

Supporting Information.

Exploiting Synergistic Effects of Intermolecular Interactions to Synthesize Hybrid Rejuvenators to Revitalize Aged Asphalt

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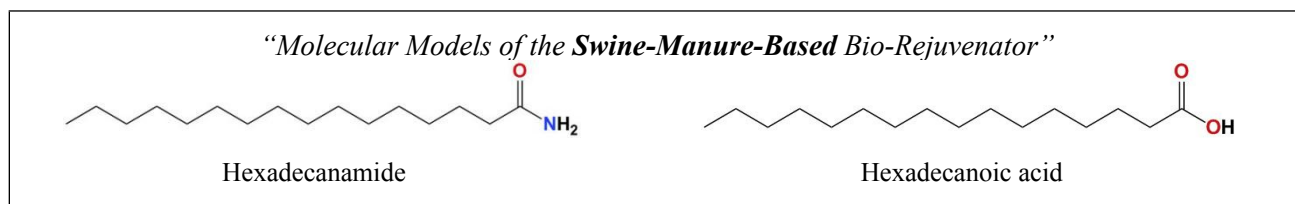
a. School of Sustainable Engineering and the Built Environment, Arizona State University, 660 S. College Avenue, Tempe, AZ 85287-3005, USA

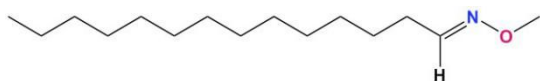
b. School for Engineering of Matter, Transport and Energy, Arizona State University, 551 E. Tyler Mall, Tempe, AZ 85287, USA

Supporting Information (SI) includes 6 pages, 2 figures, and 1 table illustrating details of molecular structure and background information.

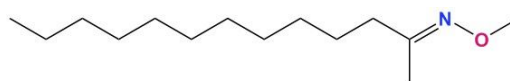
Molecular Species in the Bio-Rejuvenator Made from Swine Manure and Algae

Decomposition of a lipid-rich source such as swine manure generates compounds with higher molecular weight, including long chains of fatty acids and saturated and unsaturated linear hydrocarbons.^{1, 2} The presence of nitrogen-containing components in the form of cyclic and acyclic molecules such as indoles, quinolones, amines, and amides is the predominant feature of bio-crude oil from protein-rich biomass, such as algae, which is related to amino acid transformation through the HTL process.³⁻⁶ Amino acids decompose via decarboxylation and deamination reactions and consequently produce amines and amides.⁷⁻⁹ Some products (ammonia and amines) undergo a condensation reaction with fatty acids, the building blocks of the lipids, to give alkyl amides and nitriles.^{10, 11} Also, interactions between amines and carbohydrates produce the nitrogen-containing rings such as indoles and quinolones in the bio-oil.^{12, 13}

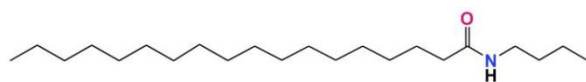




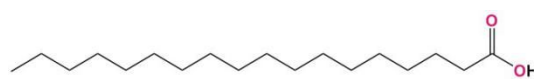
Tetradecanal o-methyloxime



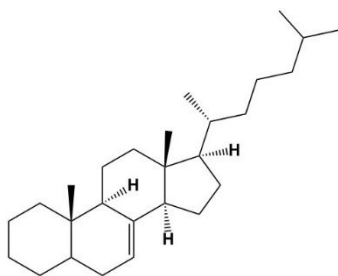
2-tridecanone o-methyloxime,



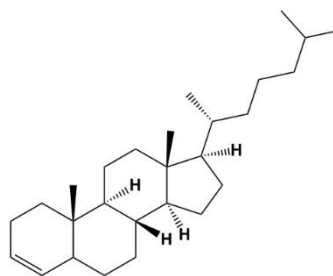
n-butyl octadecanamide



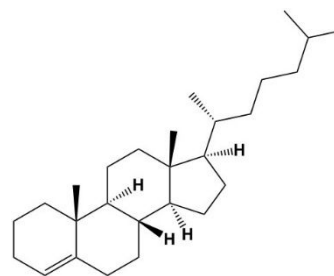
Octadecanoic acid



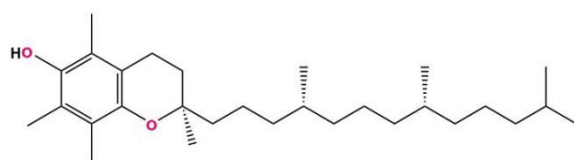
Cholest-7-ene



Cholest-3-ene

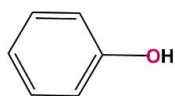


Cholest-4-ene



α-Tocopherol

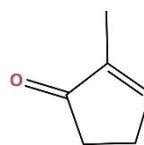
“Molecular Models of the Algae-Based Bio-Rejuvenator”



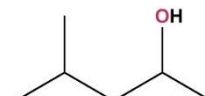
Phenol



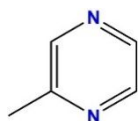
p-Cresol



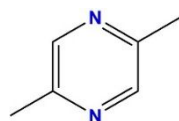
2-Methyl-2-cyclopenten-1-one



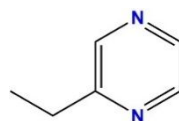
4-Methyl-2-pentanol



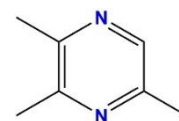
Methylpyrazine



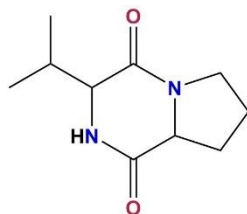
2,5-dimethylpyrazine



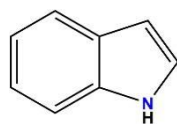
2-Ethylpyrazine



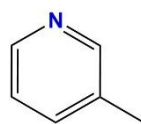
2,3,5-Trimethylpyrazine



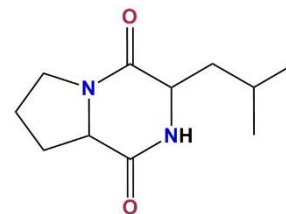
Cyclo(L-prolyl-L-valine)



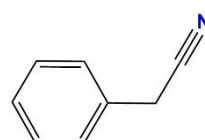
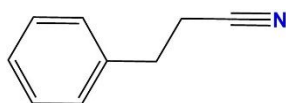
Indole



3-Methylpyridine



Pyrrolo[1,2-a]pyrazine-1,4-dione,
hexahydro-3-(2-methylpropyl)-



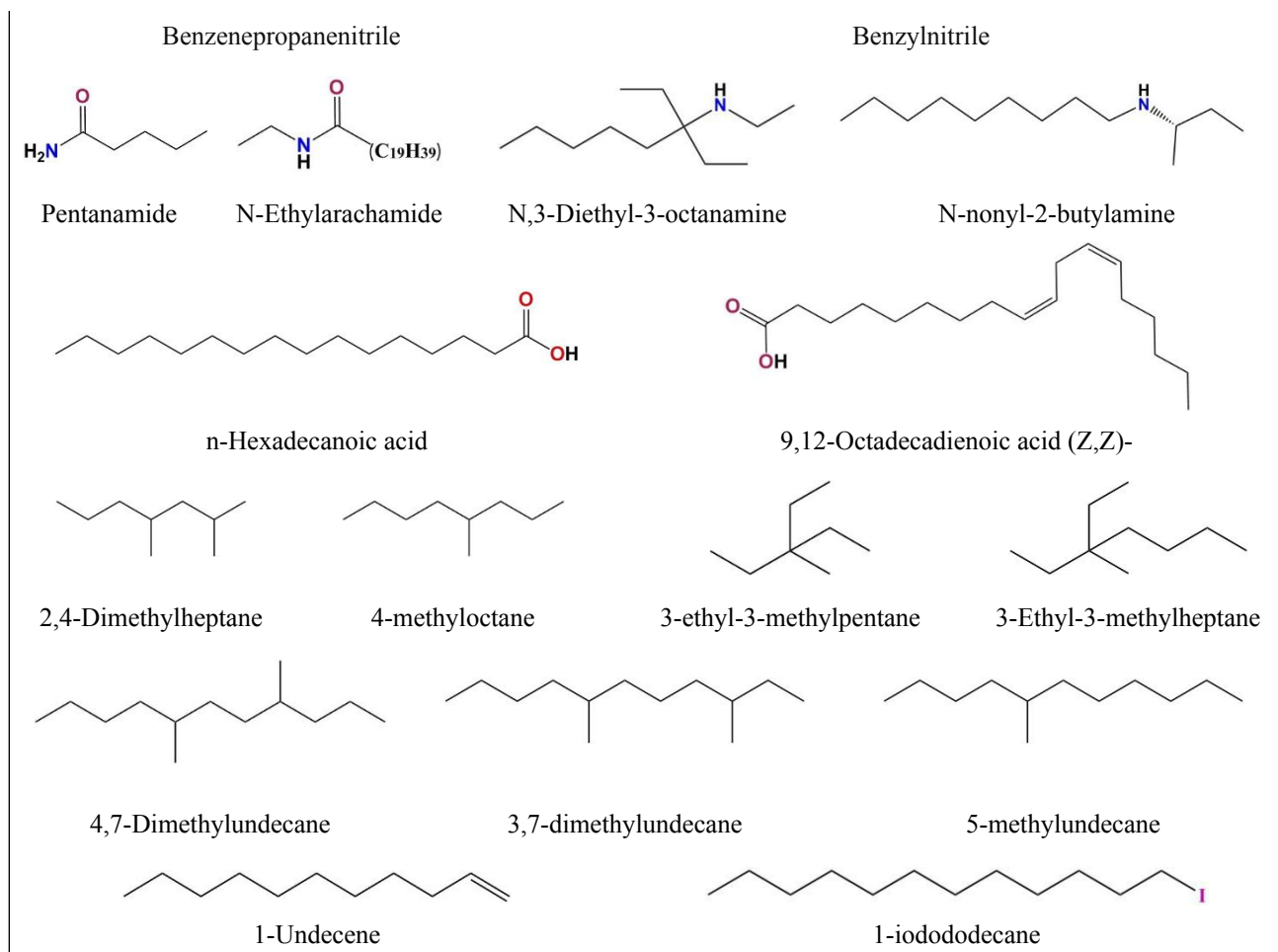


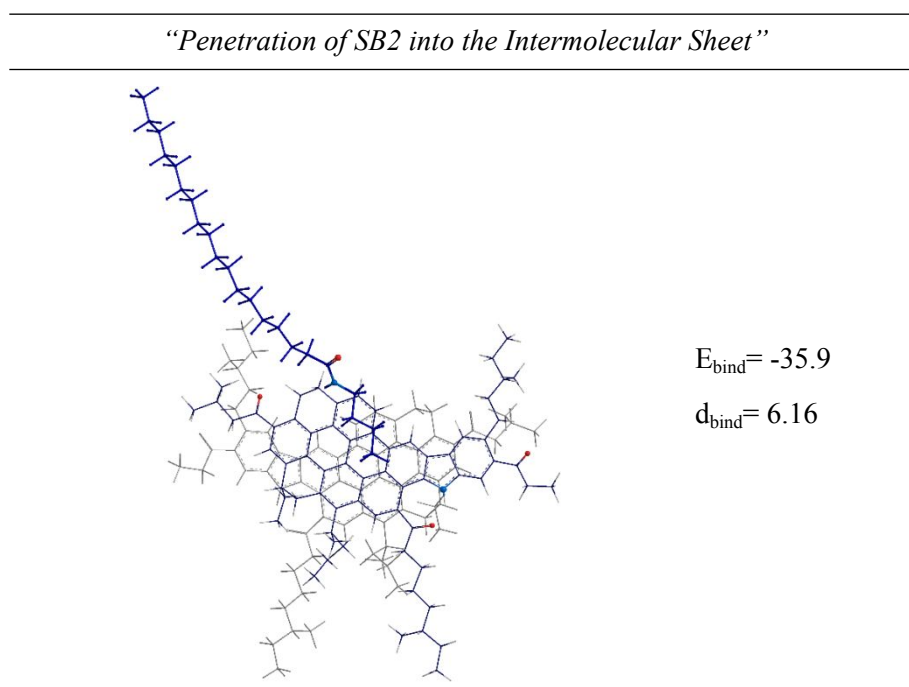
Figure S1. Molecular structures identified in swine-manure-based and algae-based bio-binders.

Intercalating Potential of the Primary and Secondary Amides, BR1 and BR2

Additional structural features whose impact on deagglomeration should be studied are the different types of amides: primary (BR1) and secondary (BR2) (Figure 2). We compared the interacting potential of the primary and secondary amides, BR1 and BR2, respectively, at Zone-C. In the secondary amide, the functional group is located between two hydrocarbon chains, so it is expected that BR2 would have more dispersion interaction from both sides of the molecular structure with the aromatic cores and subsequently more penetration into the intersheet gap in comparison with BR1. This expectation was verified in our computations for the interacting complex of an oxidized asphaltene dimer and BR2 (Table S1). The reduction in the binding energy and the increase in the binding distance of oxidized dimer of asphaltene

exposed to secondary amide (Table S1) is more than that of the primary amide (Figure 5-b). It can be expected that secondary amide molecules are more effective in the deagglomeration of asphaltene stacks in the intercalation step compared to the primary one.

Table S1. Intercalating Step: Interacting complex to evaluate the penetrating ability and opening impact of secondary amide, BR2, on the asphaltene agglomerates. Shown are the binding energy (E_{bind} , kcal/mol) and the binding distance for the oxidized dimer (d_{bind} , Å).



Density plot for population of data points falling in each range of average aggregation number

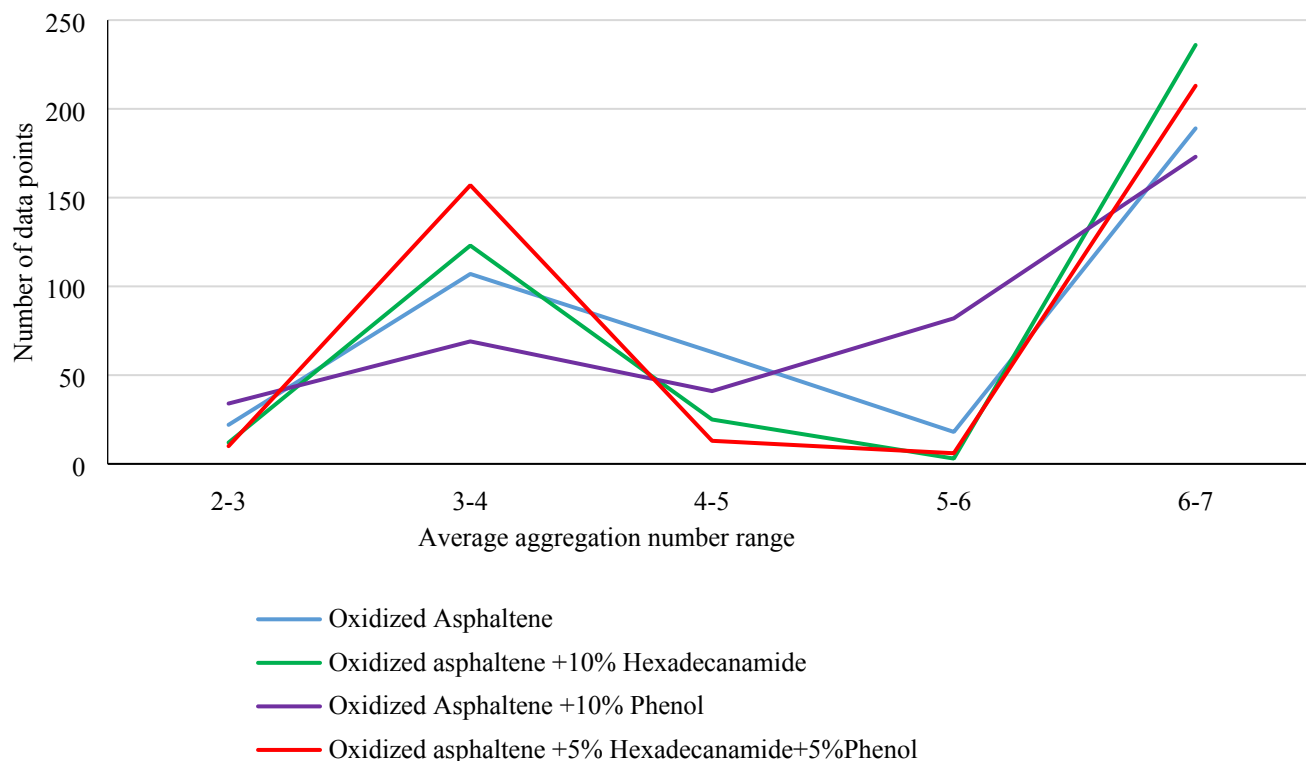


Figure S2. Density plot for data points calculated for average aggregation number from 20 to 40 ns (after addition of dopants).

References

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