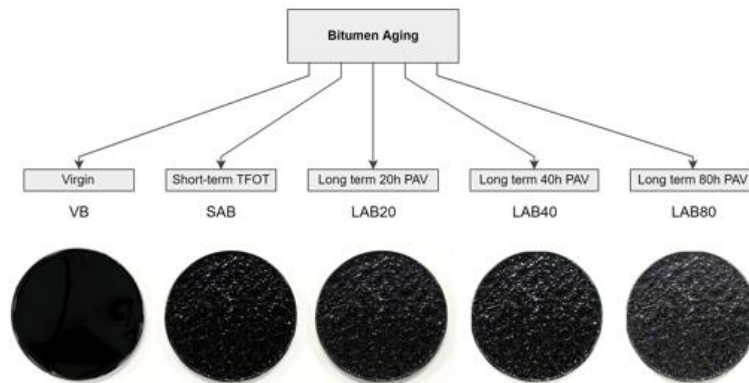


STEP 2: ESTABLISH THE MOLECULAR MODEL
 ESTABLISH BITUMEN MOLECULAR MODEL



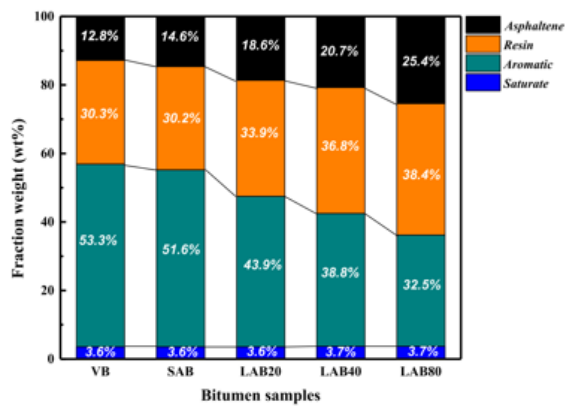
STEP 2: ESTABLISH THE MOLECULAR MODEL

01 PREPARE BITUMEN AGING CONDITIONS



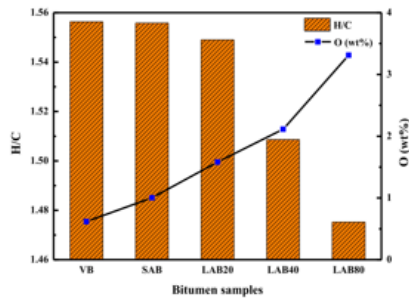
STEP 2: ESTABLISH THE MOLECULAR MODEL

02 TLC-FID: SARA FRACTIONATION ANALYSIS



STEP 2: ESTABLISH THE MOLECULAR MODEL

03 ELEMENTAL ANALYSIS

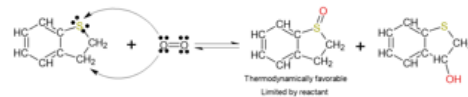
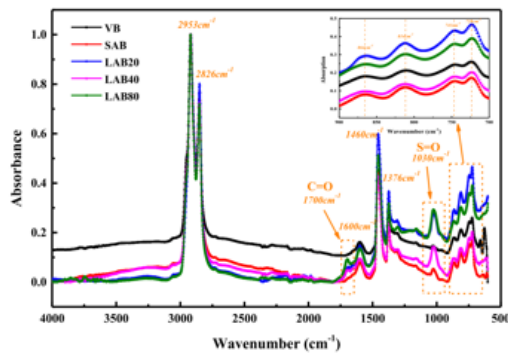


Bitumen samples	Elemental composition of Total Bitumen				
	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)
Fresh	84.08	10.90	0.618	0.90	3.52
Short-term	83.72	10.86	1.004	0.91	3.51
20h PAW	83.26	10.75	1.582	0.92	3.49
40h PAW	83.02	10.48	2.113	0.89	3.53
80h PAW	82.14	10.10	3.312	0.91	3.54



STEP 2: ESTABLISH THE MOLECULAR MODEL

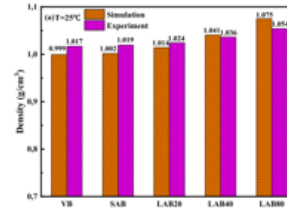
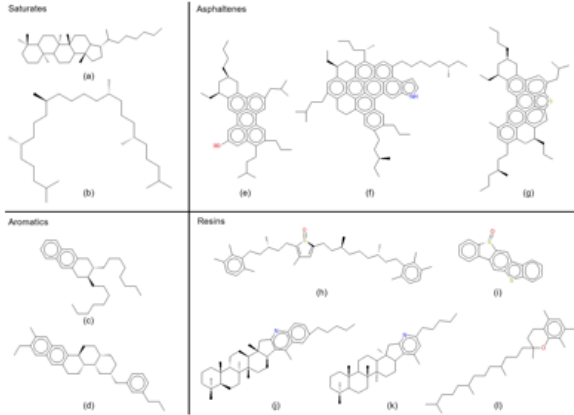
04 FTIR-FUNCTIONAL GROUPS ANALYSIS



STEP 2: ESTABLISH THE MOLECULAR MODEL

05 MOLECULES MODEL BUILD AND VALIDATION

Molecular structures:



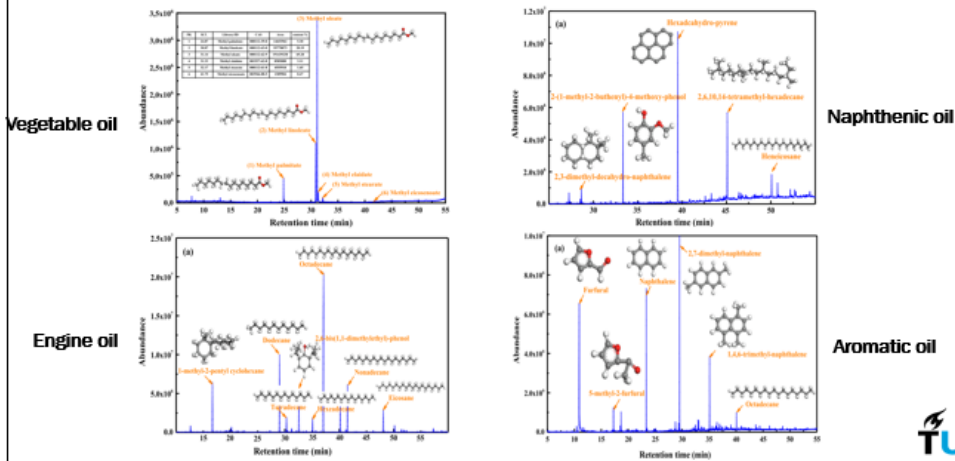
Property	Value
T (K)	298
P (atm.)	1.001
ρ (g/cm ³)	1.008
α (m ³ /kg) ($\times 10^{-4}$)	1.52
C _p (kJ/kgK)	2.10
CED (J/cm ³)	322.02
P _v (kJ/m ³)	1375.5
K _v (kJ/m ³)	831.7

Validate the molecular model based on physical parameters.



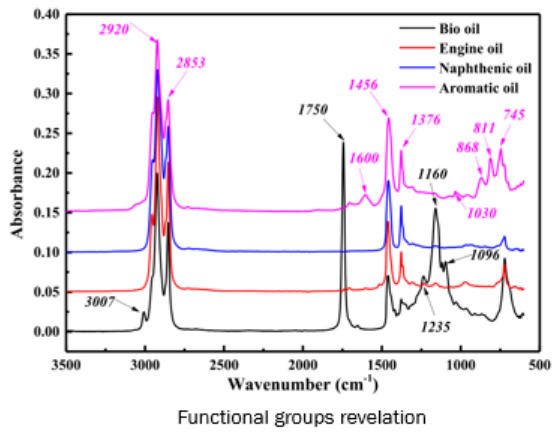
STEP 2: ESTABLISH THE MOLECULAR MODEL

01 GC-MS: MOLECULAR FRAGMENTS



STEP 2: ESTABLISH THE MOLECULAR MODEL

02 FTIR- FUNCTIONAL GROUP



STEP 2: ESTABLISH THE MOLECULAR MODEL

03 VAPOR PRESSURE OSMOMETER- MOLECULE WEIGHT

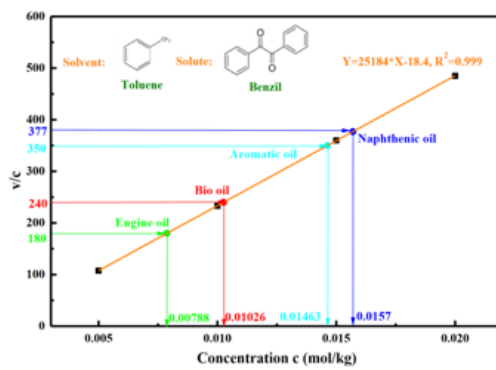


Table 3

The VPO parameters and average molecular weight of various rejuvenators.

Rejuvenators	Bio-oil	Engine-oil	Naphthenic-oil	Aromatic-oil
m_r (g)	0.0654	0.0577	0.1234	0.0710
m_s (g)	21.8250	23.0800	22.4384	11.8334
v/c	240	180	377	350
c (mol/kg)	0.01026	0.00788	0.0157	0.01463
M_n (g/mol)	286.43	316.48	357.06	409.99



STEP 2: ESTABLISH THE MOLECULAR MODEL

04 ELEMENTAL ANALYSIS

Table 2
Elemental compositions in various rejuvenators.

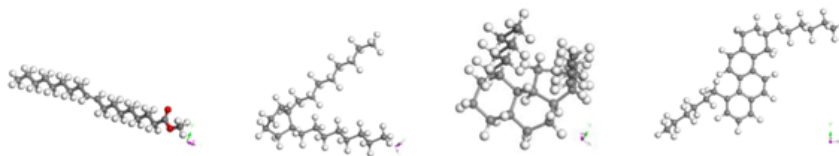
Rejuvenators	N%	C%	H%	S%	O%	H/C	O/C
Bio-oil	0.15	76.47	11.96	0.06	11.36	1.88	0.1114
Engine-oil	0.23	85.16	14.36	0.13	0.12	2.02	0.0011
Naphthenic-oil	0.12	86.24	13.62	0.1	0.1	1.90	0.0009
Aromatic-oil	0.55	88.01	10.56	0.48	0.4	1.44	0.0034



STEP 2: ESTABLISH THE MOLECULAR MODEL

05 MOLECULE MODEL AND VALIDATION

Average Molecular Model



(a) Bio-oil

(b) Engine-oil

(c) Naphthenic-oil

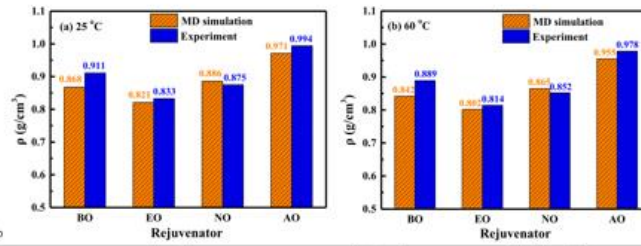
(d) Aromatic-oil

The average molecular structure of various rejuvenators



STEP 2: ESTABLISH THE MOLECULAR MODEL

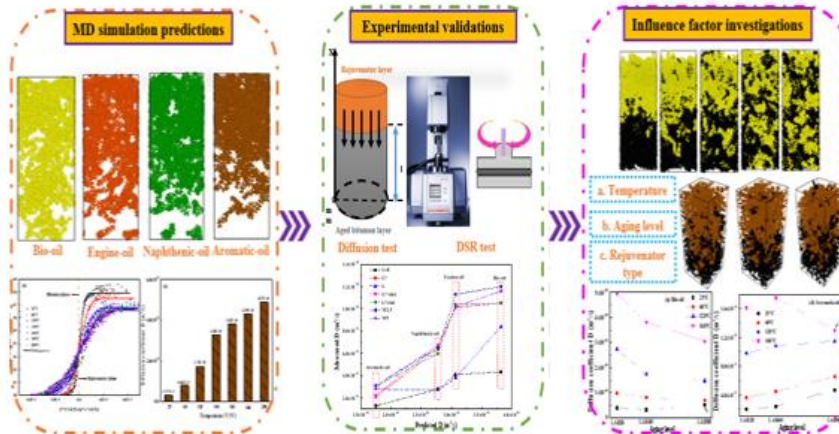
05 MOLECULE MODEL VALIDATION



Chemical and ρ	Bio-oil	Engine-oil	Naphtenic-oil	Aromatic-oil
Rejuvenators	Bio-oil	Engine-oil	Naphtenic-oil	Aromatic-oil
Appearance	Pale-yellow liquid	Brown liquid	Transparent-liquid	Dark-brown half-solid
25°C Density (g/cm ³)	0.911	0.833	0.875	0.994
60°C Density (g/cm ³)	0.899	0.814	0.852	0.978
25°C viscosity (cP)	50	60	130	63,100
Flash point (°C)	> 250	> 225	> 230	> 210
Carbon C (%)	76.47	85.16	86.24	88.01
Hydrogen H (%)	11.96	14.36	13.62	10.56
Oxygen O (%)	11.36	0.12	0.10	0.40
Sulfur S (%)	0.06	0.13	0.10	0.48
Nitrogen N (%)	0.15	0.23	0.12	0.55
Mn (g/mol)	286.43	316.48	357.06	409.99

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STEP 3: DIFFUSION BETWEEN BITUMEN AND REJUVENATOR



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STEP 3: BETWEEN BITUMEN AND REJUVENATOR
MD SIMULATION OF DIFFUSION

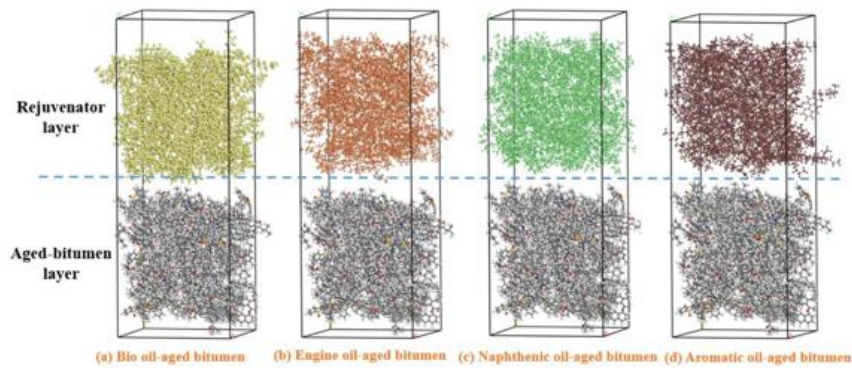


Fig. Different rejuvenator-aged bitumen diffusion molecular models



STEP 3: BETWEEN BITUMEN AND REJUVENATOR
MD SIMULATION OF DIFFUSION

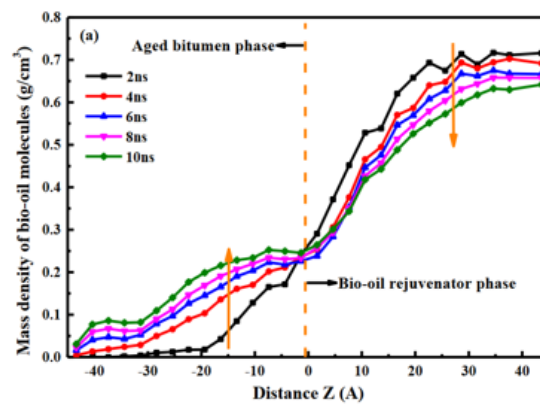
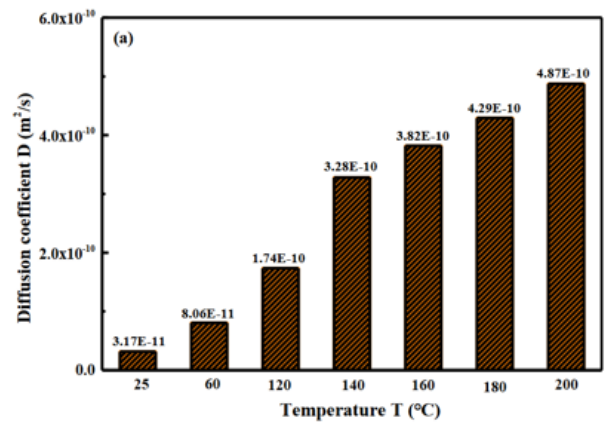


Fig Mass density profile of rejuvenators in bi-layers system



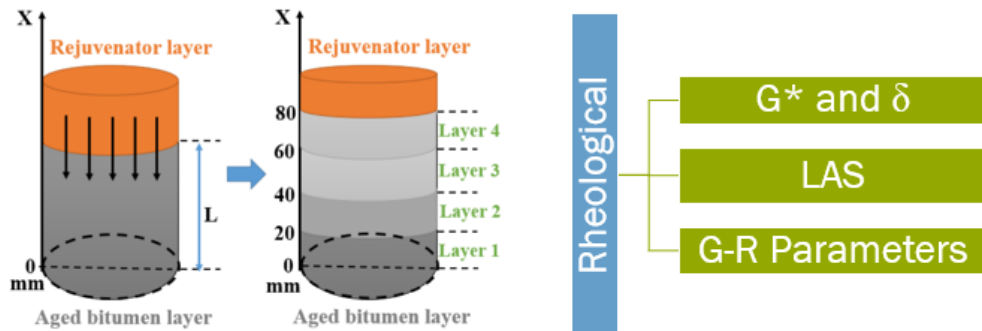
STEP 3: BETWEEN BITUMEN AND REJUVENATOR
 MD SIMULATION OF DIFFUSION



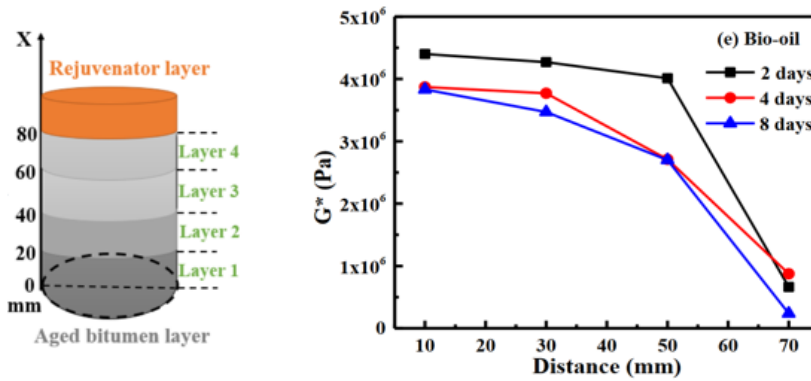
Predicted Diffusion Coefficient D based on MD simulation



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



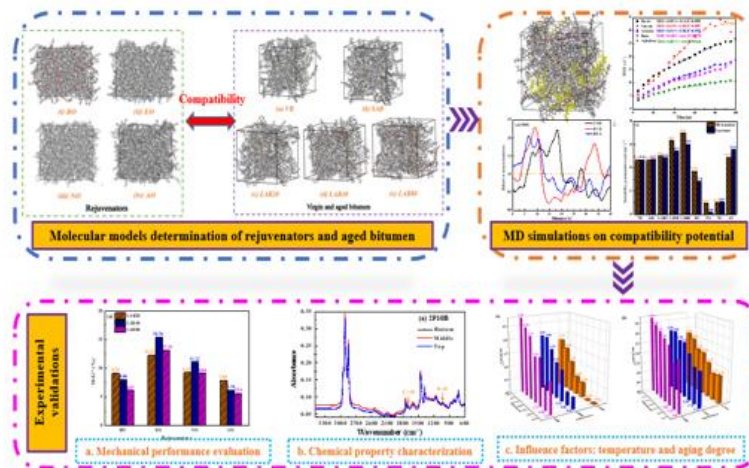
STEP 3: DIFFUSION BETWEEN BITUMEN AND REJUVENATOR
 EXPERIMENT VALIDATION OF DIFFUSION COEFFICIENT



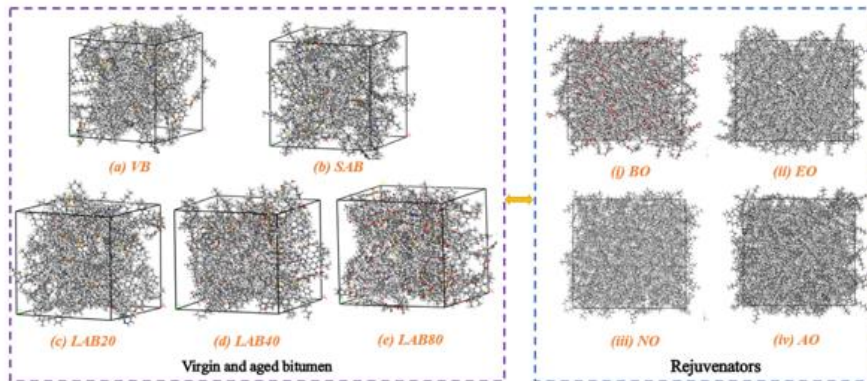
Measured Diffusion Coefficient based on Experiment



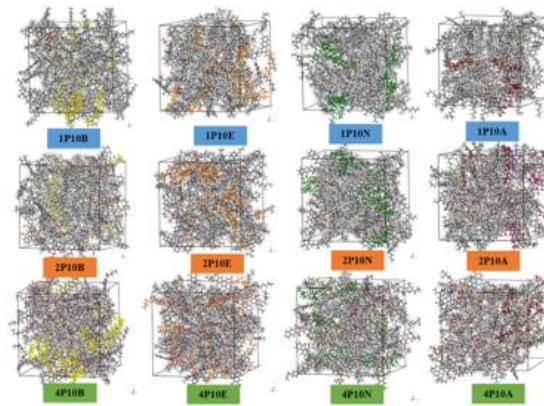
STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR



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



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



Molecule Model of Rejuvenated Bitumen



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

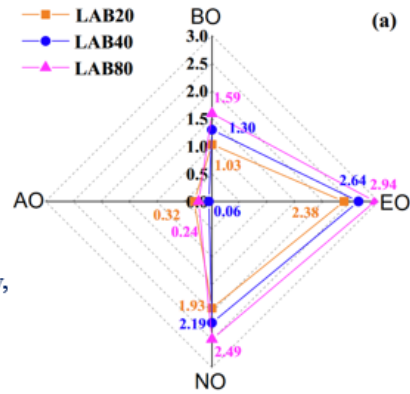
Total cohesive energy density

$$CED = \frac{E_{coh}}{V} = \frac{E_{vdw} + E_{ele}}{V}$$

Solubility parameter

$$\delta = \sqrt{CED} = \sqrt{\delta_{vdw}^2 + \delta_{ele}^2}$$

Lower $\Delta\delta$ indicates better compatibility,
 Less risk in segregation.



The solubility parameter difference $\Delta\delta$ between rejuvenators and aged binders

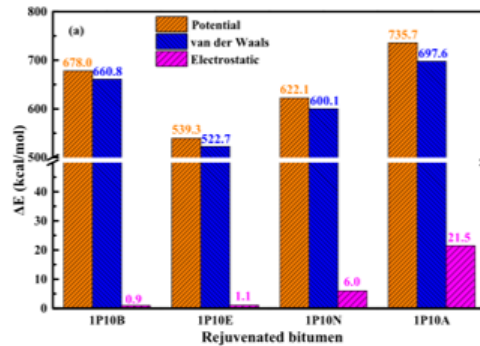


STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR
 SIMULATION OF COMPATIBILITY BETWEEN BITUMEN AND REJ

Intermolecular binding energy

$$E_{binding} = -E_{inter} = -(E_{total} - E_B - E_R)$$

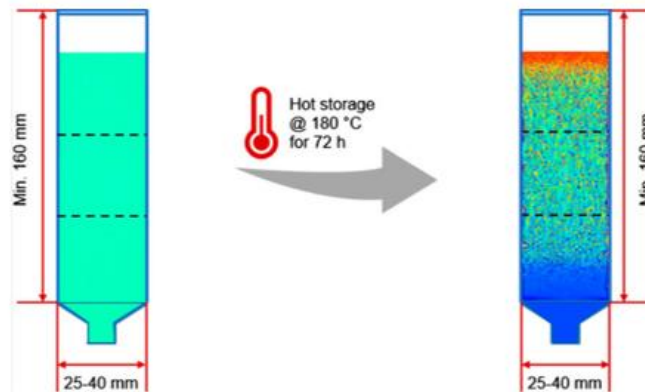
Higher $E_{binding}$ indicates better compatibility,
 Less risk in segregation.



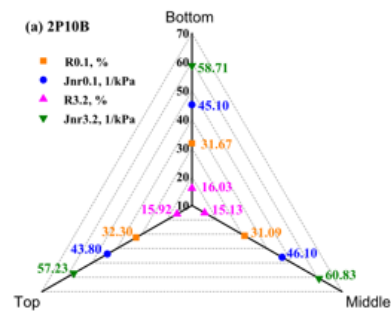
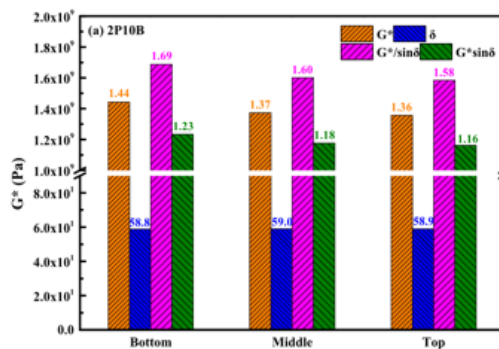
Binding energy $E_{binding}$ values of various rejuvenated bitumen



STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR
EXPERIMENT VALIDATION OF COMPATIBILITY



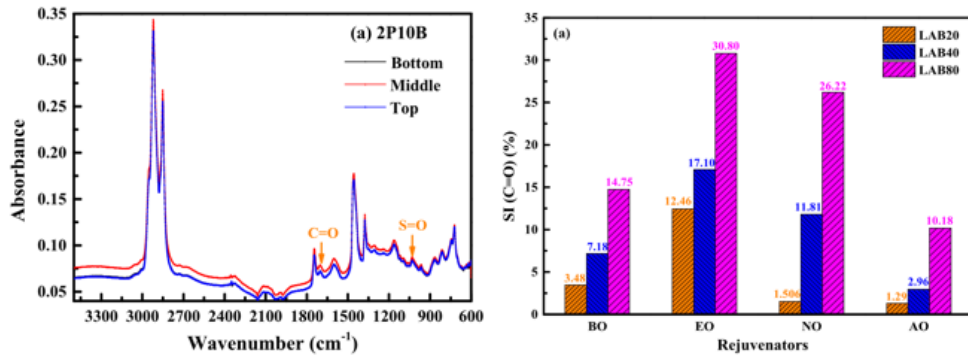
STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR
EXPERIMENT VALIDATION OF COMPATIBILITY



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



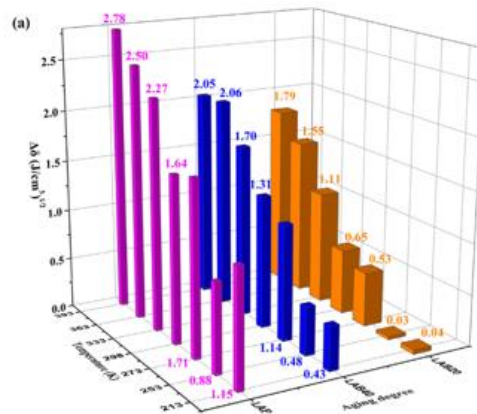
STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR
 EXPERIMENT VALIDATION OF COMPATIBILITY



Characterize the compatibility of rejuvenated bitumen based difference in functional group.
 It was found that there is a good correlation between experiment and simulation results.



STEP 4: COMPATIBILITY BETWEEN BITUMEN AND REJUVENATOR
 COMPATIBILITY PREDICTION BASED ON MD SIMULATION

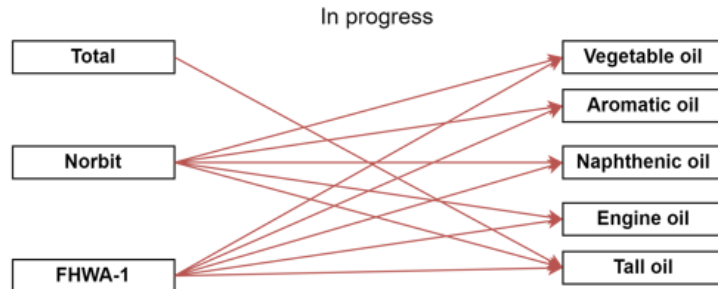


MD Simulation predict $\Delta\epsilon$, which is difficult to be characterized with experiment.



> FUTURE WORK

ESTABLISH METHODOLOGY FOR ENGINEERING APPLICATION



- Reflect the influence of bitumen and rejuvenator change on the rejuvenation mechanism and efficiency.
- Improve the MD methodology in evaluation and engineering application.



> CONCLUSIONS

- MD simulation methodology is established based on relatively **accurate bitumen** and **rejuvenator molecular model**.
- The MD simulation can predict diffusion and compatibility parameters, which are **consistent with experimental results**.
- The MD simulation methodology can partly **decrease the experiment amount** which were traditionally applied for **rejuvenator evaluation**.
- MD simulation enhances the understanding of **rejuvenation mechanism** at the molecular level. (i.e. AO and Bo can penetrate into the asphaltene cluster, while EO and NO is mostly dispersed in the aromatic/resin and saturate phase.)





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.



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- ✓ Cold Mix
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155 years of experience

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\$114,6 billion in annual revenue

Our commitments

Safe
We relentlessly work to improve the safety of our people. Reduction in injuries per 200,000 hours worked over 15 years.



Responsible
We strive to strengthen the communities where we live and work.

\$115 million
Total charitable contributions last year across 56 countries

3.2 million 10 million
Attendance at our farmer trainings for sustainable agricultural practices totaled 880,000 last year

Sustainable

- Agriculture is how we will protect the planet and our shared future.
- Climate change: Reducing supply chain emissions per ton of product 30% by 2030, and absolute operational emissions 10% by 2025
- Water resources: Achieving sustainable water management in all priority watersheds by 2030
- Land use: Eliminating deforestation in our supply chains by 2030

Glass Transition, DSC, and Asphalt

- Glass transition occurs when upon cooling, the molecular structure of amorphous material is locked into a rigid and brittle arrangement.
- There is a long history of analyzing asphalt binder via thermal analysis and glass transition.
- Tools have come along way since some earlier studies.
 - Differential Scanning Calorimeters (DSC) have been leading tool for T_g determination
 - Modulated DSC has made a significant improvement in the ability to discretize clearer transitions.
- SHRP research in the 90s, and years of research by WRI in following years has shown that asphalt T_g is the sum of multiple glass transitions.

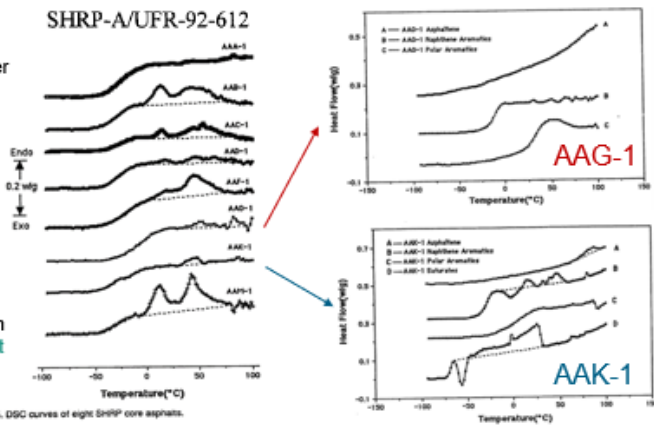
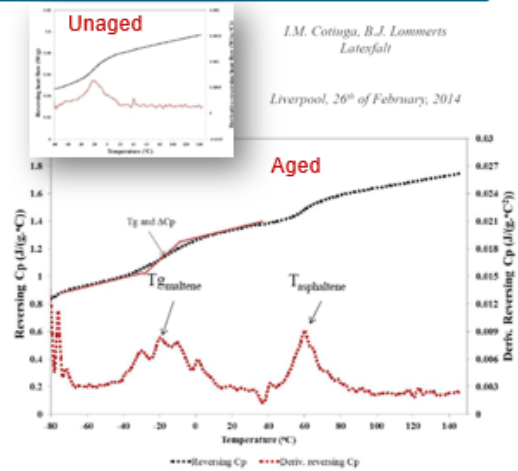
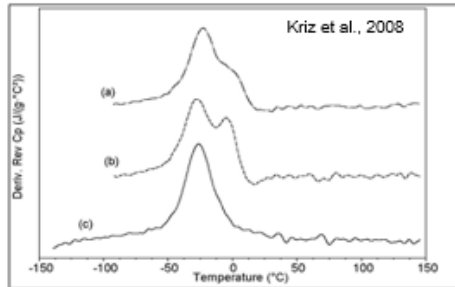


Figure 5. DSC curves of eight SHRP core asphalts.

T_g and the Impact of Aging

- Analysis of modulated T_g curves in prior studies has shown that additional T_gs form as a result of oxidative and physical aging.
- Kriz et al. (2008) showed differences in derivative peaks based on binder source and perceived compatibility.



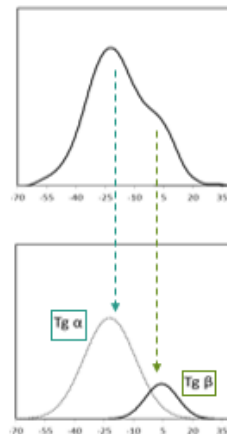
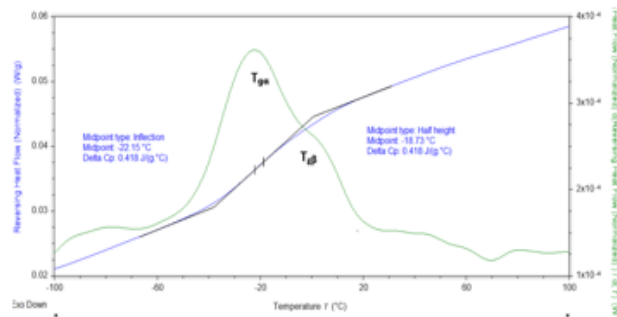
*I.M. Cotugno, B.J. Lammerts
Latexfall*

Liverpool, 26th of February, 2014

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Summing it Up: DSC, T_g, and Miscibility/Compatibility

- Miscible blends show a single combined T_g. The more clearly defined T_gs, the less miscible.
- The Derivative of DSC heat flow (dH/dT) or heat capacity is often used to detect underlying T_gs.
- Quantification of the impact of various factors on formation of multiple T_gs remains a gap.
 - Deconvoluting the derivative of DSC response is a great way to analyze miscibility!

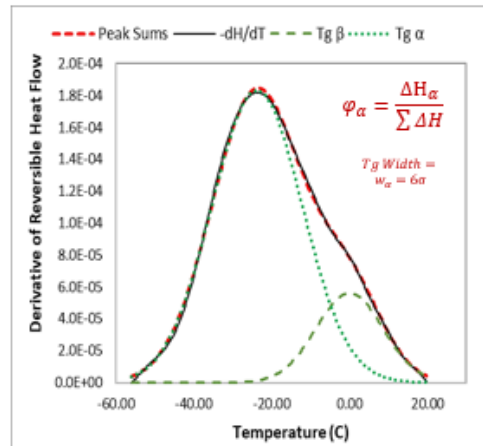
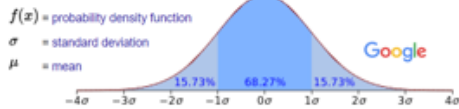


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T_g Deconvolution Method in this Study

- A **Gaussian (Normal) distribution** was assumed to describe the T_g derivative.
- The number of underlying T_gs visually defined.
 - Typically, 2 or 3 main overlapping T_gs
- Minimization of sum of squared errors used to fit distributions to experimental curve.
 - Indices can be defined based on results.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

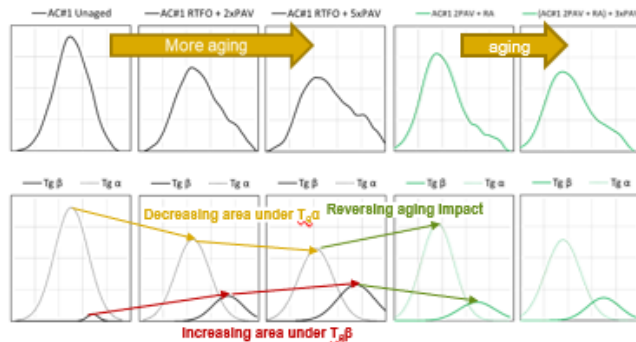


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dH/dT: AC#1 Progression of Aging ... and Rejuvenation

- **Bitumen aging increases intensity of secondary T_gs** (e.g. T_gβ)
 - Increased area fraction of T_gβ (and decreases % area of T_gα)
 - Broadens overall transition width as multiple T_gs become more resolved
- **Proper rejuvenation reverses these trends.**

Properties	AC#1	AC#2
Penetration (dmm)	51	46
Softening Point (°C)	50.9	54.5
Performance Grade (PG)	PG 64-22	PG 64-16
Continuous PG	PG 66-25	PG 68-20
ΔT _c at 20hrs PAV Aging (°C)	-0.2	-4.7
ΔT _c at 40hrs PAV Aging (°C)	-4.5	-8.6



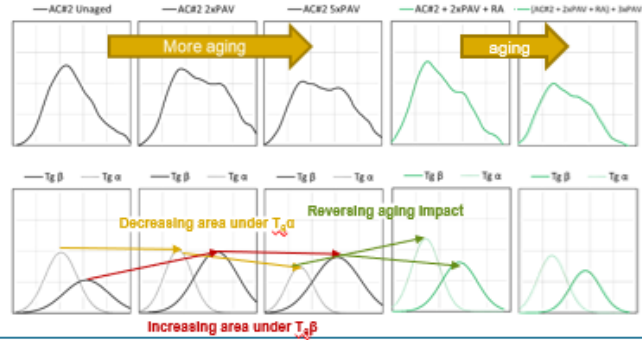
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dH/dT : AC#2 Progression of Aging ...and Rejuvenation

- Bitumen aging increases intensity of secondary T_g 's (e.g. $T_{g\beta}$)
 - Increased area fraction of $T_{g\beta}$ (and decreases % area of $T_{g\alpha}$)
 - Broadens overall transition width as multiple T_g 's become more resolved
- Proper rejuvenation reverses these trends.

Properties	AC#1	AC#2
Penetration (dmm)	51	46
Softening Point (°C)	50.9	54.5
Performance Grade (PG)	PG 64-22	PG 64-16
Continuous PG	PG 66-25	PG 68-20
ΔT_c at 20hrs PAV Aging (°C)	-0.2	-4.7
ΔT_c at 40hrs PAV Aging (°C)	-4.5	-8.6



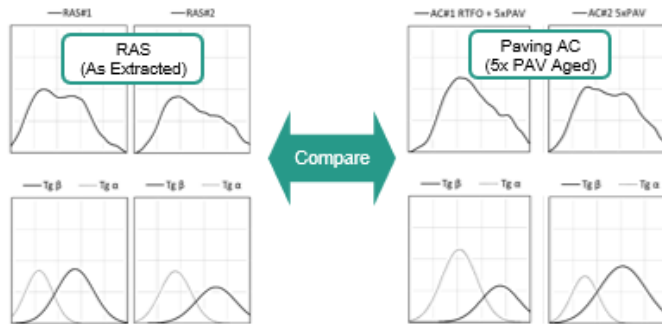
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dH/dT : RAS Glass Transition Analysis...

- Bitumen aging increases intensity of secondary T_g 's (e.g. $T_{g\beta}$)
 - Increased area fraction of $T_{g\beta}$ (and decreases % area of $T_{g\alpha}$)
 - Broadens overall transition width as multiple T_g 's become more resolved

Properties	RAS#1	RAS#2
Penetration (dmm)	7	5
Softening Point (°C)	116.7	134
Performance Grade (PG)	PG130+20	PG 148+26
Continuous PG	PG135+15	PG153+23
ΔT_c at 20hrs PAV Aging (°C)	-36.4	-47.8
ΔT_c at 40hrs PAV Aging (°C)	N/A	N/A

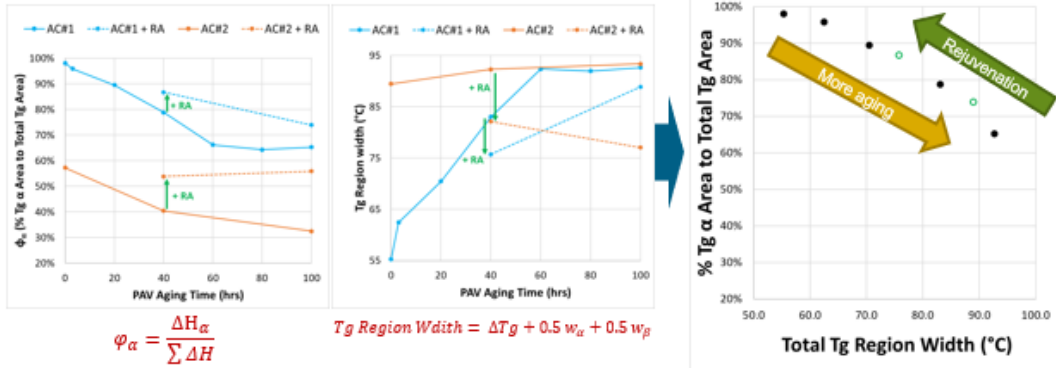


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What to Do with all of this?

Potential exists to create criteria for aging and rejuvenation impact.



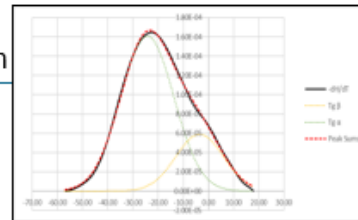
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Other Examples

Neat Bitumen

- The DSC Deconvolution method seems to provide some discrimination power when modifying bitumen with different additives.

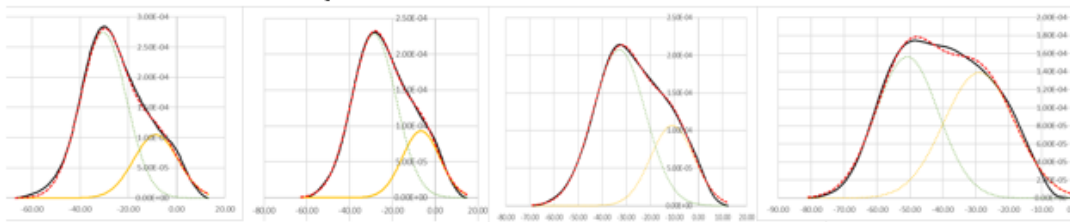


+ Aromatic Distillate

+ Bio-based (Veg) Rejuvenator

+ Paraffinic Distillate

+ REOB

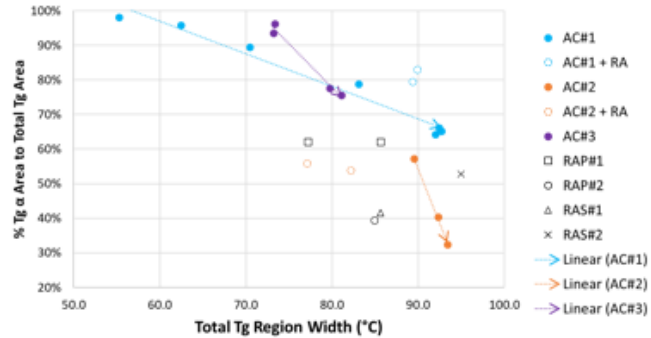


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Conclusions and Next Steps

- Degree of bitumen phase compatibility can be observed through DSC T_g analysis.
- Potential exists to create criteria for aging and rejuvenation impact.
- Method can be used as analytical verification for rheological and performance indices believed to be related to bitumen compatibility.
- Further studies underway to create such relationships and practical compatibility test specifications:



Project in Progress: AN INNOVATIVE PRACTICAL APPROACH TO ASSESSING BITUMEN COMPATIBILITY AS A MEANS OF MATERIAL SPECIFICATION

- PI: University of New Hampshire (Prof. Eshan Dave), Co-PI: Cargill

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Questions?



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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 Kumbargerri, Joe Rovani

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

WesternResearch
INSTITUTE

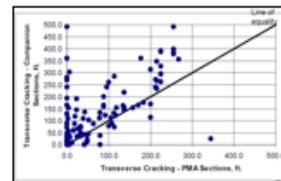
1

WesternResearch
INSTITUTE

Context - "360" Industry Changes

□ Drivers: economics, geopolitics, societal, regulatory

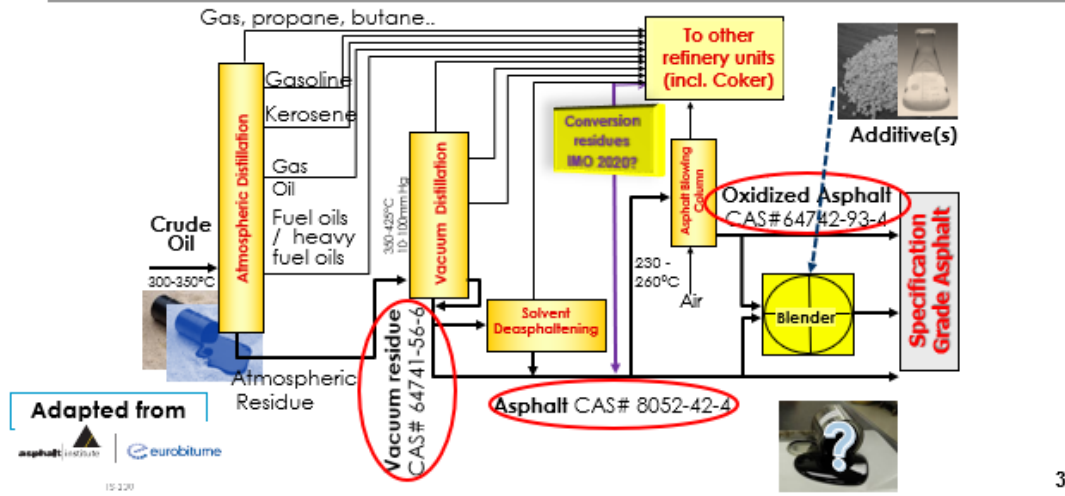
- Changes in crude oils & processes
- World of additives & modifiers
 - New chemistries, more biomass origins...
- Changes to product specifications
 - Asphalts and heavy fuels (IMO 2020)
- Market changes
 - WMA, RAP, RAS, PMA, GTR, Plastics...
- Environmental footprint of asphalts
 - EPD's, LCA, LCCA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



Base Asphalt vs. PMA performance, Von Quintus et al, 2005

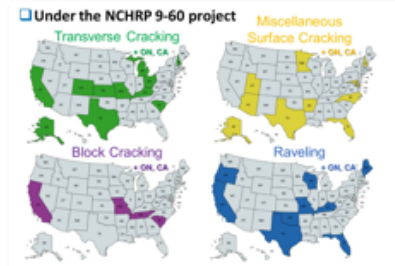
2

Asphalt/Bitumen production process (US/Europe)



Consequences of the Changes

- ❑ Unconventional binders not captured by Superpave specs
 - PG specs and test methods, from the 90's for asphalts from the 90's, not for today's and tomorrow's binders
- ❖ Binder quality impacts pavement performance
 - Note: mix design / construction... too!



	Inception-
❖ Tools and knowledge (with FHWA)	2007-
❖ “Fingerprint” project : Proof of concept – Initial Trials (with Eurovia)	2013-
❖ Validation – Industrial Perspective (Asphalt Industry Research Consortium #1)	2015-
❖ Proposed Specifications & Formulation Guidelines (NCHRP 9-60 – Agencies’ Perspective)	2016-
❖ Further Validation & Applications (AIRC #2)	2018-
❖ Proposed Specifications Framework validation (NCHRP 9-60)	2022-
❖ Evolutions: PMA/ Recycling /Alternative binders (AIRC #3)	
❖ Others...	

5

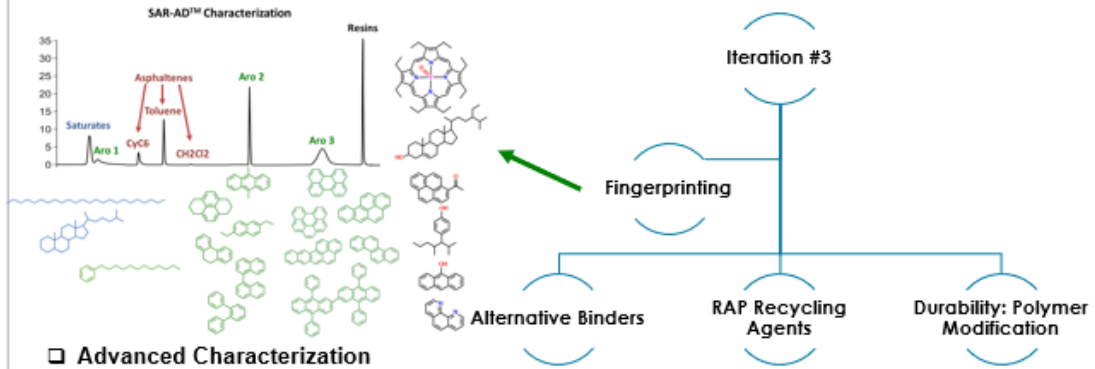
- ❑ Launched in 2016
- ❑ 2 iterations successfully completed, currently 3rd iteration beginning
- ❑ **Partners worldwide:** Road administrations, Contractors, Additive and Asphalt suppliers
- ❑ **More partners welcome to join!**



>100+ asphalt binders included in the matrix (from worldwide sources)!!

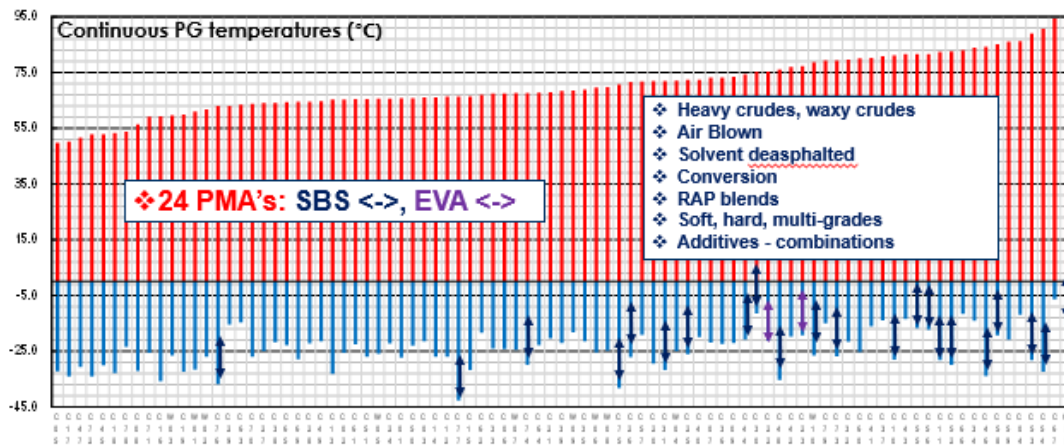
6

- Started out as fingerprinting (iteration -1)
- Now beginning iteration-3



- Advanced Characterization

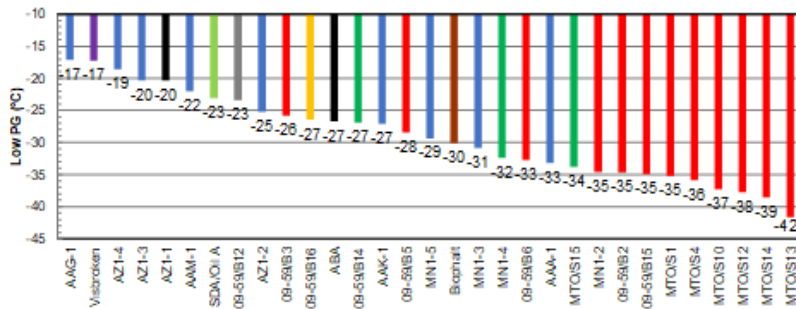
Exp: Binder Matrix, 100+ Binders



AIRC Binder Matrix - Performance Grade Mapping (°C)

Low PG Ranking after PAV20h-Aging from BBR (31 binders, here)

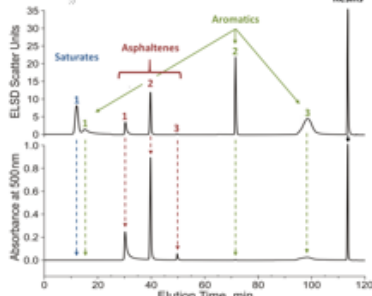
- Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken



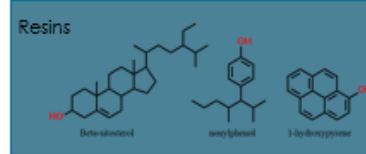
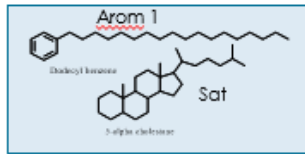
(Elwardany, Planche, and King, C&BM 2020)

	AIRC	9-60
Elemental Analysis	✓	
Saturates, Aromatics, Resins, and Asphaltene Determinator (SAR-AD™)	✓	✓
Waxphaltene Determinator (WD™)	✓	✓
Infrared Spectroscopy (FT-IR)	✓	✓
Size Exclusion Chromatography/Gel Permeation Chromatography (SEC/GPC)	✓	
Differential Scanning Calorimetry Results (DSC)	✓	✓
SuperPave Performance Grade	✓	✓
Black Space Diagram	✓	✓
Rheological LVE Parameters (ΔT_c & GR)	✓	✓
Multiple Stress Creep and Recovery Test (MSCR)	✓	✓
Asphalt Binder Cracking Device	✓	✓
Machine Learning/Regression	✓	✓

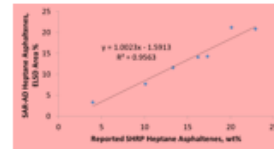
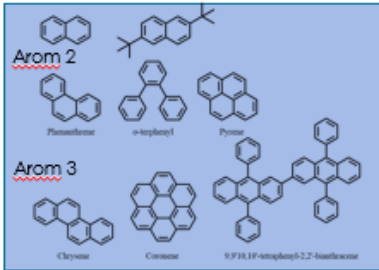
Chromatography + solubility separations to unlock the continuum



WRI, WY, 2011, SAR-AD™
Boysen, Schabron, Rovani

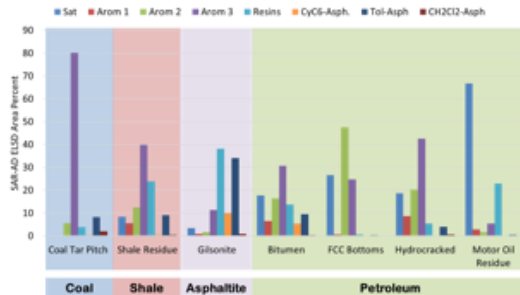


From saturated to highly aromatic and polar asphaltene molecules

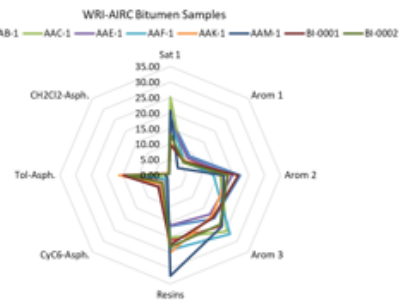


Differentiation of hydrocarbons

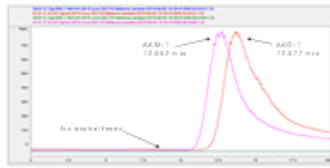
HC from various origins / processes



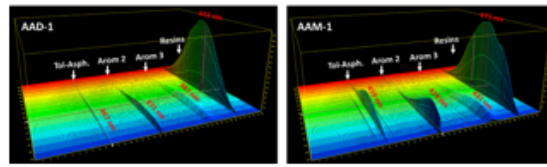
Bitumens



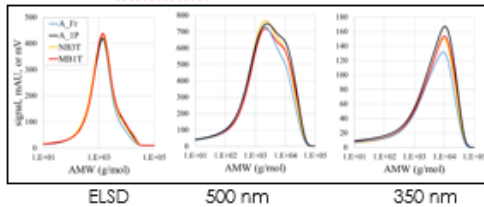
SAR-AD 2G with multiple detectors to unlock the chemistry and associations



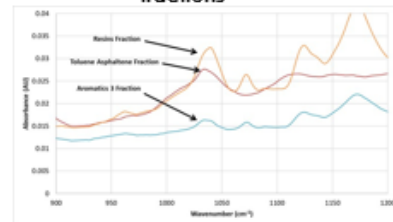
SEC of maltenes of AAG-1 and AAM-1.



Fluorescence Spectroscopy of AAD-1 and AAM-1 fractions



SEC with ELSD and VWD at 500 nm and 350 nm for 4 bitumens before (A_FR) and after field aging (A_1P, NB3T and MB1T) – ISAP 2022, *Siroma et al*

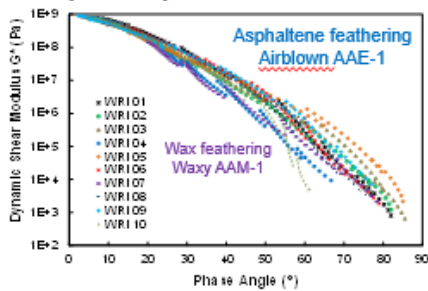


FTIR of fractions after aging showing the sulfoxide region

13

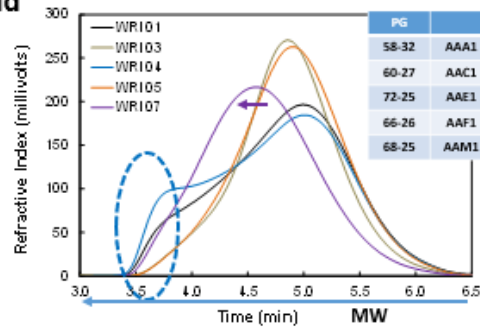
Asphalt structure and properties

Complex asphalts from the real world



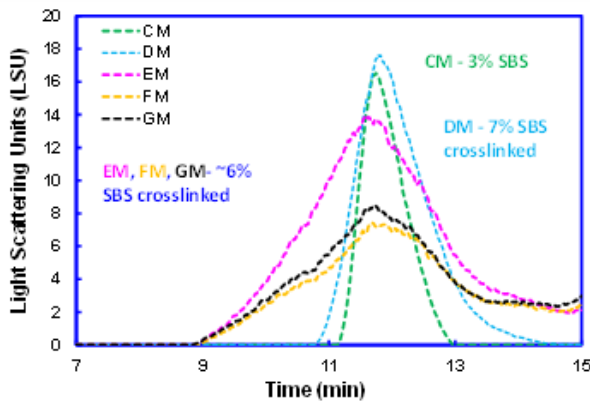
- ❖ Rheologically complex
- ❖ SAR-AD CII from 0.26 to 0.6

- “Gel” structures
- Phase transitions

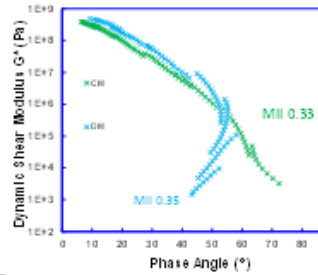
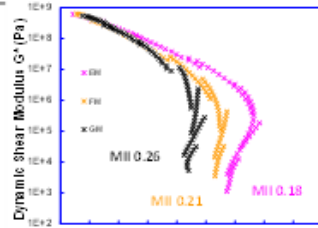


- ❖ Airblown asphaltene association
- ❖ High molecular weight maltenes

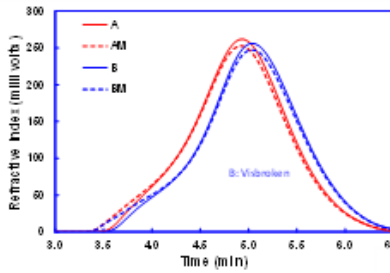
14



$$\text{Maltene Instability Index (MII)} = \frac{\text{Saturates} + \text{Aromatics 1}}{\text{Aromatics 2} + \text{Aromatics 3} + \text{Resins}}$$

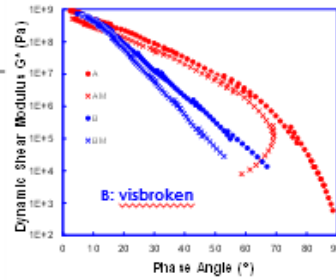


15



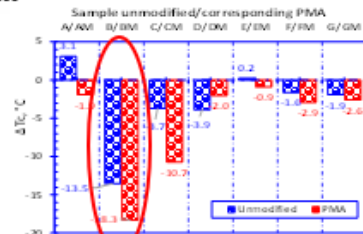
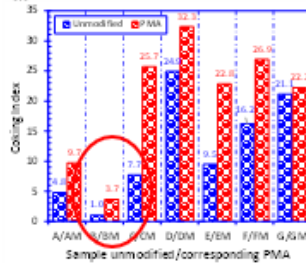
A look at visbroken binders

$$\text{Coking Index} = \frac{\text{Least polar asphaltenes}}{\text{Most polar asphaltenes}}$$



Coking Index - Index for asphaltene stability

- Higher is better
- Around 10 or higher- great!
- Around 4-5 - okay
- Around or less than 2 - BAD!

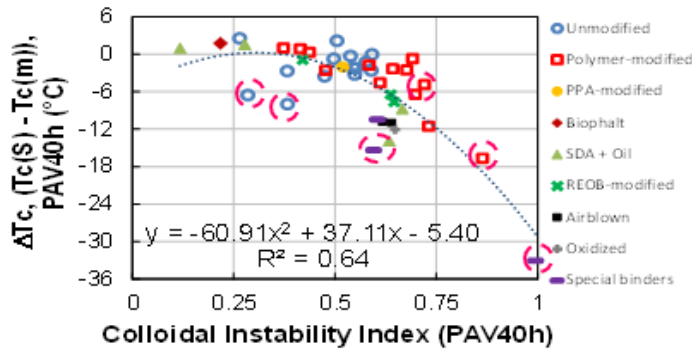


16

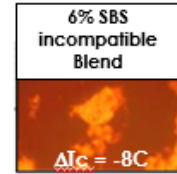
Correlations between ΔT_c (from BBR or DSR 4mm) and CII

Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Special binders

$$CII = \frac{Sat+Asph}{Arom+Res}$$



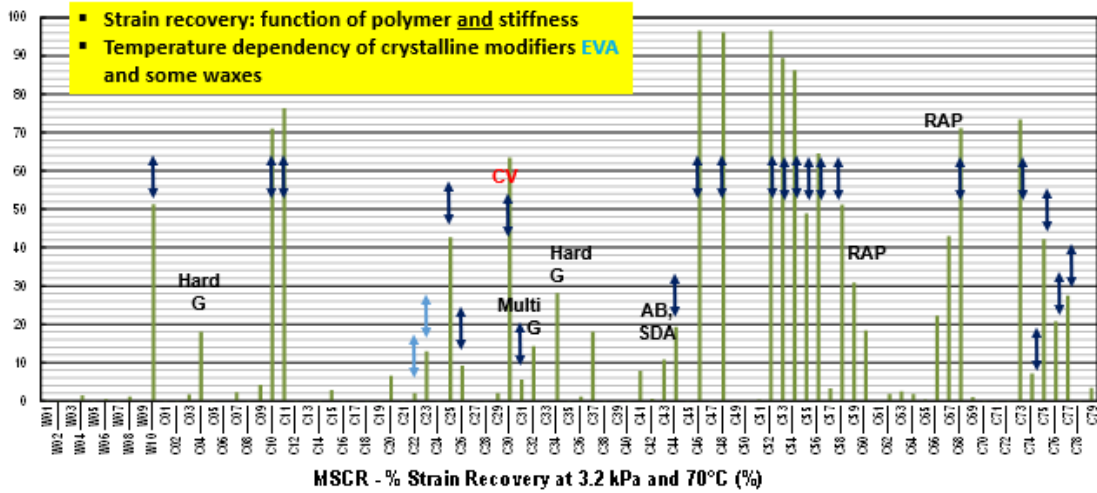
- Unconventional binders
- Waxy
 - Thermally converted
 - High asphaltenes
 - Incompatible PMA's



(Elwardany et al., C&BM 2020)

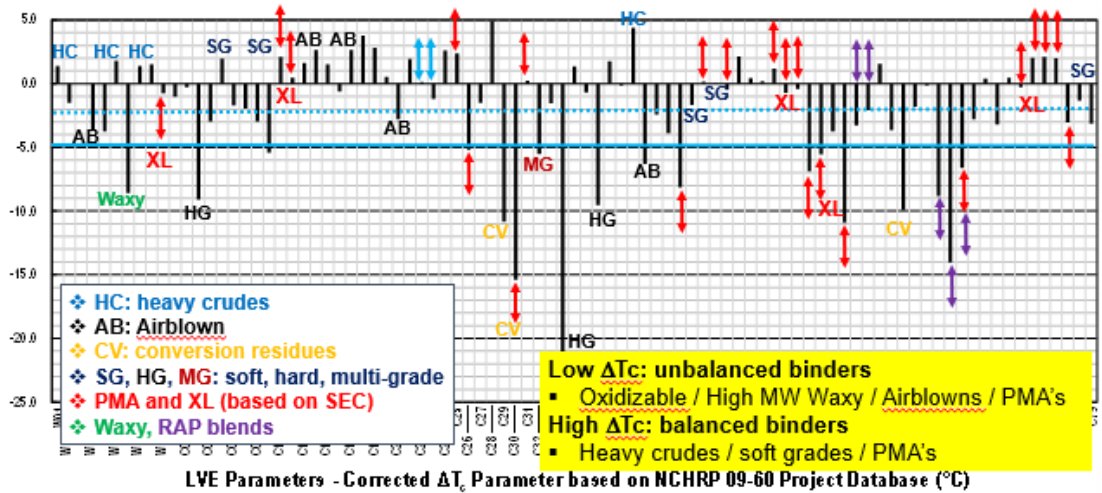
- VALIDATION
- Examples

MSCR, % Strain Recovery



19

Rheological Parameters, DSR ΔT_c



20

- Huge changes in asphalt binders since SHRP
- Most production/formulation have their own chemical, structural and mechanical features
- Specifications do not always capture performance
- Specification additives not always performance additives
- Quality inconsistency can lead to early field damage, storage issues...
- Compatibility and oxidation sensitivity are main issues
- Coping with changes needs right approach and tools
 - ❑ **Innovative Tools + Fingerprinting + Database + Machine learning = Guidelines**
- ❖ Useful to industry for research, smart formulation and control



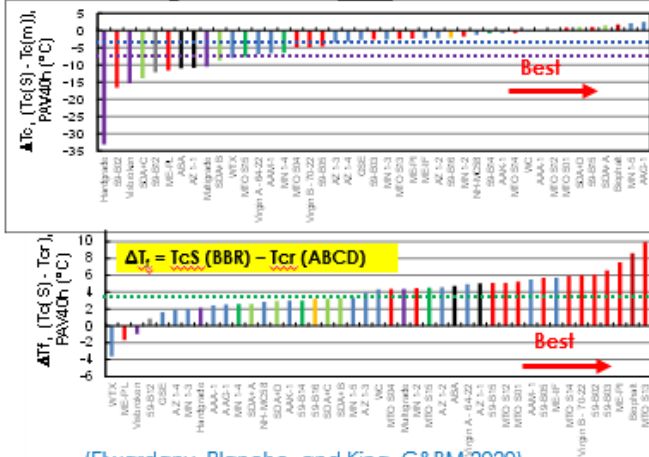
21

- ❑ **Alternative binders and modifiers are coming**
 - Thermo-reversible gelled systems - supramolecular systems
 - Aging retardant
 - Self healing
 - Packages of additives – like in the lubricant industry
 - 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
- ❑ **New approaches**
 - Failure (NCHRP 9-60 outcomes) and other properties
 - Machine learning to understand relationships
- **STAY TUNED!**

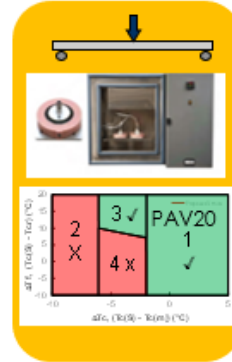
22

Ranking after PAV40h

> Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Special grades (Visbroken, Multi/Hard)



(Ewardany, Planche, and King, C&BM 2020)



60th Petersen Asphalt Research Conference Online/Onsite

**July 17-20, 2023
Laramie, Wyoming**

Thank You! - Questions?

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