Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Characterization of Tunable Carbohydrate-Based Materials for Sorption of Oil Sands Naphthenic Acids

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Results and Discussion

Synthetically engineered copolymers are receiving growing attention for sorption and possible degradation of components in oil sands processed water (OSPW). *β*-Cyclodextrin (*β*-CD) copolymers, for example, have been shown in recent studies of electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to adsorb oil sands naphthenic acid fraction components (NAFCs). Herein, we report complementary results for atmospheric pressure photoionization (APPI) for characterization of NAFCs in OSPW samples following sorption with cyclodextrin-based copolymers. The materials investigated were *β* -CD-cross-linked with three different types of diisocyanates, namely, (i) 4,4′ -dicyclohexylmethane diisocyanate, (ii) 4,4′ -diphenylmethane diisocyanate, and (iii) 1,4-phenylene diisocyanate. The APPI studies revealed variable sorption for a complementary range of NAFCs with compound classes not detected by ESI. For example, sorption was observed for new classes of NAFCs: HC, N_1O_1, N_1O_2, N_1O_3, N_1O_4, N_1O_5, N_2O_1, N_2O_2, and N_2O_3, from OSPW in accordance with the nature of the cross-linker unit of the copolymer and the structure of the NAFCs. Sorption of NAFCs in general was more pronounced for *β* -CD copolymers cross-linked with 4,4′ -dicyclohexylmethane diisocyanate, particularly for the O2 class that was amenable to negative-ion APPI detection. In contrast to the 75% attenuation of O2 species observed for sorption to the copolymer cross-linked with 4,4′ dicyclohexylmethane diisocyanate, little or no sorption was observed for the O_2 series with positive-ion APPI. The O2 series is presumably mixtures of classical naphthenic acids and dihydroxy components with a range of different structures. The complementary nature of the APPI and the prior ESI results contribute further to the quality and understanding of the sorption mechanism of the copolymers.

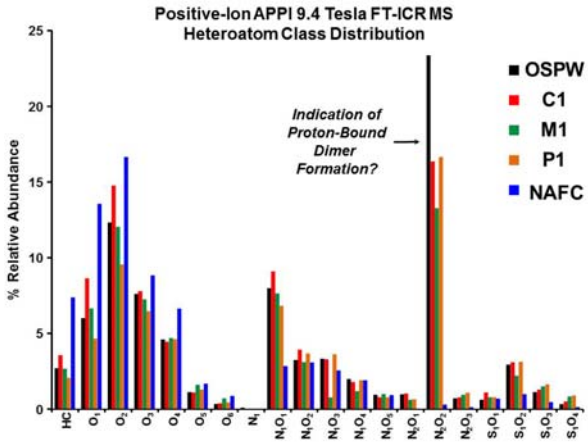

Figure 1. The positive-ion APPI FT-ICR MS data reveal the sorption of many new compound classes not observed in earlier work: HC, N_1O_1, N_1O_2, N_1O_3, N_1O_4, N_1O_5, N_2O_1, N_2O_2, and N_2O_3. The N_2O_2 class could be a proton-bound dimer of N_1O_1, although attempts were made to minimize dimer formation by running the samples at low concentration. The levels of the N_2O_2 class in the NAFC are relatively low compared to the OSPW and treated OSPW, providing further indication that those components are likely proton-bound dimers. There is also evidence for desorption of O_5, O_6, O_7, and S_1O_4 species for the M1 polymer. Those component classes are relatively minor components in the OSPW and the NAFC extract and, thus, likely originate from the polymer material. Further studies are thus warranted to determine whether or not the desorption of the compound classes affects the toxicity of the treated OSPW.

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for financial support of this research, along with the Program of Energy and Research Development (PERD), National Science Foundation (NSF) Division of Materials Research through DMR-11-57490, the Florida State University Future Fuels Institute, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida

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