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Synergistic effect of surfactants and silica nanoparticles on oil recovery from condensed corn distillers solubles (CCDS)

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ABSTRACT

Most of the oil in condensed corn distillers solubles (CCDS) is in an emulsified form and centrifugation alone is not sufficient to recover the oil in high yield. The synergistic effect between non-ionic surfactants (Tween® 80 and Span® 80) and silica nanoparticles (hydrophilic and hydrophobic) on oil recovery was investigated using 3 batches of commercial CCDS. The use of surfactant mixture with Hydrophilic-Lipophilic-Balance (HLB) value of 9.7 led to the highest oil recovery. Tween® 80/silica and surfactant mixture (HLB 9.7)/silica recovered 5–10% more oil compared with the control groups. However, Span® 80/silica was not effective. Surfactant mixture/silica made the oil recovery by centrifugation more efficient by destabilizing oil-in-water emulsion and washing out free oil droplets. The use of surfactant and silica significantly affected the distribution of different types of oil, as well as centrifugation conditions, heating and shaking. About 20% of total oil remained in the unbroken cells or germ pieces in CCDS, which is unrecoverable without additional treatment.

1. Introduction

Condensed corn distiller solubles (CCDS) is produced by evaporating thin stillage in the dry-grind corn ethanol fermentation process. It typically contains 65% moisture, 14% protein and 20% oil on a dry weight basis (Majoni et al., 2011). The oil recovery from corn fermentation has seen an impressive growth in recent years due to the thriving ethanol process and the need from biofuel industry to increase revenue. Distillers corn oil usage had 62% growth for biodiesel in 2013 and 105% growth in 2012 compared to the previous years (Scott and Weber, 2014).

Dried distillers grain with solubles (DDGS) is used as animal feed which is a dried blend of CCDS and wet cake from decanting operation. However, it has been reported that the high residual oil in DDGS may interfere with milk production in dairy cattle and lead to undesirably soft pork belly in swine (Wang et al., 2009). In this case, recovery of oil from CCDS is desirable for the dry-grind fermentation industry to make a low-fat content DDGS. The recovered oil can either be added to enrich DDGS for animals having high energy requirement or used to make biofuel. Such practice will make the dry-grind fermentation product more flexible and the fermentation process more profitable.

CCDS is a viscous mixture which contains protein, lipid, fine fiber and residual starch (Kim et al., 2007). It is relatively stable under ambient temperature but cold storage will induce phase separation. There are four possible forms of oil in the CCDS based on preliminary study and understanding (Majoni et al., 2011): (1) protein and phospholipid stabilized oil-in-water emulsion, (2) small oil droplets that are bound to hydrophobic particles or surface, (3) oil bodies in the unbroken corn particles, and (4) oil bodies released from broken cells. Centrifugation is a common means to separate oil from CCDS in corn fermentation industry (Moreau et al., 2012), but the complex interaction of oil with other components makes this method inefficient in recovering the total oil. Thus, several types of chemical demulsifying aids are currently used in corn-based ethanol plants.

Chemical aid is easy to use and relatively effective in improving oil recovery from CCDS. A number of demulsifiers have been designed for oil recovery from corn stillages, including FoodPro SA9843 corn oil yield improver (General Electric, Trevose, PA, USA), PTV M-5309 corn oil extraction aid (Ashland Chemical, Covington, KY, USA), Ashland DPI-428 (Ashland Hercules Water Technologies, Wilmington, DE, USA), and Hydri-Maize Demulsifier 300 (Hydrite Chemical Co., Waterloo, IA, USA). Such additives include alcohol-based compounds (Gallop et al., 2012), polymeric materials (Scheimann and Kowalski, 2009), and surfactants (Sheppard

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Abbreviations: CCDS, condensed corn distillers solubles; DDGS, dried distillers grain with solubles; HLB, hydrophilic-lipophilic-balance.

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et al., 2012). Addition of solid particles as an optional aid was mentioned in an US patent 20120245370 (Sheppard et al., 2012). However, detailed composition of commercial demulsifier packages and mechanism of action are lacking.

Solid particles can be used as a demulsifying agent, but it has a different mechanism of action than that of surfactants. Theoretically, the solid particles can be partially wetted by both phases in an emulsion and the preferred emulsion type is determined by the wet preference for hydrophilic or hydrophobic phase (Binks, 2002). The contact angle of the solid particle on emulsion interface is equivalent to HLB value of surfactant. Different from surfactants, which stabilize emulsions by reducing the oil-water interfacial tension, the solid particles affect the stability by providing a steric barrier at the interface and changing the rheological properties of the emulsions and interfaces (Binks, 2002). The use of mixtures of surfactants and particles for demulsification has attracted attention for possible synergistic interactions (Nesterenko et al., 2014). By adsorbing onto solid surface, surfactant molecules can transform a hydrophilic surface to a hydrophobic one and vice versa, or a charged surface to an uncharged one (Kwok et al., 1993).

Studies examining the interactive effect of surfactants and particles on emulsion stability in food and petroleum applications have been reported (Binks and Rodrigues, 2007; Tambe and Sharma, 1993; Drelich et al., 2010). However, no research has been seen to investigate the interactive behavior between surfactants and solid particles when they are blended together as an enhanced demulsifier (a term coined by industry as a de-emulsifying agent), and the demulsification behaviors of this mixture has not been systematically studied.

The objectives of this research were to understand the synergistic effect between surfactants (Tween® 80 and Span® 80) and silica nanoparticle (hydrophilic and hydrophobic) on corn oil recovery from CCDS, and to investigate the distribution of different types of oil in CCDS as affected by oil recovery treatments.

2. Materials and methods

2.1. Condensed corn distillers solubles (CCDS)

Three batches of CCDS were obtained from LincolnWay Energy (Nevada, IA) at three different times within a year, and they were stored in a walk-in refrigerator at 4 °C and used as quickly as we could. Small amount of sodium azide was added to prevent mold and bacteria growth. Commercial CCDS typically contains 65–73% moisture, 15–22% fat and 18–22% protein (dry weight basis).

2.2. Chemicals and other materials

A hydrophilic non-porous silica nanoparticle, 6808NM, and a hydrophobic silica nanoparticle, 6864HN were purchased from SkySpring Nanomaterials Inc (Houston, TX, USA). The hydrophilic nanoparticle 6808NM has 20 nm particles size and unmodified natural surface. The hydrophobic silica nanoparticles 6864HN has 10–20 nm particle size and has chemically treated superhydrophobic surface. Hexanes, Span® 80 (sorbitan monooleate), Tween® 80 (polysorbate 80), hydrochloride acid, sucrose, sodium chloride and 100% pure cotton cheesecloth were purchased from Fisher Scientific (Fairlawn, NJ, USA).

2.3. CCDS characterization

Total oil content, solid content and particle size distribution were measured for the 3 batches of CCDS. Total oil content was determined by acid hydrolysis method (AOAC, 1992), and it was used as the base to calculate oil recovery. Solid content was determined by weight difference after oven-drying at 105 °C for 5 h. The particle size distribution profiles of the 3 batches CCDS were determined by using a Mastersizer-2000 particle size analyzer (Malvern Instruments Ltd., Worcestershire, UK) with a wet module (Hydro 2000). The CCDS sample was diluted with DI water to an obscuration range of 11–14% as recommended by the manufacturer.

Table 1
HLB values of surfactant mixtures used in this study.

Surfactants (w:w)	HLB value
Span® 80, 100%	4.3
Span® 80: Tween® 80 (4:1)	6.4
Span® 80: Tween® 80 (2:1)	7.8
Span® 80: Tween® 80 (1:1)	9.7
Span® 80: Tween® 80 (1:2)	11.3
Span® 80: Tween® 80 (1:4)	12.9
Tween® 80, 100%	15.0

HLB values of Span® 80 and Tween® 80 were provided by producer; HLB value of surfactant mixtures were calculated by the equation in Section 2.4.

2.4. Effect of surfactant HLB on oil recovery from CCDS

Surfactants with different HLB values were obtained by mixing Span® 80 and Tween® 80 at following ratios by weight: Span® 80 to Tween® 80 ratio of 1:0, 4:1, 2:1, 1:1, 1:2, 1:4, and 0:1. The HLB value of the blend was calculated by using the following equation:

$$\mathrm{HLB}_a \times \mathrm{R}_a + \mathrm{HLB}_b \times R_\mathrm{b} = \mathrm{HLB}_t \text{ (ICI American, 1984),}$$

Where “*a*” is surfactant a; “*b*” is surfactant *b*; R is ratio by weight of surfactant *a* or surfactant *b*; and *t* is combined surfactant mixture.

The HLB values of resulting surfactant mixtures are shown in Table 1. Surfactant mixture of 0.04 g was mixed with 40 g of CCDS (equivalent to 1000 ppm) in a 250 mL centrifuge bottle. This application level was chosen based on the suggested dosage of commercial demulsifiers at 500–1500 ppm in CCDS. All samples were placed in a shaking water bath (Model R-76, New Brunswick Scientific Co. Inc., NJ, USA) at 80–85 °C for 10 min with 100 rpm shaking speed. Immediately following heating and shaking treatment, oil separation was completed by using a Centra MP4 centrifuge (International Equipment Company, Needham Heights, MA, USA) at 3000 × g for 10 min. The top free oil was transferred by washing the top surface of liquid with hexane (5 times of washing of top layer using 20, 20, 10, 10, 5 mL hexanes at each time). Removal of solvent was completed using an air stream at 90 °C. Residual solvent was removed by using an Isotemp oven (Fisher scientific, Fairlawn, NJ, USA) at 110 °C for 1.5 h. The weight of the oil was determined gravimetrically. Two replicates were applied for each of the three batches of CCDS.

2.5. Synergistic effect between surfactants and silica nanoparticles on oil recovery from CCDS

Surfactants, including Tween® 80, Span® 80 and Tween® 80/Span® 80 mixture at 1:1 ratio (M), were mixed with hydrophilic silica nanoparticles, or hydrophobic silica nanoparticles at 2.5, 5, 7.5, 10, 12.5% w/w of silica concentration in surfactant. The nanoparticles were dispersed in surfactant by using sonication at 30% power (Misonix Sonicator 3000, Farmingdale, NY) for 15 min and followed by mixing with magnetic stirrer overnight. Then, 0.04 g mixture of silica and surfactant was added into 40 g CCDS in 250 mL centrifuge bottle to give 1000 ppm concentration. All samples were placed in a shaking water bath, at 80–85 °C for 10 min with 100 rpm shaking speed. The oil separation procedure was the same as Section 2.4.