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Preliminary formulation development for aqueous surfactant-based soybean oil extraction

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ABSTRACT

Soybean oils are increasingly being used for a range of non-food applications, including production of biofuels and oleochemicals. While most soybean oil is produced by hexane-based extraction methods, concern about environmental and health effects from hexane extraction has led to increased interest in development of aqueous extraction methods. Among aqueous methods, surfactant-based aqueous extraction of vegetable oils has shown particular promise as an alternative to hexane-based extraction methods. The objectives of this work were to explore the use of surfactant-based methods for the extraction of soybean oils, and to test whether the use of mixed anionic–cationic and anionic–cationic–nonionic surfactant mixtures could successfully be used to reduce the salinity requirements for surfactant-based extraction. All three formulations tested were capable of producing ultra-low (<0.01 mN/m) interfacial tensions with soybean oil. One of the formulations, a four-component (three surfactant, one hydrotrope) mixture, was able to reduce the salinity requirement from 5% down to 0.75%. A range of experiments was conducted to better understand the factors influencing extraction yield for surfactant-based extraction of soybean oil. Extraction experiments were conducted with a single extended surfactant system which has been used previously for extraction of other oilseeds. Extraction yields as high as 88.6% were observed for the conditions tested. Extraction yield was strongly dependent on salinity, and was found to increase with increasing shaker agitation rate, decreasing solid to liquid ratio, and decreasing particle size.

1. Introduction

While soybean oil continues to be predominantly used in edible products, its use in non-food applications has grown rapidly over the past two decades, and now comprises a substantial fraction of all use. For example, it has been reported that 20% of soybean oil consumption in the United States in 2011 was due to non-food applications, up from only 4% a decade earlier (Gunstone, 2013; SoyStats, 2014). Much of this increase can be attributed to rapidly growing production of biodiesel and other soy-based biofuels. Data from the National Biodiesel Board indicates that biodiesel production has increased 100-fold over the past decade (Biodiesel.org, 2014). Another significant non-food use of soybean oil is the production of oleochemicals and biosurfactants (e.g., Qingyi et al., 2011).

Because solvent extraction is the primary method used for extraction of vegetable oils, the vegetable oil extraction industry is a major source of volatile organic compound emissions (Rosenthal et al., 1996). The annual hexane emissions from soybean oil extraction processes have been reported to be 210–430 million liters in the U.S. (Rosenthal et al., 1996). The use of hexane for vegetable oil extraction has led to both increased health concerns, and increased environmental regulations. Exposure to hexane has been shown to cause peripheral nerve damage, and hexane is also a potentially hazardous explosive material (Wan and Wakelyn, 1997). In 2001, the U.S. Environmental Protection Agency (EPA) established regulations on hexane emission (EPA, 2001). With rapidly increasing vegetable oil production, it has become more challenging for oilseed extraction plants to meet these regulations (EPA, 2006). Thus, there is a pressing need for development of environmentally-friendly and sustainable oil extraction technologies.

Aqueous-based oil seed extraction methods have advantages over hexane-based extraction, since aqueous extraction can be employed for either dry or wet oilseeds/plants without extensive drying of the starting material. A recently developed alternate approach has employed aqueous surfactant systems to enhance seed oil extraction (Do et al., 2009; Do and Sabatini, 2010; Phan et al., 2010a; Kadioglu et al., 2011). Surfactant-assisted aqueous extraction makes use of interfacial tension reduction between the surfactant solution and the extractable oil, mobilizing the oil

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and allowing it to pass through the disrupted oilseed cell matrix (Campbell and Glatz, 2009; Do and Sabatini, 2010). New classes of surfactants, known as extended-surfactants, are able to produce ultralow interfacial tensions with a wide range of vegetable oils, making them attractive for developing a versatile system for bio-oil extraction that can be used across widely different oilseeds or plants (Salager et al., 2005; Do et al., 2009; Phan et al., 2010a; Witthayapanyanon et al., 2010). Although recent preliminary studies of surfactant-assisted aqueous extraction have shown promising oil extraction results (e.g., 85% extraction efficiency with corn germ oil and over 90% with peanut and canola oils (Naksuk et al., 2009; Do and Sabatini, 2010; Kadioglu et al., 2011)), the fundamental processes controlling the oil release mechanisms have yet to be verified and modeled. To date, the amount of added salt required to achieve good extraction efficiency in aqueous surfactant-based extractions has been relatively high (e.g., 5–10% by weight). High salinity increases potential for corrosion in production equipment, and may lead to more challenging wastewater treatment and disposal scenarios. The need to add significant quantities of salt also can potentially increase cost, all else being equal. Improved surfactant systems will be required to reduce the salinity level. Furthermore, work has not been reported to date examining the use of aqueous surfactant-based extraction methods for extraction of soybean oil. Soybeans have been reported to be among the most challenging oilseeds to extract, due to their high phospholipid content, which can cause stable emulsification of extracted oils, requiring additional processing steps (Owusu-Ansah, 1997; de Moura and Johnson, 2009).

As such, the objectives of the present study were (1) to conduct preliminary tests of the feasibility of aqueous surfactant-based soybean oil extraction using surfactant formulations used in previous studies for extraction of other oilseeds; (2) to explore whether more complex surfactant formulations involving mixed anionic/cationic/nonionic surfactants can reduce salinity requirements for soybean oil extraction; (3) to conduct a preliminary assessment of contributions of system inputs to ultimate extraction efficiency as a starting point for future modeling efforts; and (4) to explore the potential impact of lecithin co-extraction on interfacial tension, with the aim of understanding its likely impact on surfactant solution reuse. The work described here involves a combination of interfacial tension measurements to determine the conditions necessary to create ultralow interfacial tensions with soybean oil (a requirement for high extraction efficiencies), and extraction studies under varying conditions. Parameters affecting extraction results are evaluated with preliminary Box–Behnken experiment design calculations.

The significance of this work is that it takes a critical first step toward development of surfactant-based aqueous methods for soybean oil extraction, providing a proof of concept demonstration of the feasibility of surfactant-based extraction from soybeans, and offering initial insights that will guide future optimization work. The resulting methods should be well suited to meet the rapidly expanding demand for soy-based biofuels and other non-food soybean oil applications.

2. Experimental methods

2.1. Materials

All formulations studied in this work were based on an extended propoxylated-ethoxylated anionic surfactant, $C_{10}PO_{18}EO_2$ sulfate (22.55% active), which was provided by Huntsman Chemical Co. (The Woodlands, TX). The same surfactant has been used previously in studies of the extraction of corn (Kadioglu et al., 2011), peanut and canola oils (Do and Sabatini, 2010, 2011).

Two of the three surfactant formulations studied include the cationic surfactant Arquat HTL8-MS, which was provided by Akzo Nobel (Amsterdam). One surfactant formulation also includes the nonionic surfactant Plantacare 818 UP (50% active), which was provided by Cognis, and the cationic hydrotrope Berol 563 SA (85% active), which was provided by Akzo Nobel. Surfactants and their compositions are listed in Table 1.

Anhydrous sodium chloride (>99.5% purity) used for salinity adjustment was purchased from Sigma–Aldrich (St. Louis, MO). Selected experiments explored the effect of addition of soy lecithin on interfacial tension. Soy lecithin (>99% purity) was purchased from Thermo Fisher Scientific (Waltham, MA). The soybean oil used for interfacial tension measurements was purchased from a local market in Norman, OK. All chemicals were used as received. Soybeans (9E482X) from Midland Genetics (Ottawa, KS) were used for all extraction experiments.

2.2. Methods

2.2.1. Preparation of soy flour

Soy flour was prepared by initial grinding in a nut grinder, followed by processing in a L'Equip (St. George, UT) Nutrimill Grain Mill. The resulting flour was sieved first through a 300 μm sieve, followed by a 212 μm sieve, yielding a flour with a particle size less than 212 μm. This size is comparable to sizes used on the industrial scale, where soybeans are cracked and flaked to approx. 0.2 mm using rolling mills (Campbell and Glatz, 2009; Do and Sabatini, 2010).

2.2.2. Interfacial tension measurement

Interfacial tension measurements were used to assess the abilities of surfactant formulations to produce the ultralow interfacial tensions necessary for effective extraction. Dynamic interfacial tension experiments were carried out using a spinning drop tensiometer (University of Texas, Model 500). Oil droplets 1–3 μL in volume were injected into a 300 μL capillary tube containing the aqueous surfactant solution. Interfacial tensions were recorded at 5 min intervals over the course of 30 min to ensure measurements reflected equilibrium values.

2.2.3. Aqueous oil extraction with surfactant solutions

Soybean flour was added to surfactant solution in 50-mL centrifuge tubes. Samples were placed on a Cole-Parmer (Vernon Hills, IL) Ping-Pong horizontal shaker, model 51504-00. Except where noted, samples were equilibrated on the shaker for 30 min at rates ranging from 100 to 300 rpm. Slurry pH values were monitored and found to be between pH 6.5 and 7 for all experiments. Following equilibration, slurries were centrifuged at 4000 rpm for 30 min in a Thermo Fisher Scientific CL10 centrifuge. After centrifugation, the solid portion was retained and freeze-dried in a Labconco (Kansas City, MO) FreeZone 4.5 freeze dry system for subsequent oil residual analysis. All experiments were conducted in duplicate.

2.2.4. Soxhlet hexane extraction

Hexane extraction of soy flour solids remaining after surfactant-based aqueous extraction (Section 2.2.3) was used to determine the amount of remaining oil, for calculation of aqueous extraction yield. Hexane extraction was also used to determine the initial oil content of the soy flour. Freeze-dried samples (Section 2.2.3) and prepared soy flours (Section 2.2.1) were extracted using hexane in a Soxhlet extraction apparatus following the AOCS Method 948.22 standard procedure (AOAC, 1995). After solvent extraction, excess hexane was evaporated from the extracted oil in a hot air oven at