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Carboxymethylated lignins with low surface tension toward low viscosity and highly stable emulsions of crude bitumen and refined oils



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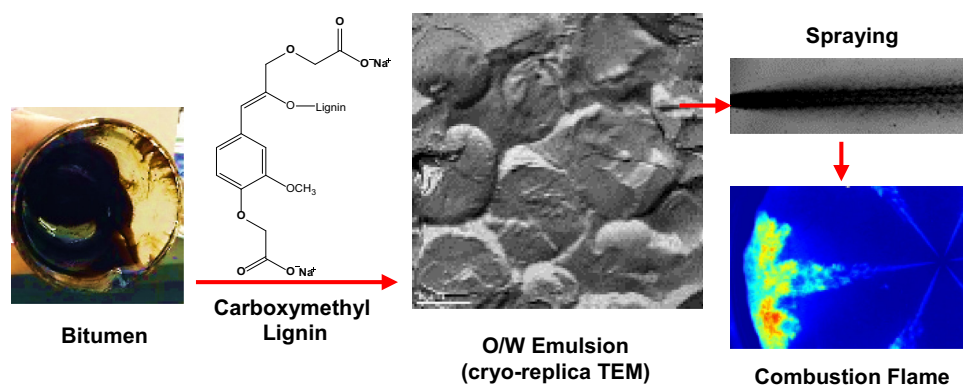
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GRAPHICAL ABSTRACT



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ABSTRACT

Kraft and organosolv lignins were subjected to carboxymethylation to produce fractions that were soluble in water, displayed a minimum surface tension as low as 34 mN/m (25 °C) and a critical aggregation concentration of ~1.5 wt%. The carboxymethylated lignins (CML), which were characterized in terms of their degree of substitution (³¹P NMR), elemental composition, and molecular weight (GPC), were found suitable in the formulation of emulsions with bitumens of ultra-high viscosity, such as those from the Canadian oil sands. Remarkably, the interfacial features of the CML enabled fuel emulsions that were synthesized in a very broad range of internal phase content (30–70%). Cryo-replica transmission electron microscopy, which was used here the first time to assess the morphology of the lignin-based emulsions, revealed the droplets of the emulsion stabilized with the modified lignin. The observed drop size (diameters < 2 μm) was confirmed by light scattering, which revealed a normal size distribution. Such characteristics led to stable emulsified systems that are amenable for a wide range of applications. Emulsification with CML afforded bitumen emulsions with very high colloidal stability (no change was noted for over one month) and with a strong shear thinning behavior. Both features indicate excellent prospects for storage, transport and spraying, which are relevant in operations for power generation, which also take advantage of the high heating value of the emulsion components. The ability of CML to stabilize emulsions and to contribute in their combustion was tested with light fuels (kerosene, diesel, and jet fuel) after formulation of high internal phase systems (70% oil) that enabled operation of a fuel

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engine. A significant finding is that under certain conditions and compared to the respective pure fuel, combustion of the O/W emulsions stabilized by CML presented lower NO_x and CO emissions and maintained a relatively high combustion efficiency. The results highlight the possibilities in high volume application for lignin biomacromolecules.

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1. Introduction

Heavy crude oils (API < 20) are dense and highly viscous [1,2] hydrocarbons that are used for power generation. According to the U.S Energy Information Administration (US EIA), the worldwide largest heavy crude oil deposits, with over 500 billion barrels, are located at the Orinoco Petroleum Belt, covering over 20 thousand square miles in eastern Venezuela and are joined by the oil sands found in Canada [3]. The heavy oil reserves are more than twice those of conventional light crude oil. However, they cannot flow easily for operation under normal conditions with centrifugal pumps or other method [4]. Due to the difficulties and costs in extraction, transport, and refining, the price of heavy oils is generally discounted in the market. Bitumen, in particular, is a good example of extra heavy oils (API gravity > 10 and reservoir viscosity of ~10,000 mPa·s) that fit these characteristics [5]. They are complex hydrocarbon mixtures formed from the biological degradation of original oil with the light components (commonly C1 to C10) largely absent, making them tacky and semi-solid yet representing a worldwide consumption of ~102 million tons per year [6]. Their primary application is in road paving, around 85% of total use, where they act as binder mixed with particle aggregates to produce asphaltic concrete [6]. Other uses include bituminous waterproofing products for roofing felt and for sealing flat roofs [7]. Used as fuels, bitumen fractions produce combustion products that may include inorganic fine solids, heavy metals, and heteroatoms, which represent a contamination challenge [8]. Moreover, even after refining, the lighter fraction of bitumen may still display a high viscosity and cannot be burned for conventional power generation or transportation. Therefore, a light, often volatile diluent is added to facilitate flow.

In recent years, fuel emulsions have been explored as an alternative, relatively inexpensive fuel with reduced pollution impact. Bitumen-based emulsions such as Orimulsion[®], from the Orinoco Petroleum Belt, have been stabilized by polyethoxylated nonylphenol surfactants [9] and was used as a commercial boiler fuel in power plants. However, the synthetic surfactants used in such fuel emulsions may result in unburnt residues inside the boiler and cause corrosion. Moreover, depending on surfactant molecular composition, some exhaust emissions including sulfur oxides and other pollutants can be produced. Besides the fact that some synthetic surfactants are being banned, their typical low heating values reduce the combustion efficiency and increase the total price of the emulsions.

Most important to this study is the fact that wood-derived lignins can be considered as an alternative to synthetic surfactants in related applications; they show not only the required surface activity but they are inexpensive, green macromolecules that are widely available [10]. Lignin is the second major component of wood consisting of three main coupled units including *p*-coumaryl, coniferyl, and sinapyl alcohols that produce *p*-hydroxyphenyl, guaiacyl, and syringyl residues, respectively [11]. The relative contents of these three species vary depending on the plant species [12]. Lignin's building blocks can be linked, for example by β -O-4 and other linkages, in over ten different ways; all together and even if one excludes the linkages with carbohydrate fractions, it is apparent that the extraordinary complex structure of lignin results

in varying detailed molecular features [13]. Thus, it is only logical that lignin utilization is challenged by its complexity, which limits its main use to energy recovery in pulp mills where it is burned as main component of the solid fraction of highly alkaline "black liquors" [14]. Annually, lignin is produced at around 50 million tons with only a small fraction (ca. 2%) used commercially, including 1 million tons of lignosulfonate and less than 0.1 million tons of kraft lignin [15,16]. Sulfur-free lignins from organosolv, acid hydrolysis and steam explosion and, more generally, those from biorefinery processes have captured interest considering their possible uses [17].

Despite lignin's complex structure, it can be considered as an inexpensive, multifunctional macromolecule that can be upgraded for high-value applications. Lignin contains both hydrophobic and hydrophilic groups presenting, depending on the conditions, which makes it surface-active. Some treatments can make lignin to act as emulsifier, such as in the case of lignosulfonates [18,19]. Moreover, the high carbon content of lignin (~66%) [20] correlates with a higher heating values (HHV) of ~23–26 MJ/kg [21], making a good case for consideration as far as energy prospects.

Utilization of lignin in the area of fuel emulsions, as proposed here, can offer several benefits. From the viewpoint of energy, lignin provides a heating value that is higher than that of synthetic surfactants. From the environmental perspective, lignin is non-toxic and can be burned with minimum pollutant exhaust emissions. To this end and in order to reduce the emission of sulfur oxide, carboxymethylated lignin is a good alternative to available lignosulfonates. Economically, lignin is less expensive than the synthetic surfactants used in fuel emulsions. Overall, it is proposed that lignins can be exploited in complex, upgraded fluids, for example, in fuel emulsions for power generation.

In this work we used carboxymethylation to modify low sulfur kraft lignin in order to extend its water solubility at neutral pH. An organosolv lignin was also modified and used as a reference. The modified lignins (carboxymethylated lignins, CML) were characterized in terms of their degree of substitution (³¹P NMR), elemental composition, and molecular weight (GPC). The CML displayed a relatively low surface tension and was used to emulsify different oils with water. Bitumen crude oil as well as light oils (kerosene, diesel, and jet fuel) were used to formulate oil-in-water (O/W) emulsions with varying water-to-oil ratio (WOR), from 30:70 to 70:30. The properties of the fuel emulsions were characterized, including drop size and size distribution, stability, and rheological behavior. Moreover, the emulsion fuel was evaluated based on the combustion analysis to measure heating value, exhaust gaseous emissions, and combustion efficiency.

2. Materials and methods

2.1. Carboxymethylated lignin (CML)

Pine kraft (Domtar, Plymouth, NC) and organosolv (Alcell, Lignol, Vancouver, Canada) lignins were used as precursors to obtain carboxymethylated lignins (CML). In general, the procedure includes initially alkalization of phenolic hydroxyl groups with sodium hydroxide (Sigma Aldrich, St. Louis, MO) to form ionized nucleophiles. The phenol ions then react with monochloroacetic

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