

Dr. Ellie Fini, Ph.D., P.E., F. ASCE

- Associate Professor at Arizona State University
- Invention Ambassador of AAAS
- Fulbright Scholar of Aalborg University of Denmark
- Senior Sustainability Scientist at Global Institute of Sustainability and Innovation
- Director of the Innovation Network for Materials, Methods and Management

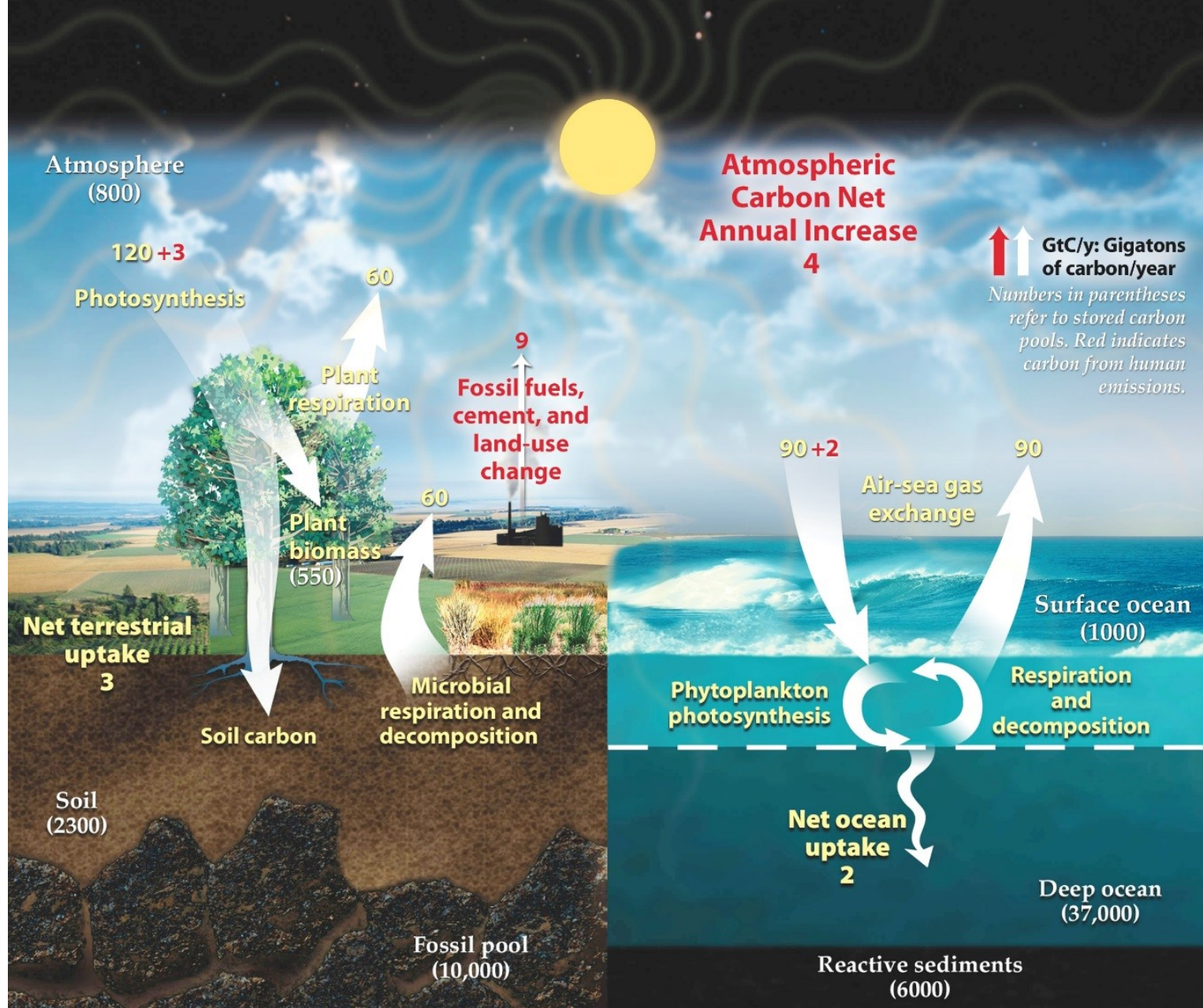
Arizona State University
E-Mail: efini@asu.edu
<https://isearch.asu.edu/profile/3333499>





Towards Carbon Negative Built Environment: The Use of Critical Aging Point in Asphalt Pavements

Ellie H. Fini, Ph.D., P.E. F.ASCE
Arizona State University



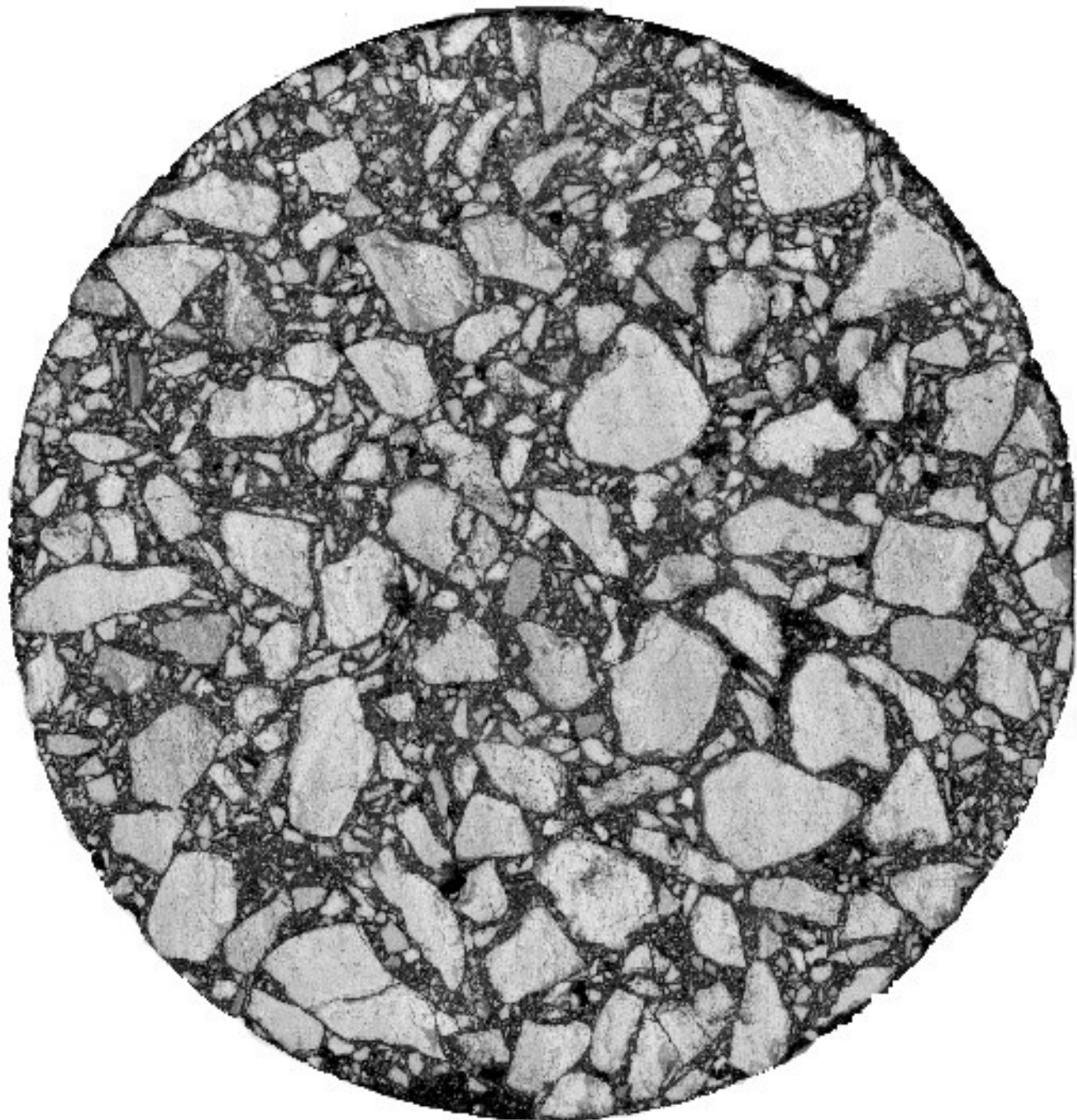
Carbon & Pavements!?

- **Energy usage** per lane mile of pavement typically ranges from 3-7TJ (equivalent to yearly energy consumption of **41 U.S. household**, 0.1 TJ/year/household)
- **CO₂ emissions** per lane mile of pavement construction is equivalent to yearly carbon emissions of **20 U.S. household**
- With more than 4million miles of roads in the US, pavements account for about 70% of state and local \$100B roadway expenditures¹

Sustainability in Roadway Construction

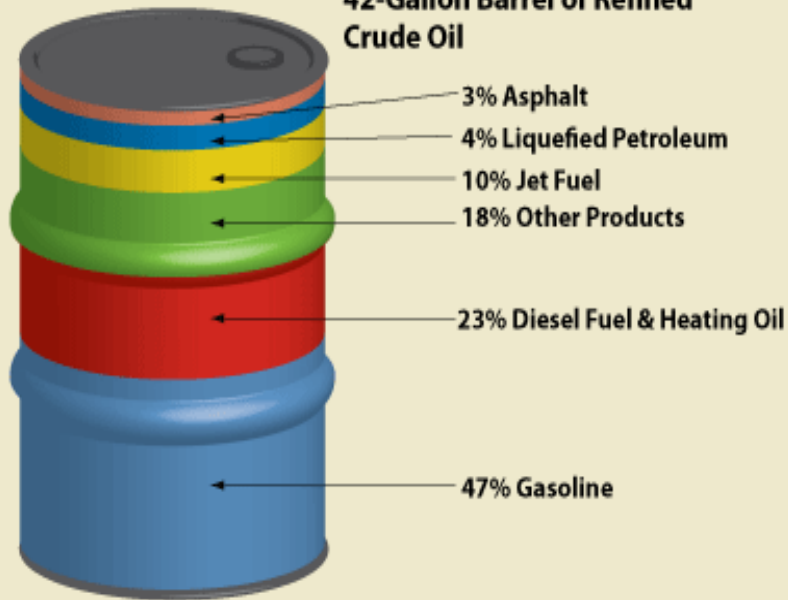
- Pavement Construction
 - Material Production
 - Construction Process
 - Transportation associated with construction
 - Maintenance

	Energy	CO ₂
Material Production	70	75
Construction	5	5
Transportation	20	10
Maintenance	5	10



Binder Source?

Products Made from a Barrel of Crude Oil



Source: U.S. Department of Energy.

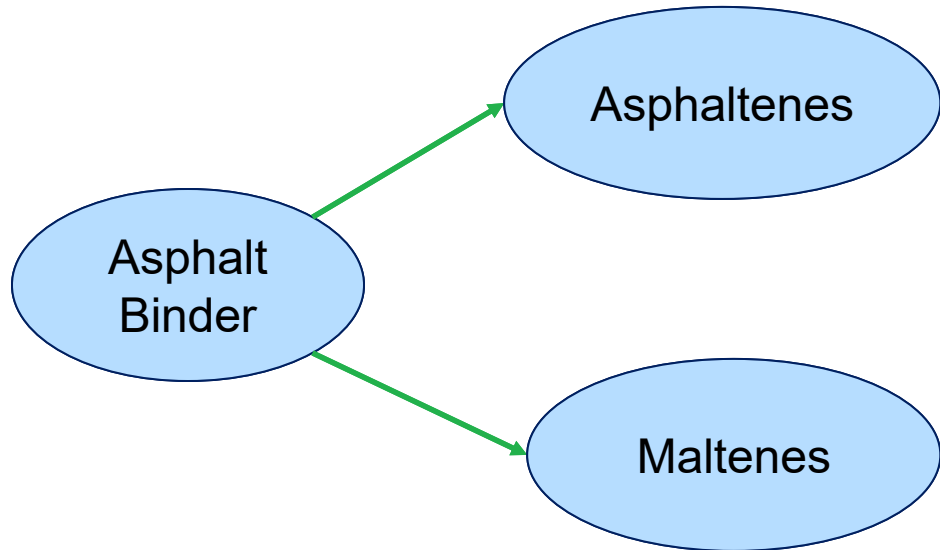


Basic properties of bio-binders*

Properties	CO	CS	MS	WP	WVO
Density (g/cm ³)	0.881	1.250	1.050	1.230	0.898
C (%)	77.80	61.6	65.77	61.05	77.30
H (%)	12.66	7.28	7.31	6.93	12.08
O (%)	9.46	30.16	26.25	31.81	10.50
N (%)	0.08	0.96	0.67	0.21	0.12
Saturates (%)*	20.95	6.8	6.22	3.46	0.00
Aromatics (%)*	0.00	3.73	8.56	2.93	87.19
Resins (%)*	78.17	67.49	60.47	76.21	12.80
Asphaltenes (%)*	0.87	21.96	24.47	17.38	0.00

*Zhou, T., F. Kabir, L. Cao, E. H. Fini, 2021, Journal of Resources, Conservation & Recycling, <https://doi.org/10.1016/j.resconrec.2021.105626>

Composition of Asphalt Binder



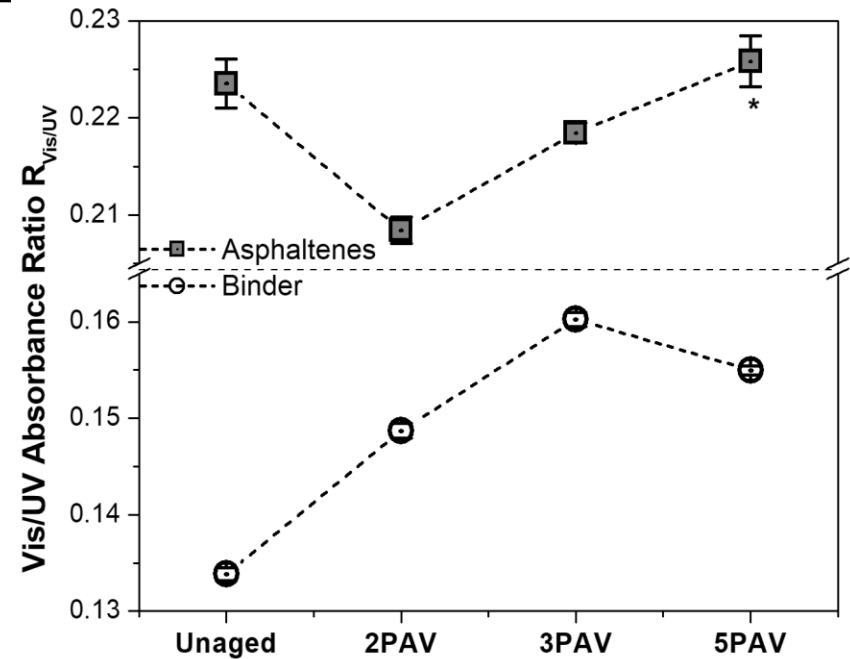
- Polar compounds (Resins)
- Aromatics (Naphthene aromatics)
- Saturated hydrocarbons

Polarity: **Asphaltenes >> Resins > Aromatics | Saturates**

Hung, A. and E. H. Fini, 2019, Absorption spectroscopy to determine the extent and mechanisms of aging in bitumen and asphaltenes, *Fuel* 242: 408-415

Asphalt Compounds Age Differently

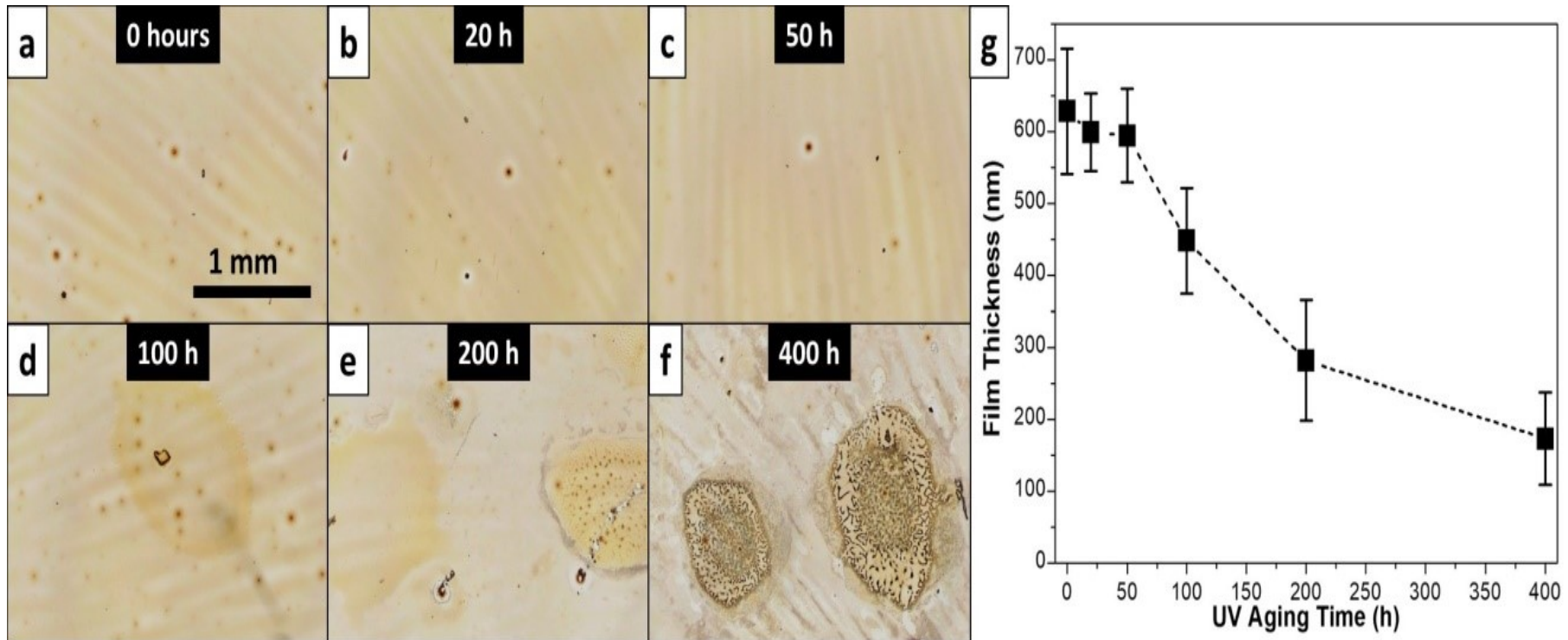
How asphalt binder constituents react with oxygen defines asphalt susceptibility to oxidation.



%	Unaged	2PAV	3PAV	5PAV
Saturates	12	10	10	2
Aromatics	19	17	36	7
Resins	50	45	23	62
Asphaltenes	19	28	30	29

Hung, A. and E. H. Fini, 2019, Absorption spectroscopy to determine the extent and mechanisms of aging in bitumen and asphaltenes, *Fuel* 242: 408-415.

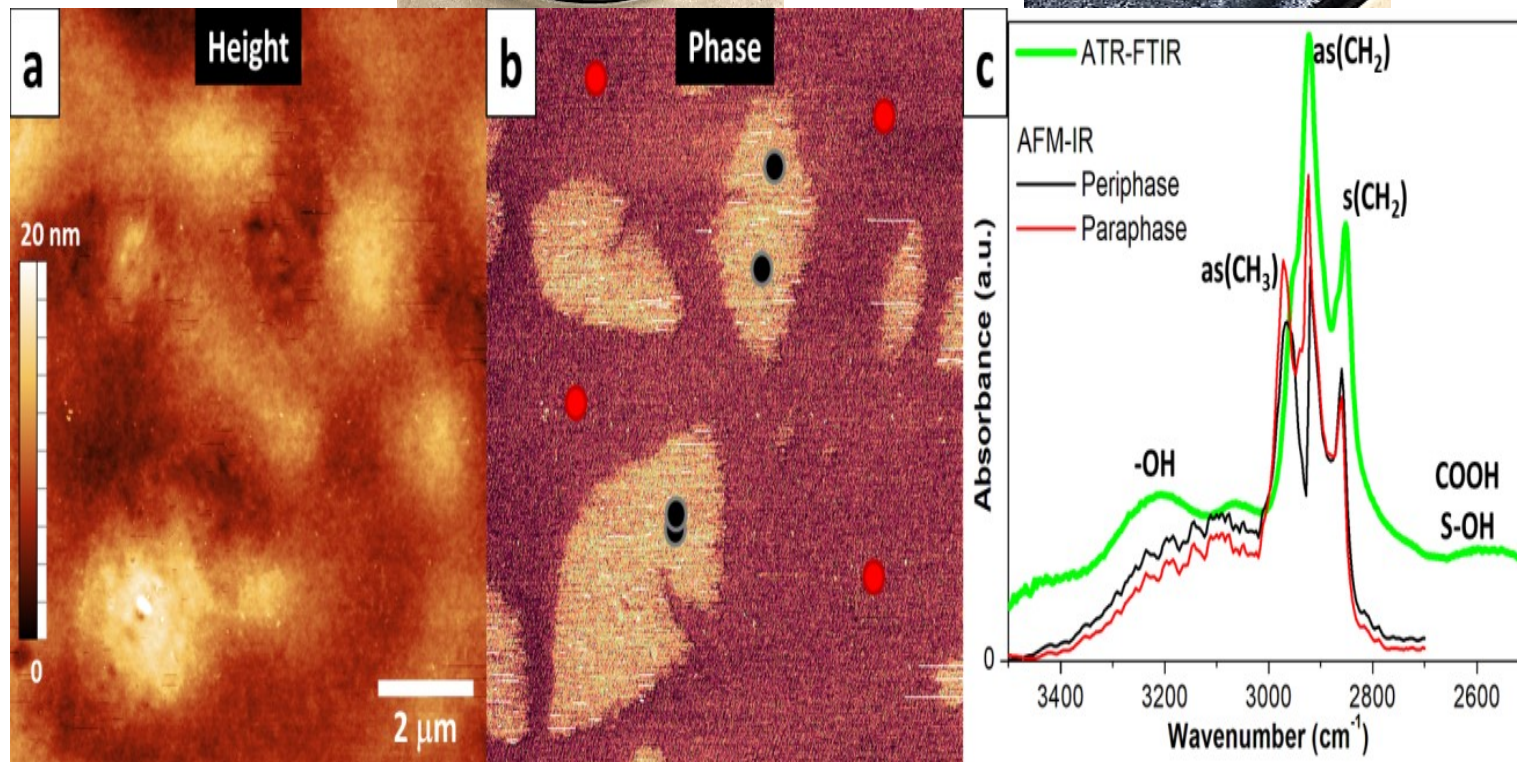
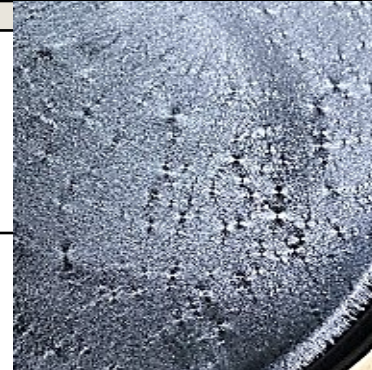
Asphalt Changes Due to Aging



Hung, A., and E. H. Fini, 2020, Surface Morphology and Chemical Mapping of UV-Aged Thin Films of Bitumen, *ACS Sustainable Chemistry & Engineering*, doi.org/10.1021/acssuschemeng.0c03877

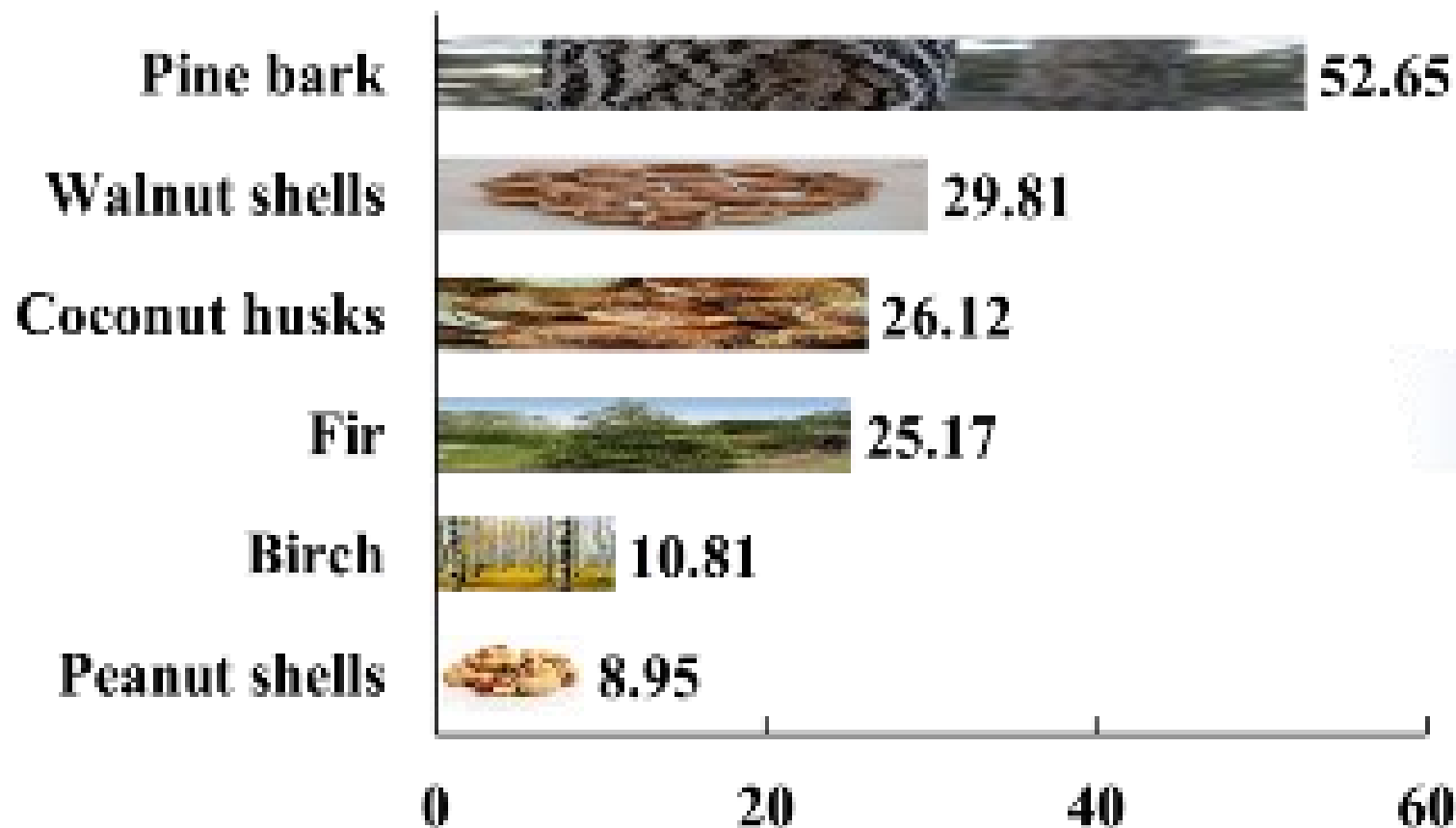


Solution 1: Delay Aging



Hung, A., and E. H. Fini, 2020, Surface Morphology and Chemical Mapping of UV-Aged Thin Films of Bitumen, ACS Sustainable Chemistry & Engineering, doi.org/10.1021/acssuschemeng.0c03877


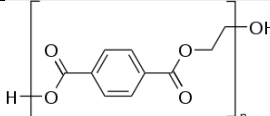

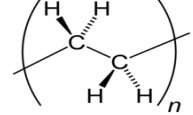

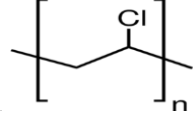

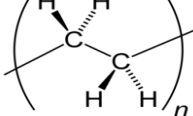

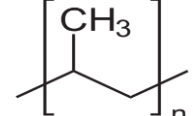

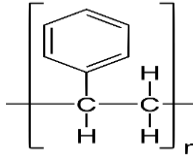

Phenol-rich Bio-oils from Various Sources



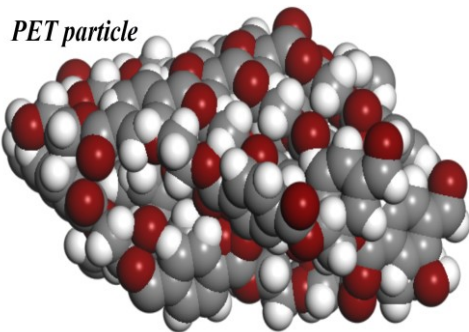
Park, K-B. J-S Kim, F. Pahlavan, E. Fini, 2022, Biomass Waste to Produce Phenolic Compounds as Antiaging Additives for Asphalt, ACS Sustainable Chem. Eng. 2022, 10, 12, 3892–3908, <https://doi.org/10.1021/acssuschemeng.1c07870>

Waste plastic: a carrier for bio-oil

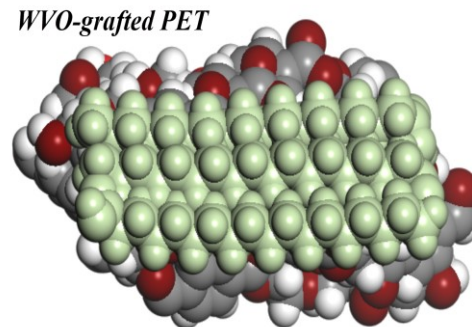
- Not all types of plastics are equally recyclable
- Polyethylene Terephthalate (PET) and High-density Polyethylene (HDPE) are the most widely used plastics.
- PET can undergo monomer recycling and mechanical recycling.

Polymer name Symbol	Chemical structure	Uses	Can be recycled
polyethylene terephthalate  PET		soda bottles, water bottles, medicine jars, and salad dressing bottles	yes
high-density polyethylene  HDPE		soap bottles, detergent, and bleach containers, and trash bags	yes
polyvinyl chloride  PVC		plumbing pipes, cables, and fencing	limited
low-density polyethylene  LDPE		cling wrap, sandwich bags, and grocery bags	limited
Polypropylene  PP		reusable food containers, prescription bottles, and bottle caps	limited
Polystyrene  PS		plastic utensils, packaging peanuts, and Styrofoam	no
other plastics (e.g., acrylic, polycarbonate, etc.)  Other	-	water cooler bottles, baby cups and fiberglass	no

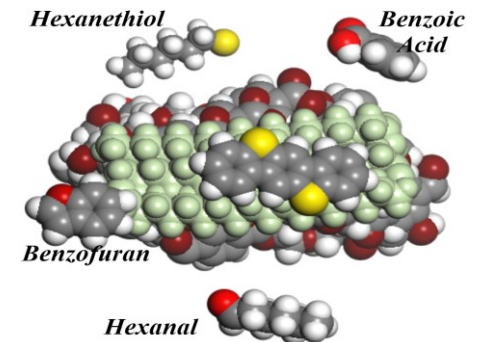
Delay Asphalt Aging with Bio-grafted PET



polyethylene terephthalate (PET) particle

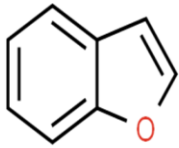


Binding of a molecular assembly of waste vegetable oil (WVO) on the PET surface (WVO-grafted PET)

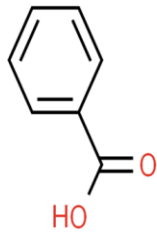


WVO-grafted PET surrounded by some volatile organic compounds.

Delay Asphalt Aging with Bio-grafted PET



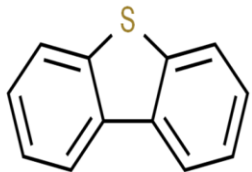
Benzofuran



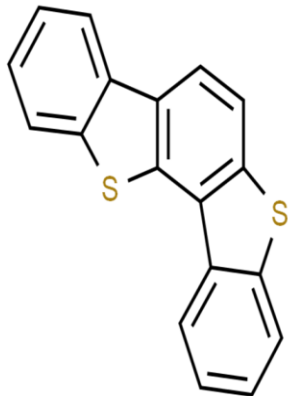
Benzoic acid



Hexanal



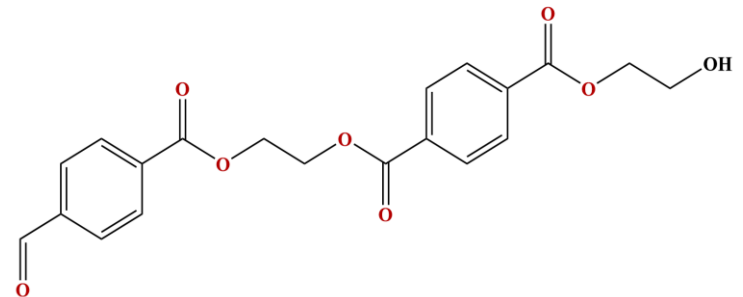
Dibenzo-thiophene



Benzo[1,2-b:4,5-b']bis[b]
benzothiophene



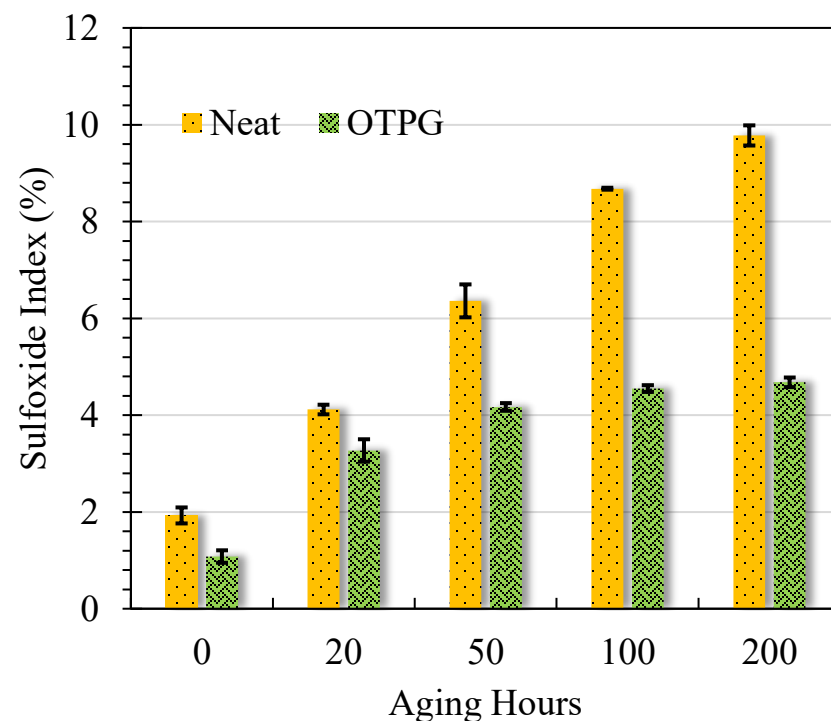
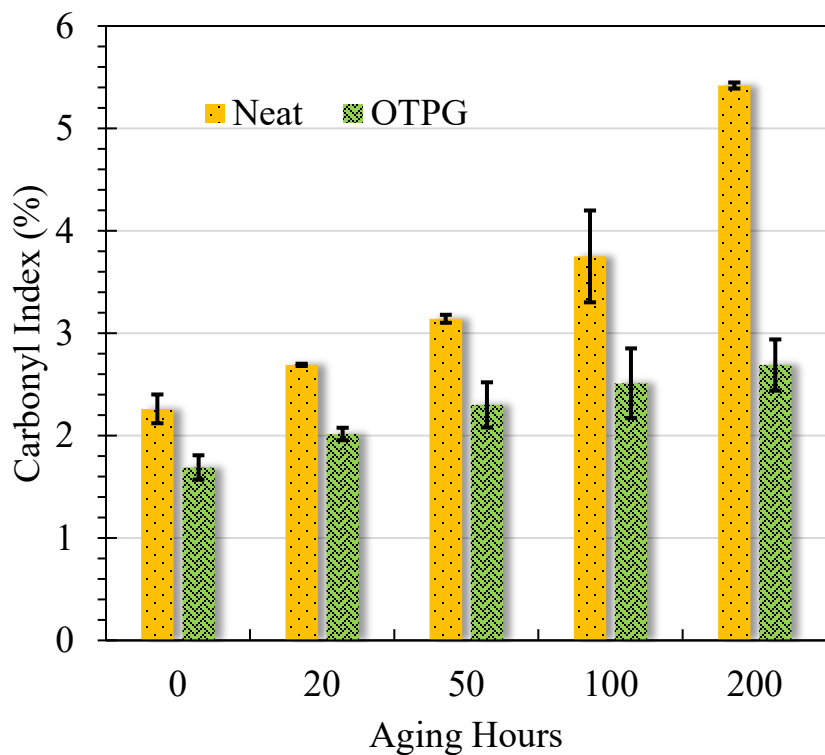
Hexanethiol



Molecular structure of a PET thermoplastic model containing two repeating units used in this study.

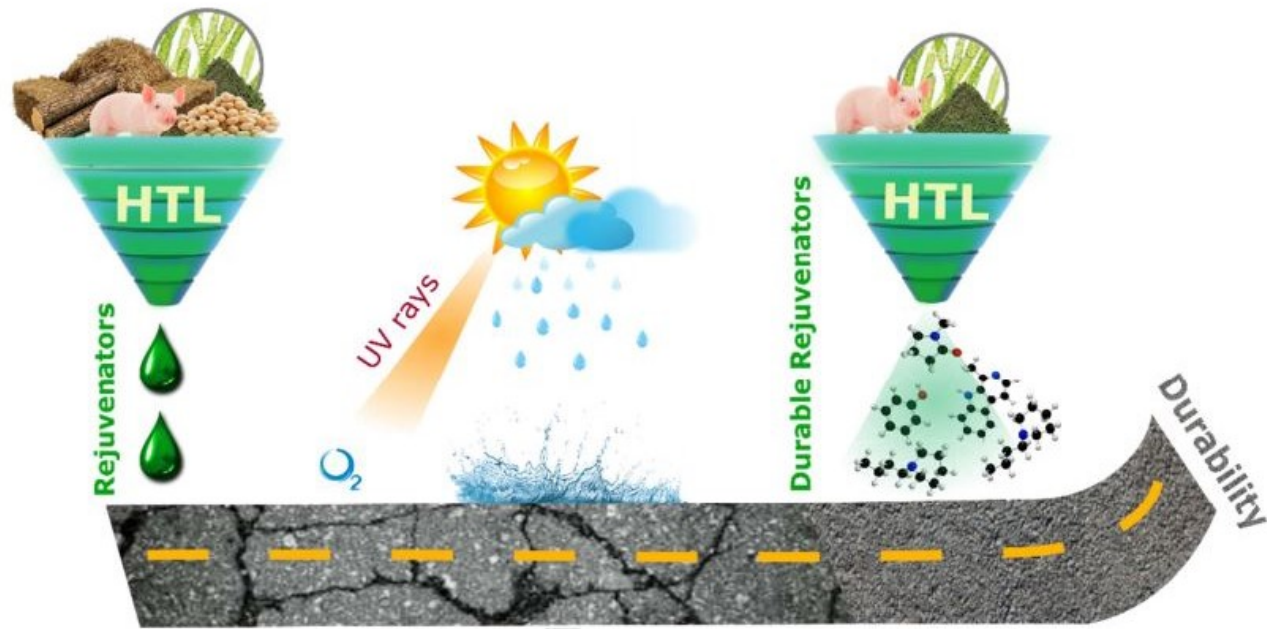
volatile compounds of bitumen

Bio-grafted PET granules delay aging



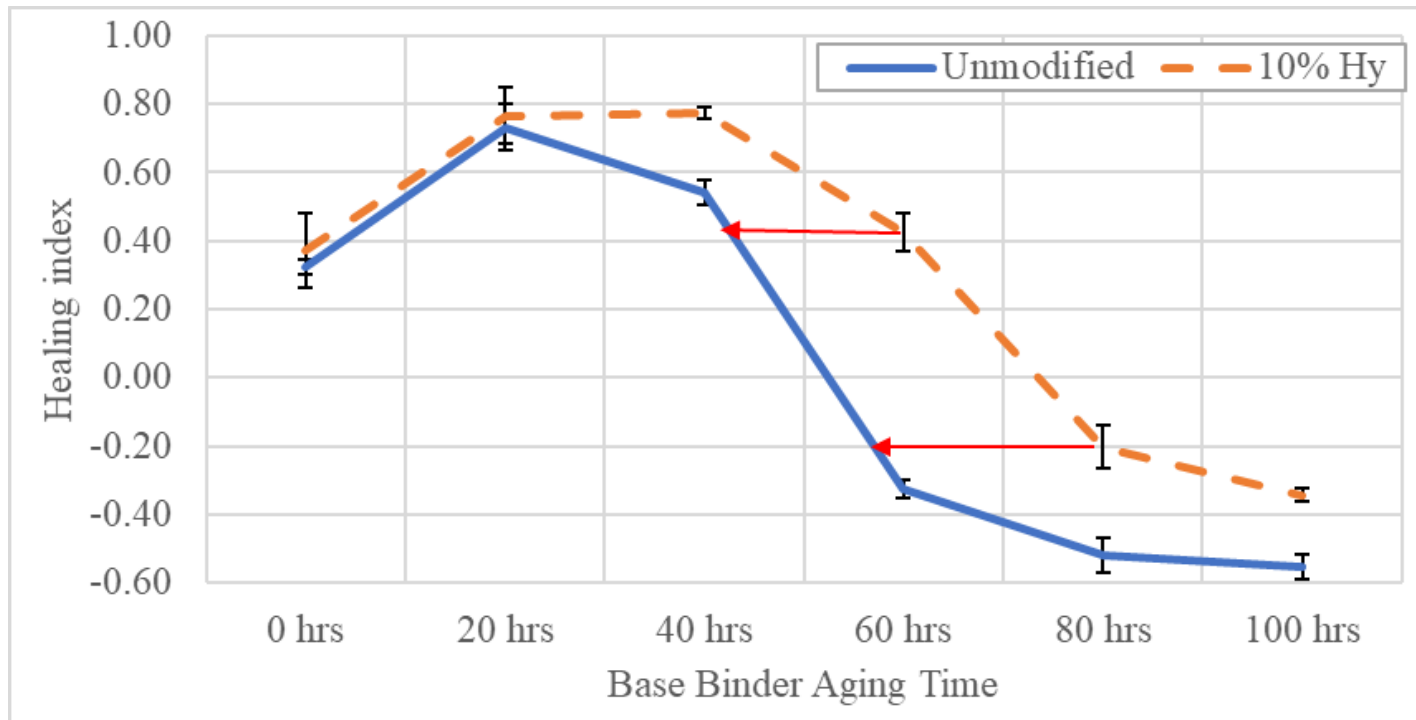
Mousavi, and E. H. Fini, 2021, Preventing Emission of Hazardous Organic Compounds from Bituminous Composites Using Functionalized Polyethylene-Terephthalate, *Journal of Cleaner Production*, <https://doi.org/10.1016/j.jclepro.2022.131067>

Solution 2: Rejuvenation



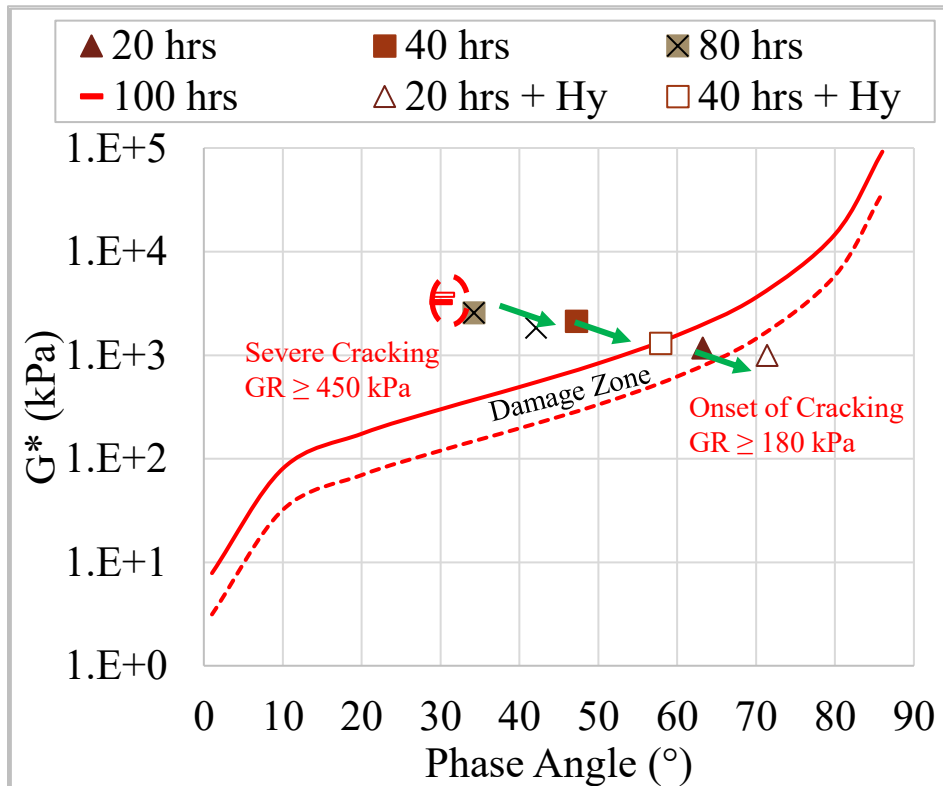
Why Do We Need Rejuvenator?

it enhances healing capacity ...

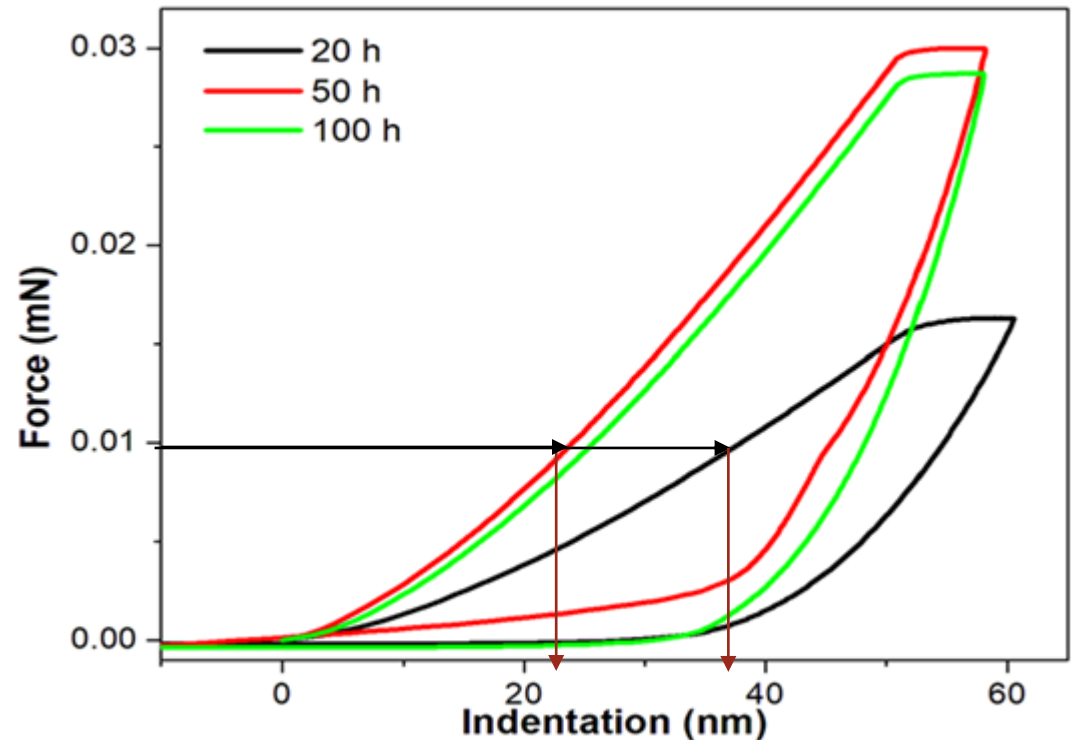


Why Do We Need Rejuvenator?

it enhances cracking resistance...

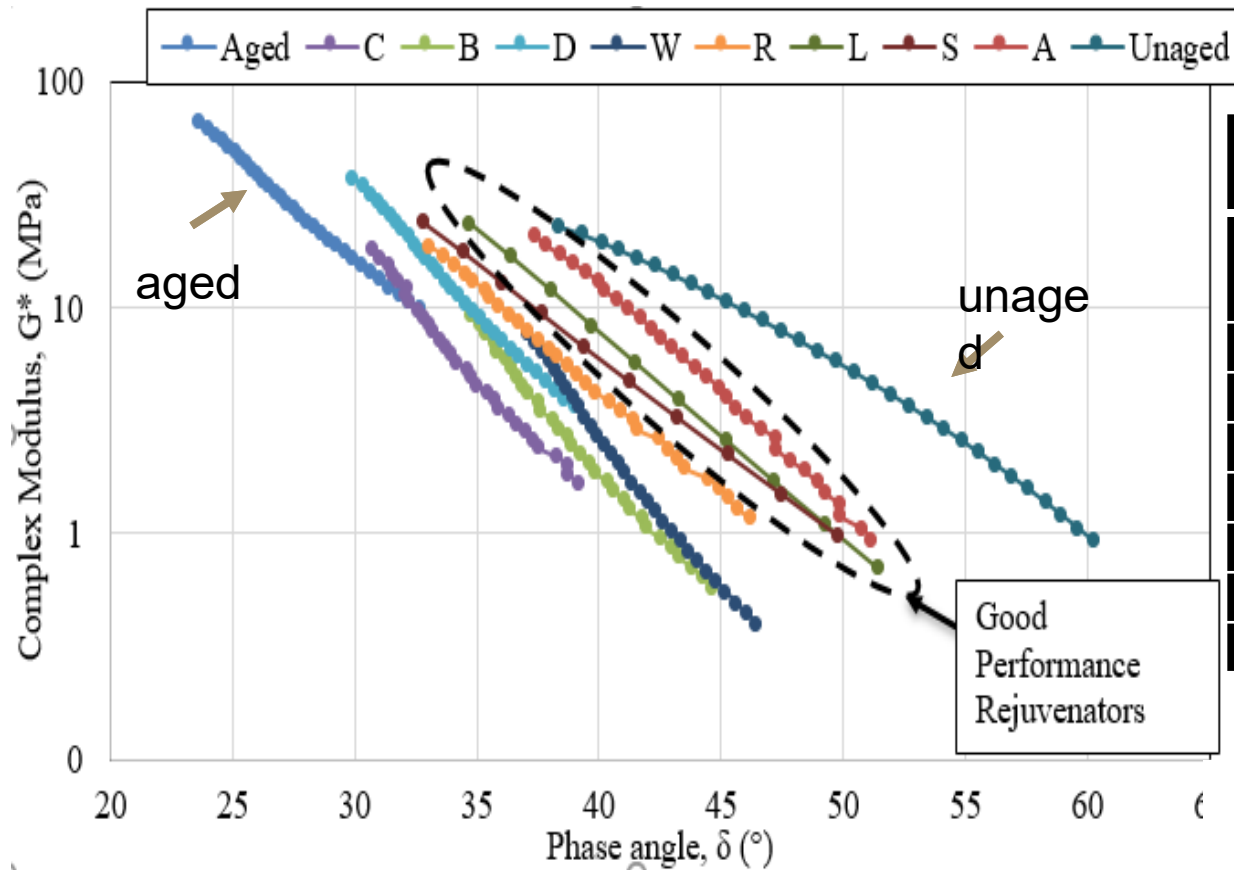


Aged Asphalts React Differently to Loading



Hung, A. M., M., Kazembeyki, Ch. G. Hoover, E. H. Fini, 2019, Evolution of Morphological and Nanomechanical Properties of Bitumen Thin Films as a Result of Compositional Changes Due to Ultraviolet Radiation, *ACS Sustainable Chemistry & Engineering*.

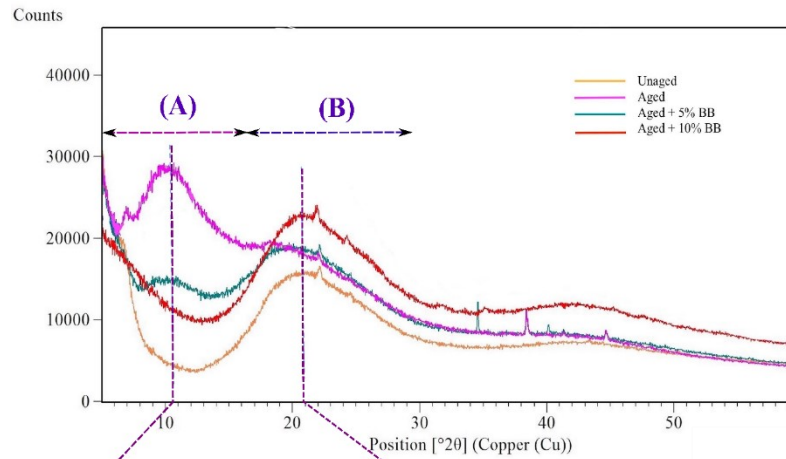
How do we know which rejuvenator is right?



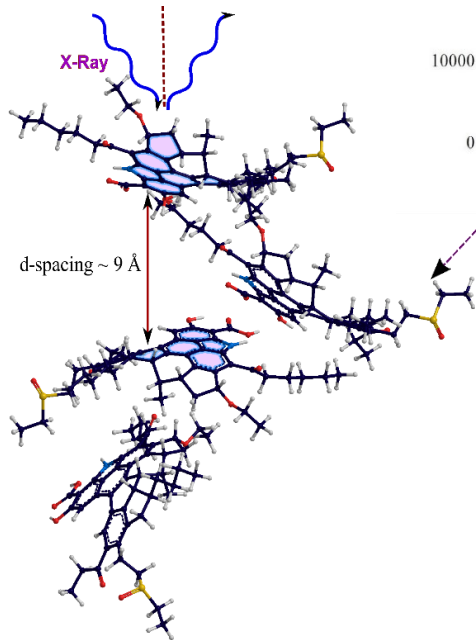
Rej	Source
A	plant extract (rosin, fatty acid, vegetable oil)
B	vegetable oil
C	soy-based oil
D	petroleum-based
W	waste vegetable oil
R	rubberwood oil
S	swine manure
L	algae

Schematic Representation of the Oxidized Agglomerates

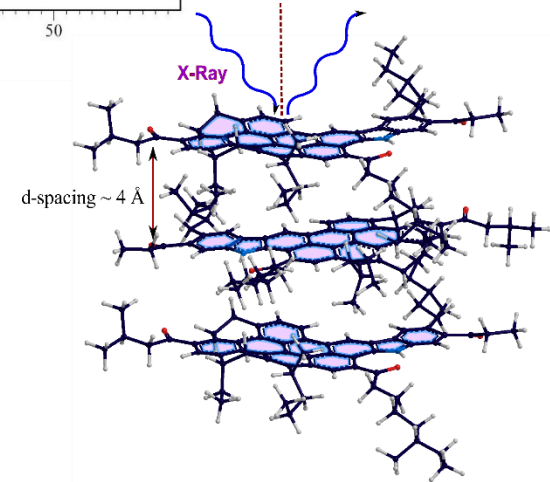
XRD Peaks



“GO-like Structuring”

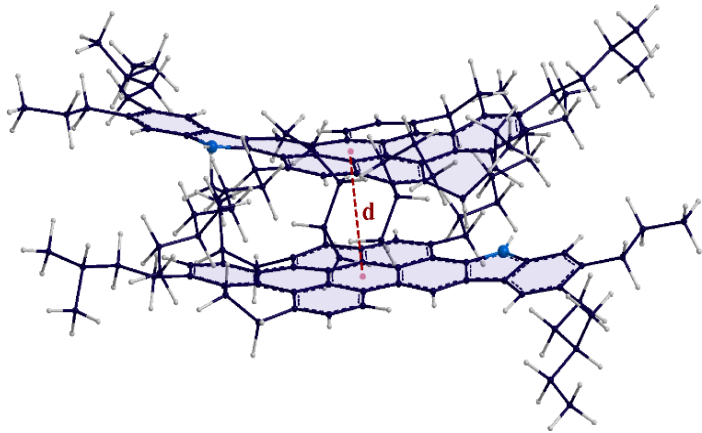


“Asphaltene Aggregation”



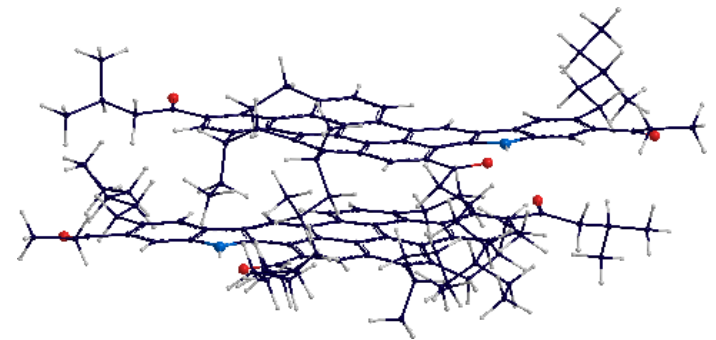
Aging Promotes Agglomeration of Asphaltenes

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Virgin Asphaltene Dimer

$$E_{\text{bind}} = -44.1 \text{ kcal/mol}$$
$$d_{\text{bind}} = 3.54 \text{ \AA}$$

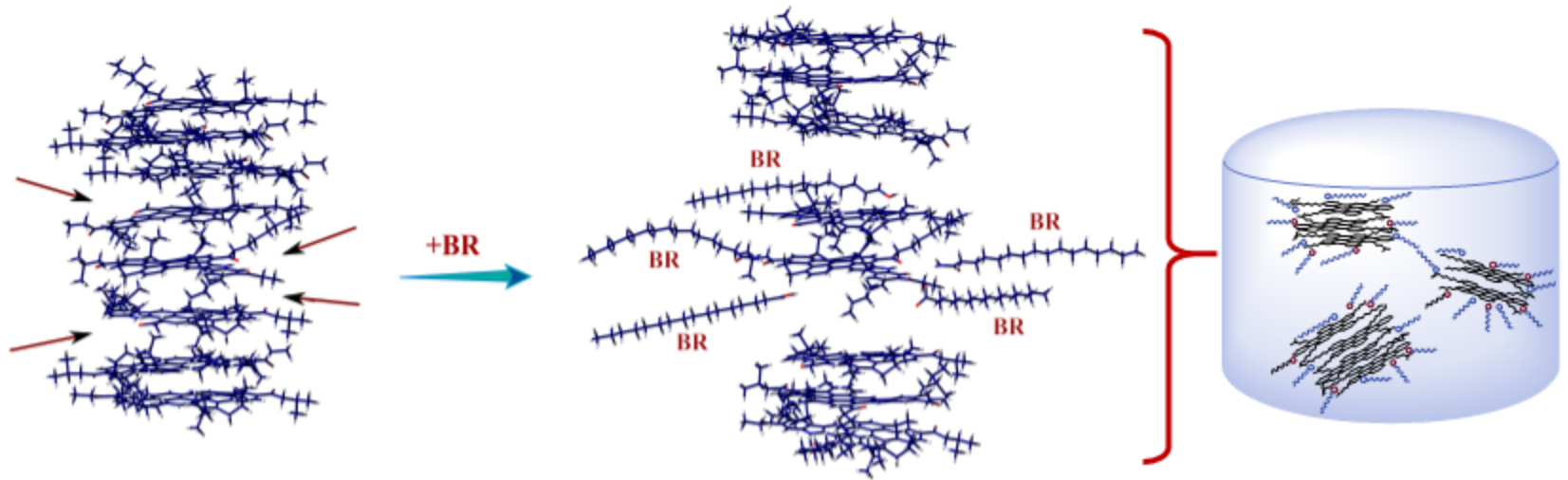


Oxidized Asphaltene Dimer

$$E_{\text{bind}} = -48.8 \text{ kcal/mol}$$
$$d_{\text{bind}} = 3.48 \text{ \AA}$$

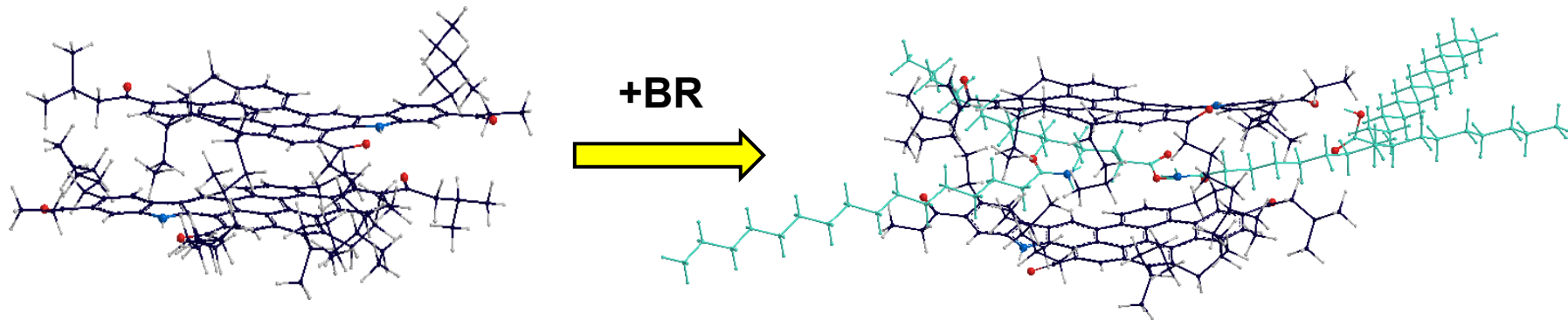
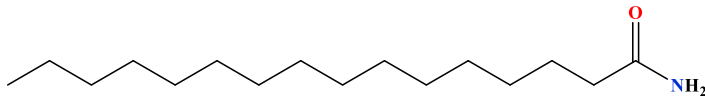
Solution 2: Rejuvenate Aged Asphalt

Schematic representation of BR action on the oxidized asphaltene agglomerates



Effect of Amides on Deagglomeration

Bio-Rejuvenator: hexadecanamide

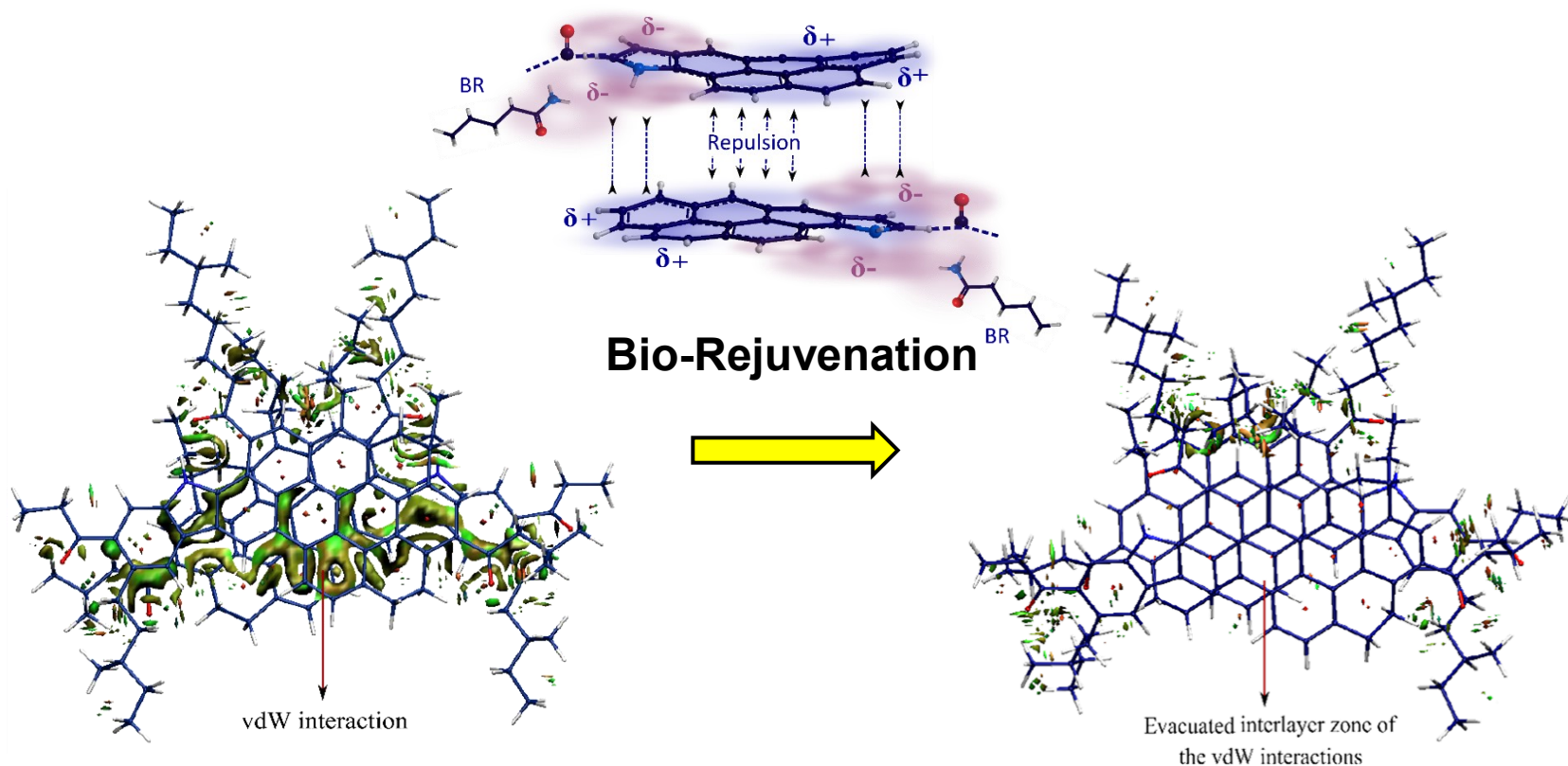


$$E_{\text{bind}} = -48.8 \text{ kcal/mol}$$
$$d_{\text{bind}} = 3.48 \text{ \AA}$$

$$E_{\text{bind}} = -15.0 \text{ kcal/mol}$$
$$d_{\text{bind}} = 7.17 \text{ \AA}$$

Effect of Amides on Deagglomeration

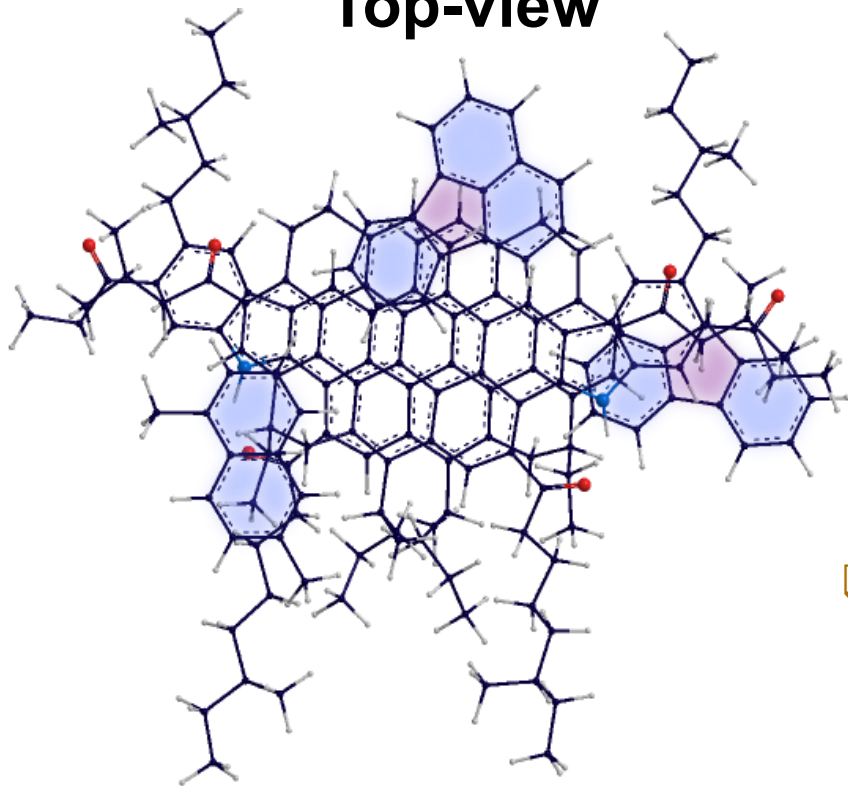
Electronic Perturbation Induced by hexadecanamide in Asphaltene Sheets



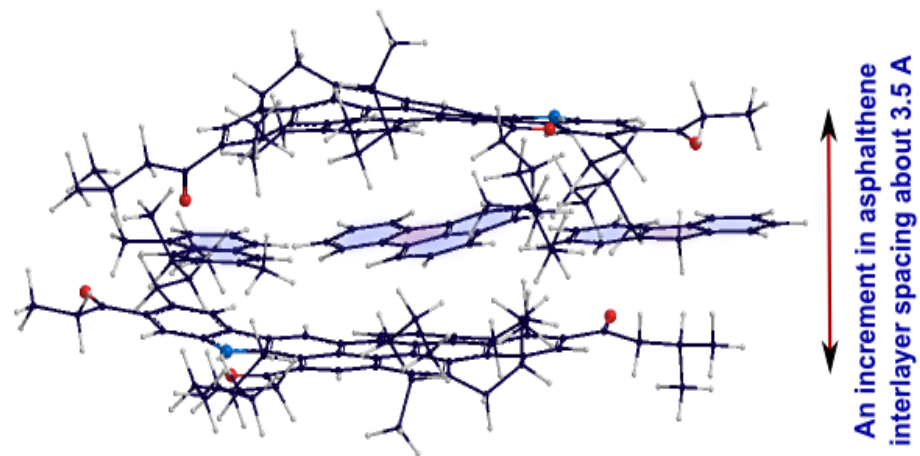
Effects of Aromatics on Deagglomeration

29

Top-view

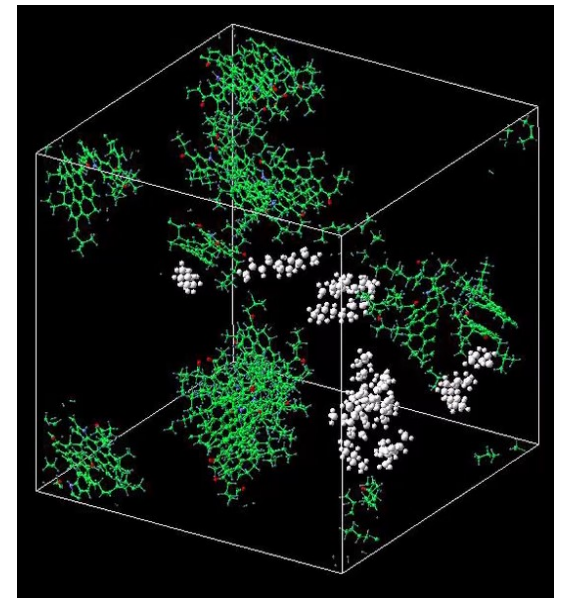
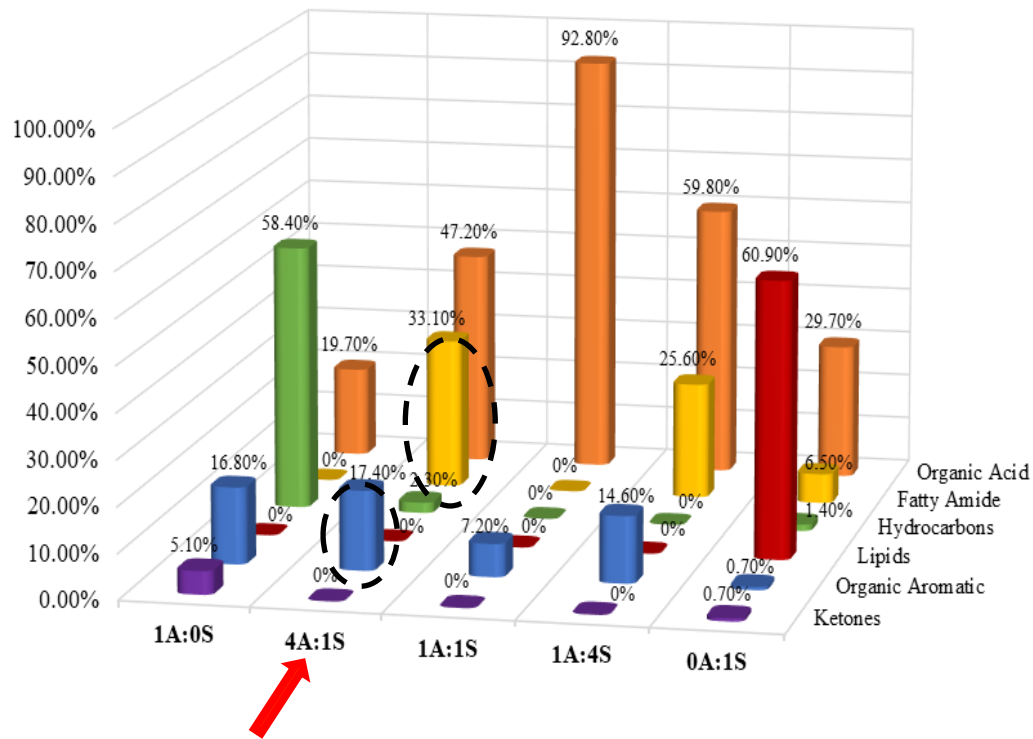


Side-view



- ❑ **Weakening effect** on the intermolecular interactions between asphaltenes and obvious **deagglomeration**

Having a **reliable test** which measures extent of true rejuvenation, we can
synthesize right rejuvenator from known and **abundant building blocks**...



Swilgae

A patent pending technology to rejuvenate aged asphalt

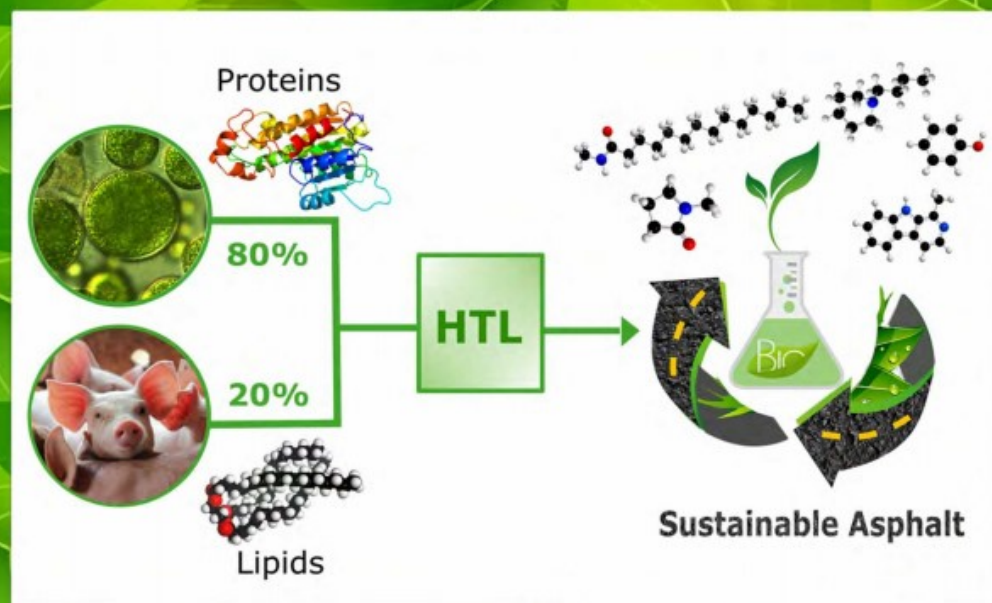
Pahlavan, F., A. I. Rajib, E. H. Fini,
ACS Sustainable Chemistry & Engineering,

<https://doi.org/10.1021/acssuschemeng.0c01100>

ACS Sustainable Chemistry & Engineering

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Pahlavan, F., A. I. Rajib, E. H. Fini, 2020, Using the Synergy between Lipid-rich and Protein-rich Biomass to Synthesize Effective Bio-Rejuvenators for Oxidized Asphaltenes, ACS Sustainable Chemistry & Engineering, <https://doi.org/10.1021/acssuschemeng.0c01100>.

- Rajib, A.I., Pahlavan, F., E. H. Fini, 2020, Investigating Molecular-Level Factors That Affect the Durability of Restored Aged Asphalt Binder, Journal of Cleaner Production.
- Fini, E., A. I. Rajib, D. J. Oldham, A. Samieadel, Sh. Hosseinneshad, 2020, Role of Chemical Structure and Composition of Recycling Agents on Their Interactions with Oxidized Asphaltene Molecules, ASCE Journal of Materials in Civil Engineering, 32:9.
- Fini, E., A. Samieadel, A. I., Rajib, 2020, Moisture Damage and Its Relation to Surface Adsorption/Desorption of Rejuvenators, Industrial and Engineering Chemistry Research, 59 (30): 13414–13419. doi.org/10.1021/acs.iecr.0c02534
- Pahlavan, F., A. Hung, and E. H. Fini, 2018, Evolution of Molecular Packing and Rheology in Asphalt Binder during Rejuvenation, Fuel, 222: 457-464
- Pahlavan^x, F., Sh. Hosseinneshad, A. Samieadel, A. Hung, and E. H. Fini, 2019, Fused Aromatics To Restore Molecular Packing of Aged Bituminous Materials, Industrial and Engineering Chemistry Research, 58(27):11939-11953, <https://doi.org/10.1021/acs.iecr.9b01397>
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