Water-Soluble Asphaltenes

Poster Presentation Prepared for

Workshop on Asphaltene Properties and Processing

NATIONAL PARTIAL UPGRADING COMMITTEE

THURSDAY, FEBRUARY 25, 2021, 09:00-15:00 MST

By

Dr. Makhlouf Laleg, Owner of ML Papchem Solutions Inc., Pointe-Claire QC, Invited Scholar at McGill University, Montreal QC

And

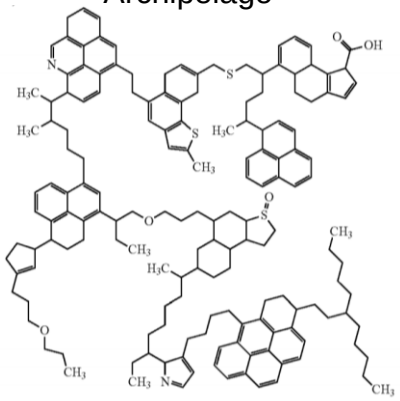
Prof. Theo van de Ven, Sir William C. Macdonald Chair in Chemistry, Director Quebec Centre for Advanced Materials, McGill University, Montreal QC

mlaleg@videotron.ca
theo.vandeven@mcgill.ca

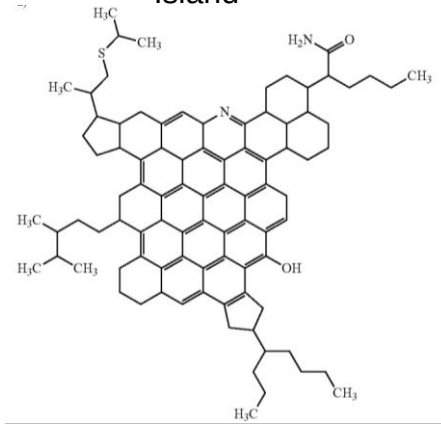
Asphaltenes

- Non-polymeric materials, made of complex polydisperse planar molecules, not straight chains
  - thermally stable aromatic “sites” with aliphatic chains linking the sites or connecting them by thermally unstable bonds and contain heteroatoms **S** (in sulfoxide, thiophene), **O** (in carboxylic acid, hydroxyl, carbonyl groups, phenol, etc.) and **N** (in pyrrole, pyridine) along with trace amount of coordinated heavy metals (**V, Ni, Fe**) --- heteroatoms give the polar nature

Archipelago

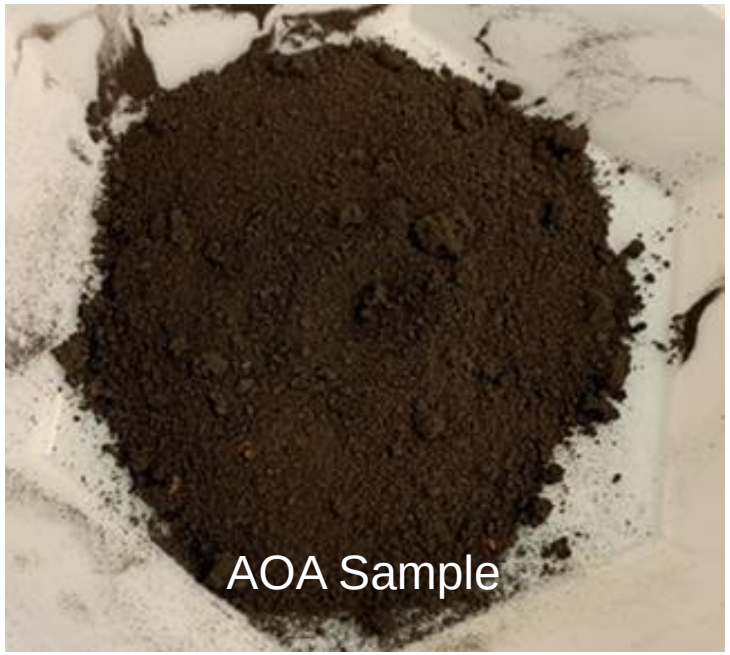


Island



different other types of structures have been postulated

- **Solvent extracted Asphaltenes** are dark brown to black friable solids products made of stable dense aggregates (through acid-base interactions and hydrogen bonding, metal coordination complex, π−π stacking)
  - **Thermoplastic character:** particles soften on heating, melt at 180 – 232°C (300°C)→ high viscosity, on cooling toward RT it harden to very brittle solid “dense” product
  - **Polar nature**: negative and positive charged heteroatoms allows particles dispersion in water
  - **Soluble or “partially” soluble in**: Carbon disulfide, Pyridine, Quinoline, Methyl chloride, O-dichlorobenzene, Nitrobenzene, Dimethylacetamide, Tetralin, Xylene, Toluene, Benzene, Carbon tetrachloride, Ethylbenzene, Cyclohexane, Dichloromethane, Tetrahydrofuran, .. Tend to precipitate over time even at low concentrations
  - **Insoluble or “slightly” soluble in**:
    - Paraffin naphthas, n-pentane, n-hexane, n-heptane, petroleum ether, cyclopentane, acetone, MEK, n-methyl pyrrolidone (NMP), dimethylformamide (DMF), cyclic carbonates, ..
    - Not soluble in neutral, acid or alkaline water – low to high T or high salt (ionic strength)



Asphaltene solubility is a complicated business

Our Objective

Develop a method to make **asphaltene (AOA)** easy to dissolve in water and/or some VOC exempt (acceptable) solvents → **for creating new application opportunities**

- Stable asphaltene solutions
- Asphaltene should keep most of its structural property
- Has desirable properties (reactivity, compatibility, adhesion, melting) needed for many different applications
- Has potentially reduced (S, N, V, Ni)

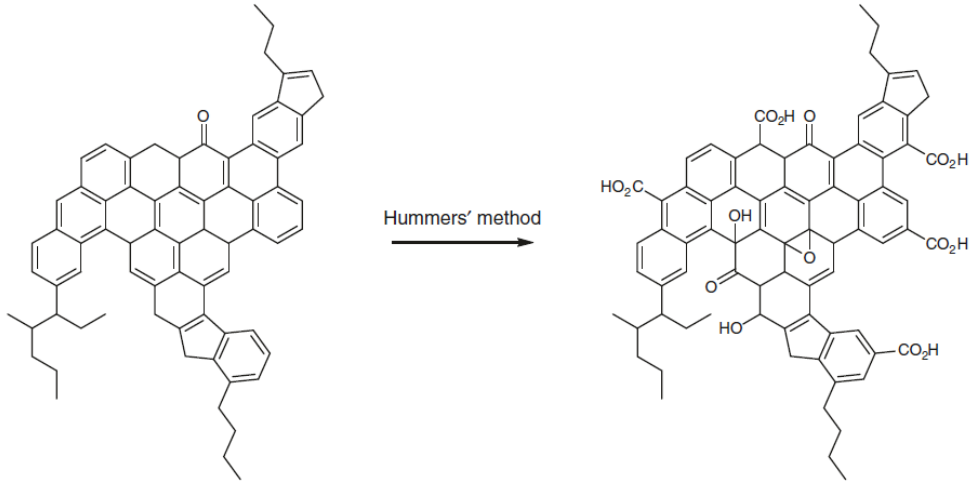
VOC: Volatile Organic Compounds

Potential **Oxidation** Approaches to Make Water-Soluble Asphaltenes

Several chemistries:

- Water-free mixture of concentrated sulfuric acid H_2SO_4, sodium nitrate $NaNO_3$ and potassium permanganate $KMnO_4$, H_2O_2, HCl (2019) -- (used Hammer's method 1958) → no solubility data
- Simplified Hummer's method: sulfuric acid and nitric acid HNO_3, NaOH, without the presence of the $KMnO_4$ (2020) → no solubility data
  - Both permanganate approaches are complicated, hazardous, expensive
- Sulfuric acid and oleum "fuming sulfuric acid" (references 1963 to 2010) → no solubility data
- Sulfuric acid (2016) → no solubility data
  - Both acid approaches are complicated and hazardous
- Nitric acid (1963) → solubility +
- Nitric acid (1985) → solubility +

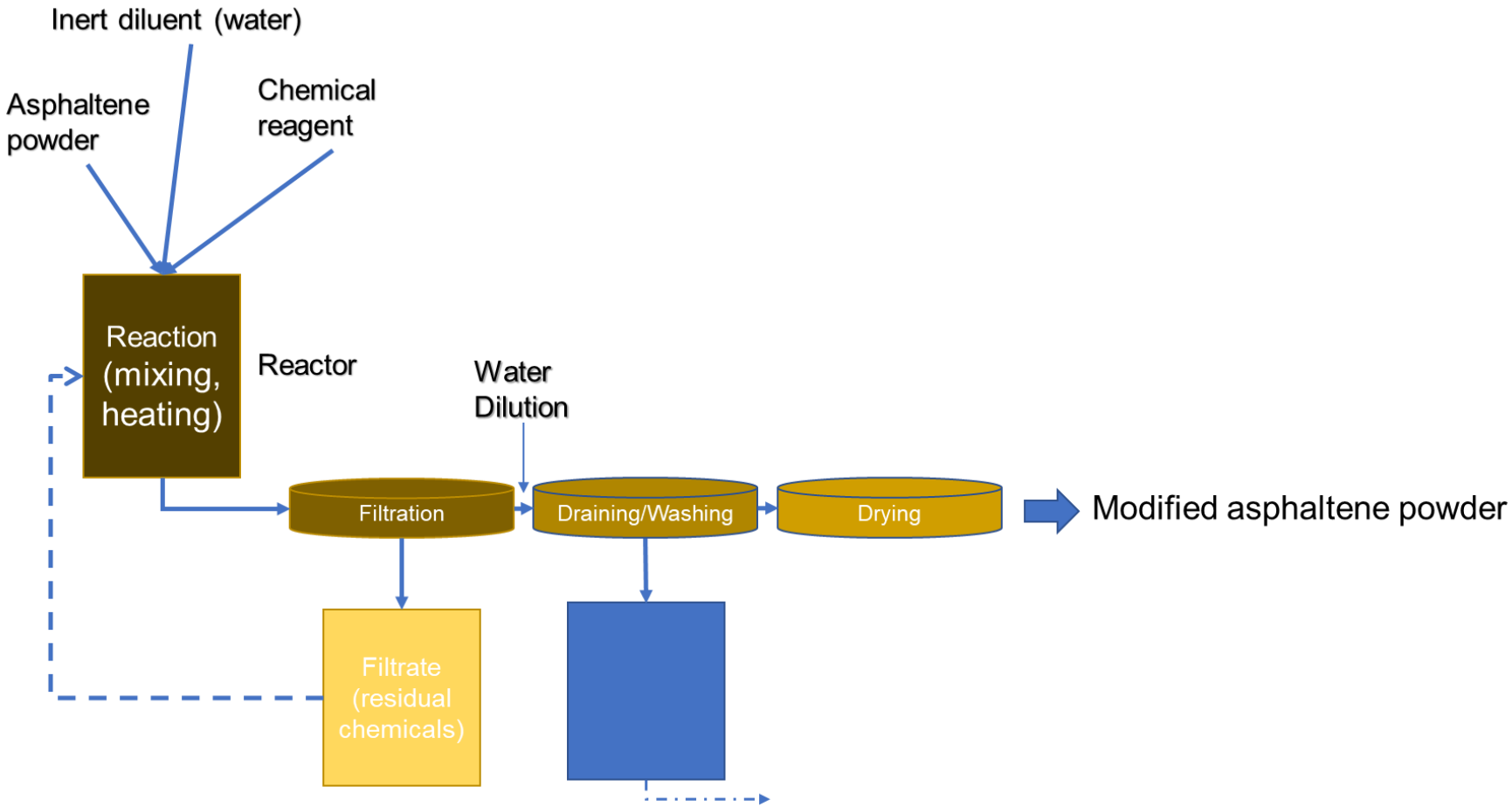
Nitric acid treatment causes degradation of aromatic structure, formation of acidic molecules (low Mw), no information on melting characteristics



Representative structure of oxidized asphaltene using Hummers' method "commonly used to oxidize graphite to Graphite Oxide"

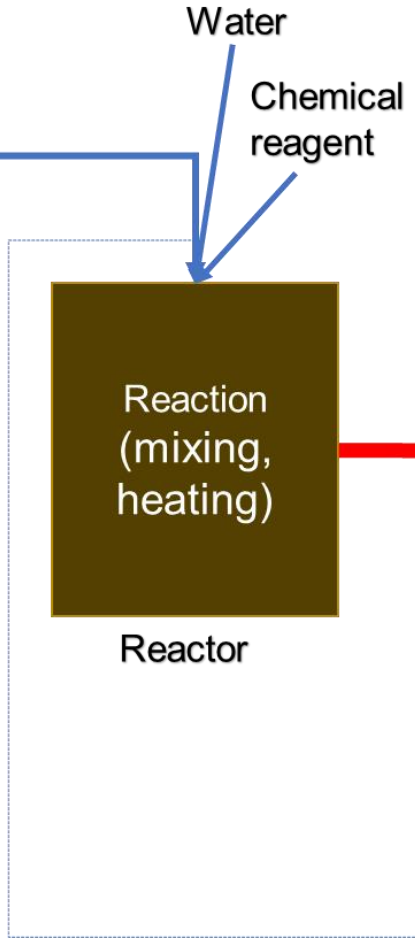
Novel Approach

Identified a cost-efficient aqueous chemistry that safely modifies AOA powder and renders it soluble in water and in several polar / polar aprotic solvents



Making the Chemically Modified Asphaltene Powder

AOA powder as received



Modified AOA powder

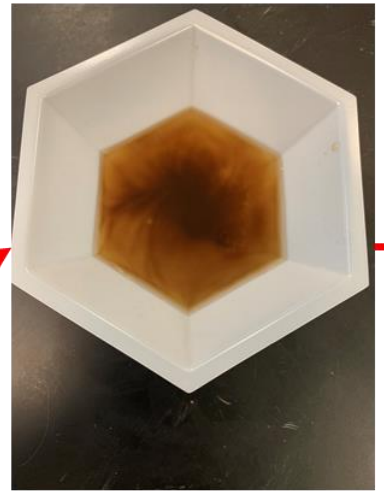
FTIR: Clear evidence of functionalization → Carboxyl (COOH) and hydroxyl (-OH) functional groups – **H-Form**

Modified Asphaltene

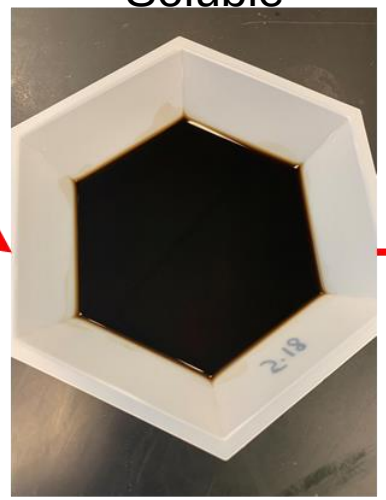
In neutral water
or acidified water

In alkaline solution

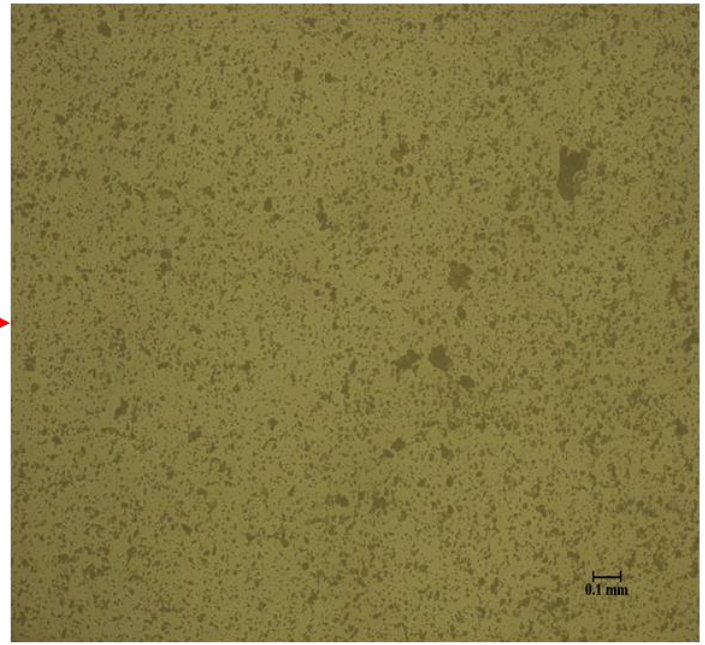
Insoluble

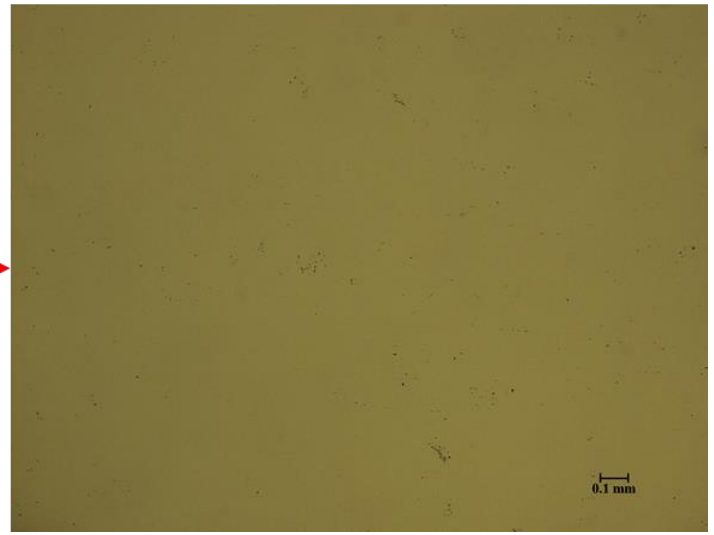


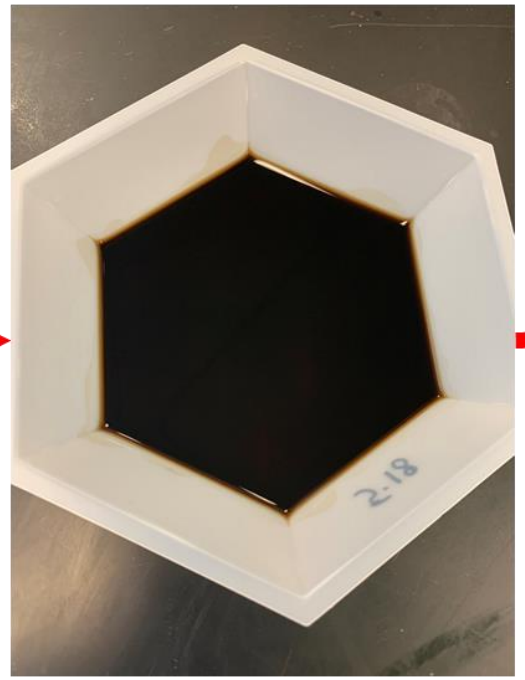
Soluble



Optical microscopy images



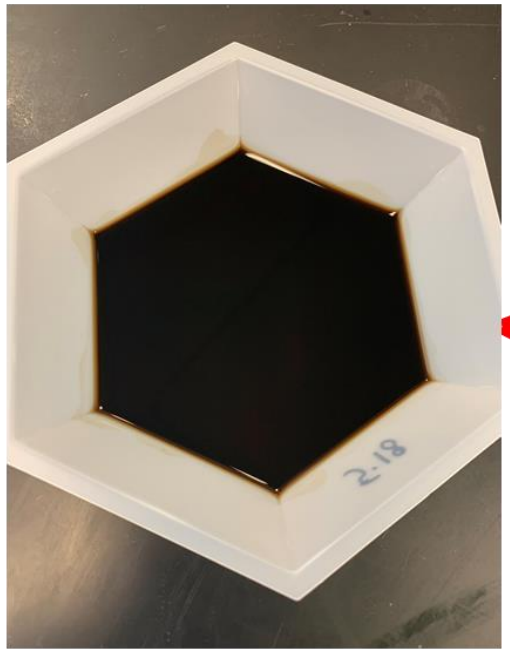




Modified Asphaltene Dissolved in Alkaline Solution

Na-form Modified Asphaltene (water soluble)

- Not soluble in acid or neutral water, increased hydrophilicity
- Slightly soluble to insoluble in alcohols
- Soluble in Acetone, MEK, NMP, DMF, cyclic carbonates, ..
- Not soluble in Toluene (aromatic solvents) and Paraffin naphthas



Modified Asphaltene dissolved in alkaline water solution

Diluted in neutral water (80 mL)

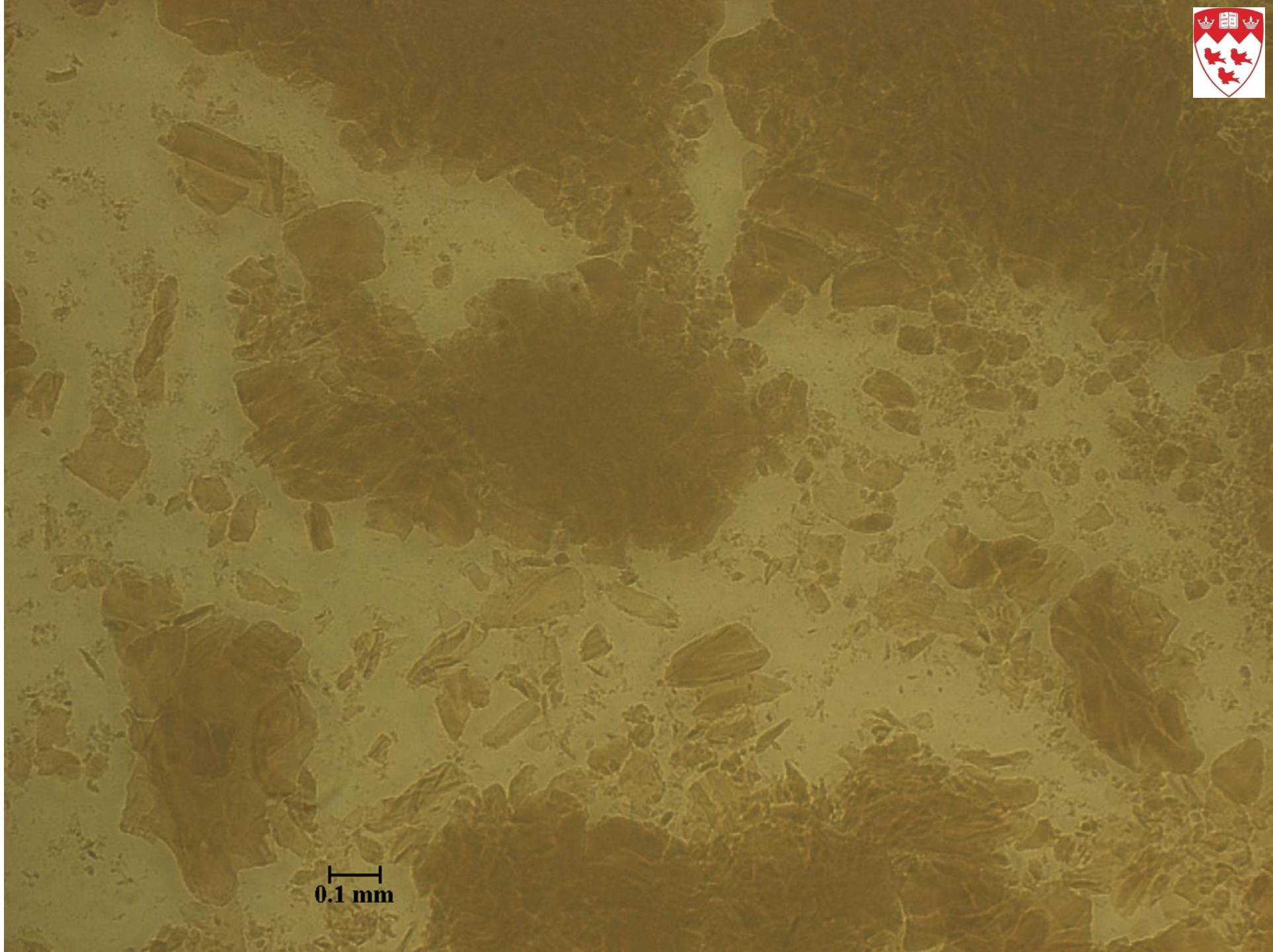
Stable solution

Diluted in acidified water (80 mL)

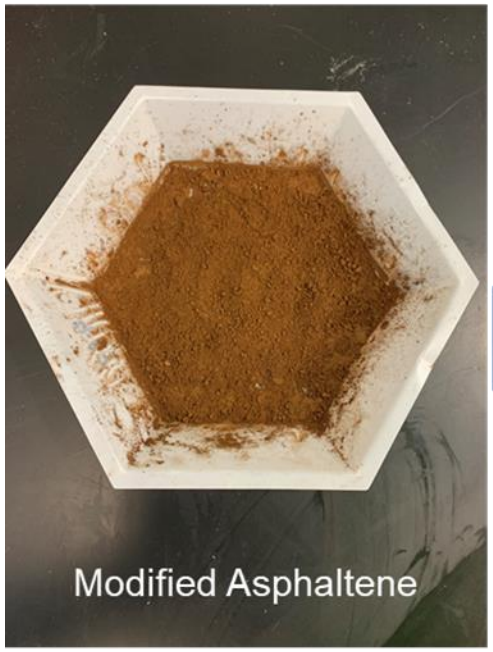
Precipitation to particles

Filtration then drying give a cleaner H-form product

Microscopy image of acid-precipitated modified AOA obtained from alkali dissolved modified AOA



Asphaltene Solutions and their Possible Blending with Resins, Latexes, Polymers, Adhesives, Coatings ….



Dissolution

Aqueous or solvent solutions of modified asphaltene

Blending Material

Filtration

For several application areas

Summary of preliminary results and Next Steps

- The novel approach provided modified asphaltene powder of **H-Form** and **Na-Form**
- Ability to form stable solutions in water and some organic solvents (VOC exempt)
- Treatment method could be optimized to cost-efficiently produce enhanced asphaltene products useful for several potential applications

Next steps

1. Conduct further analyses on the modified asphaltene samples
2. Optimize chemical reaction (dosages, time, temperature, ..)
3. Application demonstration
4. Look for collaboration an industrial partners

Acknowledgments

We thank Dr. Md Shahidul Islam, McGill and Dr. Mohammadhadi Moradian, McGill for their help in the experimental work and sample analysis

and Alberta Innovates for providing AOA sample through the CFGC program