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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.

Keywords

Condensed corn distillers solubles (CCDS), oil distribution, oil recovery, silica nanoparticle, Span® 80, synergistic effect, Tween® 80.

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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 distribution of different types of oil was significantly affected by centrifugation conditions, heating, shaking, and surfactant and silica addition. About 20% of total oil remained in the unbroken cells or germ pieces in CCDS, which is unrecoverable without additional treatment.

Keywords: Condensed corn distillers solubles (CCDS), oil distribution, oil recovery, silica nanoparticle, Span® 80, synergistic effect, Tween® 80.

Highlights:

- The use of Tween® 80/Span® 80 mixture led to highest oil recovery at ratio 1:1, w:w;
- Synergistic effect between surfactant and silica nanoparticles was demonstrated;
- CCDS properties contributed to the oil recovery performance;
- Processing treatments, including centrifuge, heating, shaking and demulsifier addition, significantly affected distribution of different types of oil in CCDS.

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 et al., 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 the oil from CCDS is desirable for dry-grind fermentation industry to make a low fat content DDGS. The recovered oil can be either adding back to DDGS for animal having specific energy requirement or making biofuel. That will make the dry-grind fermentation product more flexible to be used and more profitable for the producers.

CCDS is a viscous mixture which contains protein, lipid, fine fiber and residual starch (Kim et al, 2007). 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 et al., 2009), and surfactants (Sheppard 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, and the demulsification behaviors of this mixture has not been systematically studied yet.

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. These three batches of CCDS 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 6864 HN has 10-20 nm particle size and has chemically treated super-hydrophobic 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.

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:

$$HLB_a \times R_a + HLB_b \times R_b = HLB_t \text{ (ICI American, 1984),}$$

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 xg 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.

2.6 Effects of treatments on distribution of different types of oil in CCDS

The CCDS samples were treated by different treatments (Table 2), including different centrifuge force (3000 xg and 4000 xg), heating (85°C) and shaking (100 rpm), and demulsifier (Tween® 80/Span® 80 mixture at 1:1 ratio with 2.5% hydrophilic silica). The effects of these treatments on the distribution of different types of oil in CCDS were evaluated with the following method.

The method for separating different types of oil in CCDS was adapted based on Kapchie and others' work (Kapchie et al., 2008). CCDS of 10 g was mixed with 7 mL NaCl-sucrose solution

(1M NaCl and 0.8M sucrose) in a 50-mL centrifuge tube. The mixture was shaken gently by hand for 15 s and was centrifuged at 4000 xg for 30 min to separate the different types of oil as illustrated in Figure 1. Four layers were formed after centrifugation, including free oil, oil body, oil-in-water emulsion and solid residue, and the free oil in this section was the same with “total oil recovery” in other sections. The top free oil was removed by hexane washing (4 times with 5 mL for each time). Following hexane washing, the oil body (fat pad) and oil-in-water emulsion was filtered by using 4 layers cheesecloth. The residue on cheesecloth was oil body which was transferred into a 250-mL Erlenmeyer flask together with one layer of cheesecloth. The liquid fraction was oil-in-water emulsion and remained in a 250-mL Erlenmeyer flask. The solid residue in centrifuge tube was transferred into a 250-mL Erlenmeyer flask with water. The total oil content in oil body, oil-in-water emulsion and solid residue were determined by the acid hydrolysis procedure (AOAC, 1992). The amount of oil in free oil layer was measured gravimetrically after removing solvent.

2.7 Statistical Analysis

Significant differences among treatments were tested by using the statistical analysis software IBM SPSS statistics 19 (Armonk, NC, USA) and One-way analysis of variance (ANOVA). The Least significant differences (LSD) were calculated at $P = 0.05$.

3 Results and Discussion

3.1 CCDS characteristics

For the different batches of CCDS, solid content ranged from 27 to 30%, total oil contents ranged from 17 to 24% on dry weight basis as shown in Table 3. Particle size distributions of the 3 batches CCDS are shown in Table 5. The third batch of CCDS had significantly smaller

particle size and more particles distributed under small particle size than the first and second batches of CCDS. The second batch CCDS had no significant difference from the first batch CCDS. However, a numerically smaller particle size of second batch CCDS was found comparing with that of the first batch.

3.2 Effect of CCDS characteristics on oil recovery

No relationship was found between total oil content and oil recovery in these three batches of CCDS (Table 3). The third batch of CCDS had the lowest oil content but the highest oil recovery. The first batch had similar total oil content but significantly lower oil recovery compared to the second batch.

However, oil recovery may relate to the average particle size and particle size distribution in CCDS. The first batch of CCDS had a larger average particle size and followed by the second batch of CCDS, and the third batch of CCDS had the smallest particle size. Unlike the demonstrated effect of corn meal particle size on corn fermentation and oil recovery, for which the smaller meal size did not help oil recovery from fermentation beer (Wang et al., 2009), the smaller particle size of the CCDS related to higher amount of oil recovered. Part of corn oil and oil body in CCDS was trapped in unbroken germ cells, and attached to broken cell wall or corn protein complex (Majoni et al., 2011). When the particle size was reduced, the size of these complexes may have been reduced and released the trapped oil.

3.3 Effect of surfactant HLB on oil recovery from CCDS

The optimal HLB value for demulsifying CCDS was investigated. Non-ionic surfactants, Tween® 80 and Span® 80 used in various ratios gave a set of different HLB values of the resulting surfactant mixtures. The HLB value had significant effect on oil recovery from CCDS as shown in Figure 2. In first batch of CCDS, the oil recovery was increased when the HLB

value was increased from 4.3 to 9.7 and decreased when HLB was higher than 9.7. A similar trend was found in the second batch of CCDS but not in the third batch. The third batch of CCDS had significantly higher oil recovery (72%) than the first (55%) and the second (65%) batches of CCDS when no surfactant was added, which may weaken the effect of surfactant due to less extra recoverable oil in CCDS. Rondon et al (2006) reported an observation in a demulsifying water-in-oil emulsion study, and indicated that the optimum demulsifier formulation was the surfactant mixture having the same affinity for both hydrophilic and hydrophobic phases. Our HLB of 9.7 being the best agreed with this observation.

The HLB value is an empirical scale which intends to describe the balance of the hydrophilic and lipophilic groups of a surfactant (Rondon et al., 2006). Based on emulsifier's performances in making emulsion, it is widely accepted that $HLB < 8$ indicates a hydrophobic compound that results in a water-in-oil emulsion. On the other hand, if a surfactant's HLB is greater than 12, it is a hydrophilic surfactant and will best form an oil-in-water emulsion. Moreover, a systematic research by Boyd et al (1972) indicated that there is a minimum HLB for stability of oil-in-water emulsions, which is about 10. In our system, protein is the major stabilizer for oil-in-water emulsion in corn fermentation co-product, CCDS. Surfactant is very surface active and can replace a portion of protein on the emulsion interface (Wilde et al., 2004). However, surfactant with HLB 9.7 is not a good emulsion stabilizer, instead, it breaks the emulsion and release the oil after replacing a portion of protein on the emulsion interface. The finding from this optimization experiment provides new information to the industry in modifying their current use of Tween® 80 demulsifier, i.e., to make it more hydrophobic for achieving the best oil recovery.

3.4 Synergistic effect between surfactant and silica nanoparticle on oil recovery from CCDS

Commercial demulsifying agents may contain hydrophobic solid particles, such as hydrophobic silica and wax particles, probably due to the synergistic effect between them (Sheppard et al., 2012). However, no evidence has been shown that hydrophilic silica cannot work when mixed with surfactant. Therefore, we conducted a systematic study to investigate the interaction between surfactant and silica nanoparticles for their effect on oil extraction.

As shown in Figure 3, Tween® 80 had significantly synergistic effect with both hydrophilic and hydrophobic silica in oil recovery. However, this effect was influenced by CCDS characteristics. The oil recovery was significantly improved when Tween® 80 and silica (of both hydrophilic and hydrophobic) mixture was added in the first and the second batch of CCDS. No effects of silica concentrations were found when Tween® 80 mixed with hydrophilic or hydrophobic silica was used for the third batch CCDS. Due to the high oil recovery in the control of the third batch of CCDS, only a numerical but not significant increase was found.

No significant synergistic effect was found between Span® 80 with either hydrophilic or hydrophobic silica as shown in Figure 4, except for Span® 80 and hydrophobic silica in first batch CCDS, which had significant improvement only when >7.5% silica concentrations were used. Nonetheless, Span® 80 was not as effective as Tween® 80 at the same conditions.

Synergistic effect was found in both surfactant mixture (1:1)/ hydrophilic silica and surfactant mixture (1:1)/ hydrophobic silica as shown in Figure 5. Addition of surfactant mixture can significantly improve oil recovery compared to the control group, except for the third batch. The consistent (low standard deviation) and significant increases were observed in most of CCDS samples when hydrophilic silica or hydrophobic silica were added comparing with

surfactant alone. However, increasing silica concentration in surfactant did not help in recovering more oil.

The mechanism of surfactant destabilizing the protein-stabilized emulsion is reported in literatures. Protein forms a viscoelastic layer which can influence the stability of emulsions (Murray and Dickinson, 1996). A higher concentration of protein on the interfacial surface contributes to a stronger interaction among protein molecules and this interaction affects the stability of protein stabilized emulsion (Mackie et al., 1999). Low-molecular weight surfactants are often more surface-active than proteins and will, therefore, compete for a position on interfacial surface with protein (Wilde et al., 2004). CCDS contains 14-18% protein and these proteins stabilize the interface of oil-in-water emulsion in CCDS (Majoni et al., 2011). When surfactants are added in CCDS, they compete with protein on the oil-in-water interfaces and partially replace the protein and break the protein-protein interaction to release oil from the emulsion.

Span® 80 and its mixture with silica did not work as well as the other surfactant and combinations did. The type of interaction between Span® 80 and protein on the emulsion interface may play an important role. Cornec et al. (1996) reported that β -lactoglobulin had less possibility to be replaced by Span® 80 on emulsion interface compared with β -casein, which is more hydrophilic than β -lactoglobulin. Moreover, protein on interface was easier to be displaced by surfactant with large hydrophilic head group, such as Tween 20 (Cornec et al., 1996). Corn zein protein is a hydrophobic protein (Argos et al., 1982), and it comprises 45-50% of the protein in corn (Shukla and Cheryan, 2001). Span® 80 may tend to adsorb on the hydrophobic zein protein but not replace it. More hydrophilic surfactant is needed to replace hydrophobic proteins more efficiently as discussed by Cornec et al. (1996).

Silica nanoparticle addition significantly improved oil recovery comparing with Tween® 80 and surfactant mixture alone. That may be attributed to the similar function of hydrophobic oil and solid particle in anti-foaming action. In an anti-foaming research, Koczko et al. (1994) suggested that solid particle or hydrophobic oil alone has much lower penetration ability on emulsion interface than a mixture of these two. Denkov (1999) also suggested an “oil bridge model” to explain the hydrophobic oil and silica combination on anti-foaming. The silica particle can increase the penetration depth of hydrophobic oil in the lenses and the formed oil bridge is unstable which makes the foam break. Foam is air-in-water system which is very similar to oil-in-water emulsion, and the surfactant/silica combination may play a similar role in breaking oil-in-water emulsion. With the presence of silica nanoparticle, surfactant may penetrate the interface and replacing protein more efficiently. When the surfactant replaces the position of a protein on the interface, a “surfactant bridge” which is similar to “oil bridge” in anti-foaming may be formed. This surfactant bridge with the particles imbedded in is unstable which would break the emulsion.

However, results from this study seemingly will not explain why the same surfactant mixture had synergistic effect with both hydrophobic and hydrophilic silica, and thus led to similar oil recovery improvements when used in CCDS. Our speculation is that since the surfactant mixture is 1:1 ratio of the highly hydrophobic and highly hydrophilic compounds, such a mixture would work well with either hydrophobic or hydrophilic particles. The interactions would be similar, only that an opposite orientation or arrangement of molecules or particles on the interface would occur. Further study is needed to explain this phenomenon.

It's worth mentioning that we also tested our Tween® 80 combined with 5% hydrophilic silica nanoparticles in comparison to one of the commercial products, a demulsifier package (the

name cannot be revealed) mentioned in the introduction section. Both of the agents were used in 1000 ppm concentration in CCDS. The oil recovery from these two treatments are statistically the same, and they were much higher than the two controls, which were CCDS alone and with Tween® 80 addition alone.

3.5 Effects of treatments on distribution of different types of oil in CCDS

Results presented in above sections and that obtained during preliminary experiments indicated that oil in CCDS cannot be recovered fully, i.e., 100%. Depending on the batch of CCDS, about 25- 35% of total oil was not extracted. Therefore, we wanted to investigate the forms of oil present in CCDS and how our treatments affect the distribution of various forms of oil.

The three batches of CCDS had significantly different amount of free oil and oil-body distribution, but they had similar oil-in-water emulsion and oil-in-solid distribution when they were treated at same condition without the use of surfactant and silica, as shown in Figure 6. The third batch of CCDS had the highest free oil content and lowest oil body content, and the first batch of CCDS had the lowest free oil content and highest oil body content. This result paralleled with oil recovery in control groups of three batches of CCDS, which had the highest oil recovery in the third batch and the lowest in the first batch. Moreover, particle size distribution may also relate to the free oil and oil body proportion change among batches of CCDS.

Different treatments, including temperature, shaking, surfactant and silica addition and centrifugation condition, had significant effect on oil distribution in CCDS as shown in Figure 6. The first and second batch of CCDS were chosen for this experiment due to its appropriate oil body and free oil content. When there was no heating and shaking and surfactant and silica applied, increasing centrifuge condition from 3000 xg, 10 min to 4000 xg, 30 min significantly

improved free oil recovery and decreased oil-in-water emulsion, but no significant difference was found in oil body and oil in solid content. When 83° C heating with 100 rpm shaking for 10 min was applied before 3000 xg and 10 min centrifugation, free oil content was significantly improved, and other three types of oil contents were significantly decreased comparing with 3000 xg and 10 min centrifugation alone. This indicates heating is very effective in breaking the emulsion and oil body. When surfactant mixture (1:1, w: w, HLB 9.7) was added during heating and shaking, the free oil recovery was significantly increased again and oil content in emulsion and solid were further decreased. This indicates surfactant and silica is effective in improving free oil recovery.

Higher centrifugation force and longer centrifugation time can break the oil-in-water emulsion in CCDS at room temperature, but they can't affect oil body stability due to the special structure of oil body which is stabilized by phospholipid layer and protein (Iwanaga et al., 2007). However, the oil body in CCDS became extremely unstable after heating and shaking treatment. The treatment conditions for CCDS in ethanol plants, including 80~85° C temperature, pump transferring, blending and centrifugation of CCDS, may be already sufficient for breaking oil body. It is non-necessary to add any extra additives or steps in current dry-grind corn ethanol fermentation procedure for breaking oil body. Surfactant and silica mixture addition further improved oil recovery by breaking residual emulsion and washing out small oil droplets which are attached on the surface of cell debris. Moreover, we found there was still 25~ 35% corn oil in CCDS that cannot be recovered in this work, and this part of oil may be trapped in a protein and unbroken cell complex which was not accessible to the surfactant and silica particles. Further study should be conducted to focus on this part of trapped oil in corn fermentation.

It should be noted that the free oil recovery of 70.4% from treatments 3000 xg centrifugation plus heating and shaking, and that of 75.1% from 3000 xg centrifugation plus heating and shaking, and surfactant and silica use, were higher than oil recovery from same treatments in synergistic study of this report. This may be caused by the effect of storage on CCDS stability. The heterogeneous CCDS is a dynamic system, and precaution has to be made to prevent system destabilization. In our study, a complete set of treatments was applied to the same CCDS, so that proper conclusion on treatment effect can be drawn.

4 Conclusion

The optimal HLB value for demulsifying CCDS was about 9.7. Tween® 80 and surfactant mixture (HLB of 9.7) had synergistic effect with both hydrophilic and hydrophobic silica nanoparticles, and they significantly improved oil recovery. However, Span® 80 did not show these effects. Different treatments, including heating and shaking, surfactant and silica addition and centrifugation condition, had significant effect on distribution of different types of oil in CCDS. Comparing with conventional centrifugation method to recover oil, the use of surfactant and silica particle combination led to 5~10% more extracted oil depending on CCDS conditions. Although the synergistic effect between surfactant and silica nanoparticle was investigated for oil recovery from CCDS, this technology will have potential to be applied to other systems where there is a need to break oil-in-water or water-in-oil emulsions.

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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.

Table 2. Conditions used to study effects of processing on distribution CCDS oil

Treatment	Heating and shaking	Demulsifier	Centrifugation condition
4000 xg	No	No	4000 xg, 30 min
3000 xg	No	No	3000 xg, 10 min
3000 xg+ HS	Yes	No	3000 xg, 10 min
3000 xg + HS + D	Yes	Yes	3000 xg, 10 min

HS: Heating and Shaking; D: Mixture of Span 80 and Tween 80 at ratio by weight 1:1, with 2.5% hydrophilic silica addition

Table 3. CCDS characteristics and oil recovery

CCDS	Total solid content	Total oil content (dry weight basis)	Particle size distribution				Oil recovery
			D(0.1)	D(0.5)	D(0.9)	Volume weighed mean	
1 st batch	28.38 ± 0.97 A	22.06 ± 0.88 A	4.28 ± 0.05 B	22.26 ± 0.65 AB	420.97 ± 38.45 A	119.07 ± 8.16 A	56.27 ± 1.40 C
2 nd batch	26.88 ± 0.38 B	23.51 ± 0.63 A	4.20 ± 0.04 C	23.19 ± 0.74 A	388.41 ± 39.73 A	114.03 ± 8.47 A	66.17 ± 3.04 B
3 rd batch	29.51 ± 0.87 A	17.38 ± 0.25 B	4.72 ± 0.06 A	21.55 ± 0.63 B	296.12 ± 50.13 B	92.95 ± 8.94 B	73.12 ± 0.71 A

Data sharing the same letter in the same column did not have significant difference ($P>0.05$). D (0.1) is the diameter where 10% of the distribution is below; D (0.5) is the diameter where 50% of the distribution is below; D (0.9) is the diameter where 90% of the distribution is below. Oil recovery data in this table was collected from no surfactant and silica added group.

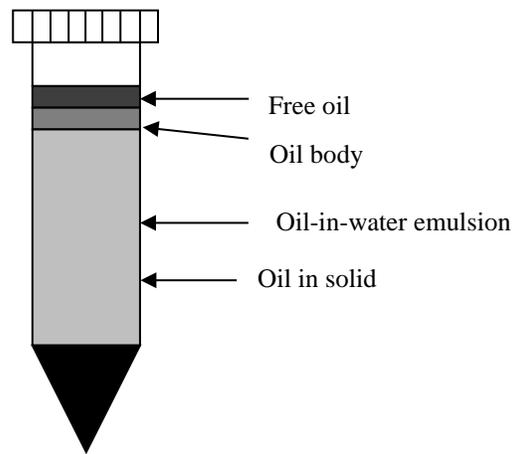


Figure 1. Separation of different types of oil after centrifugation

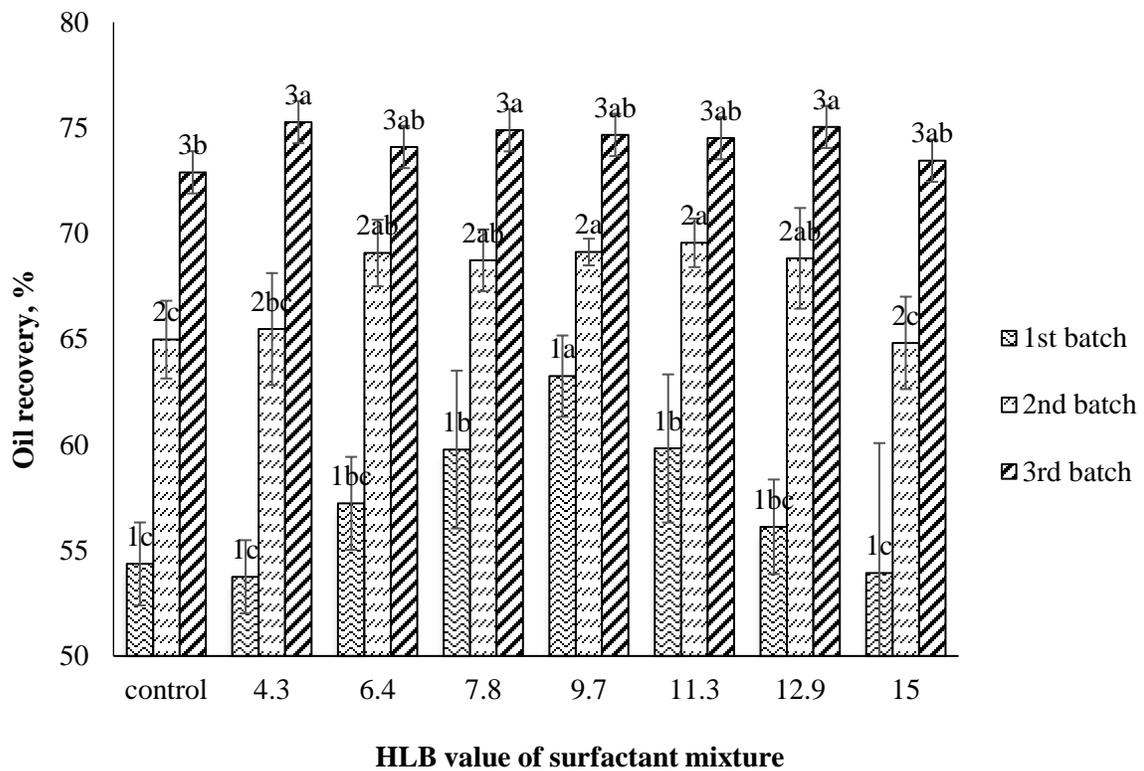


Figure 2. Effect of surfactant HLB value on oil recovery from the 3 batches of CCDS. Data sharing the same letter in the same batch of CCDS did not have significant difference ($P > 0.05$).

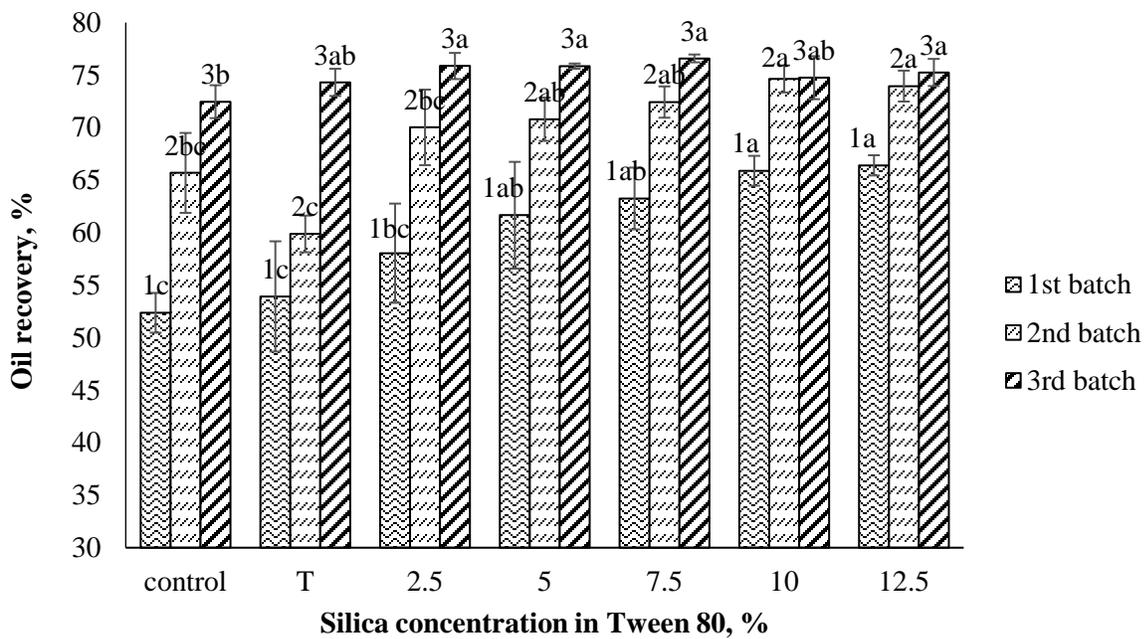
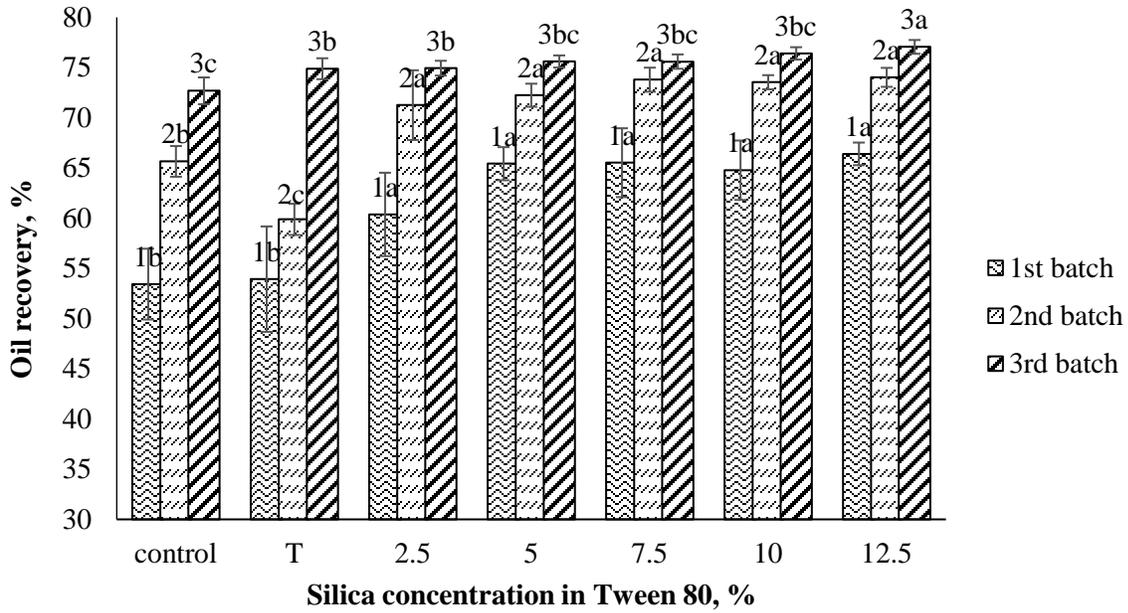


Figure 3. Synergistic effect of Tween® 80/ hydrophilic silica (upper chart) and Tween® 80/hydrophobic silica (lower chart) on oil recovery from the 3 batches of CCDS. T is Tween® 80 alone. Data sharing the same letter in the same batch of CCDS did not have significant difference ($P > 0.05$).

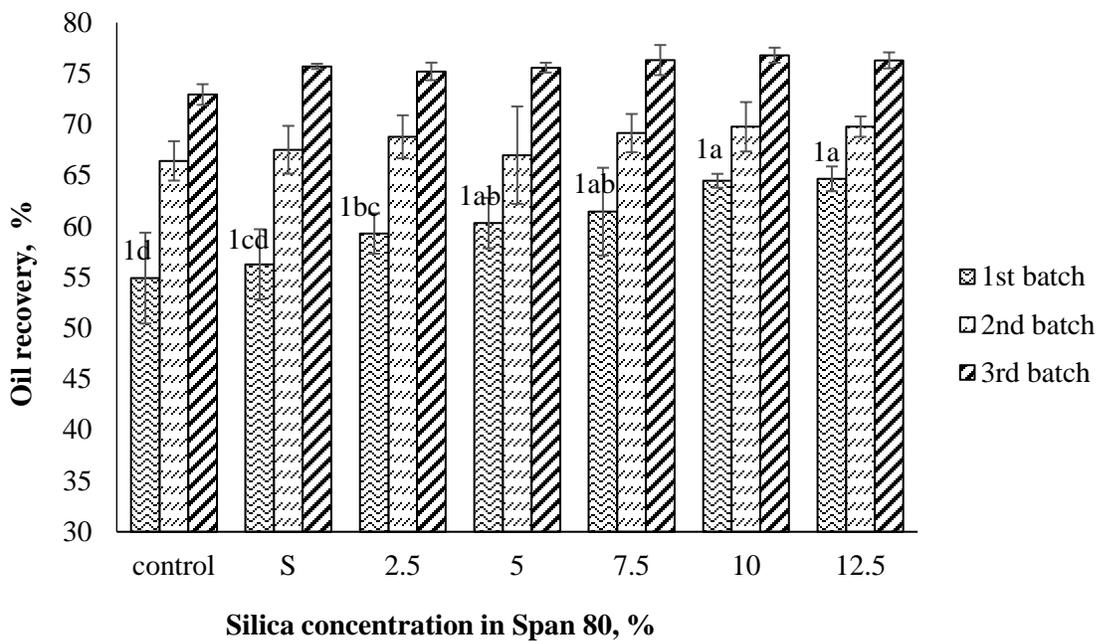
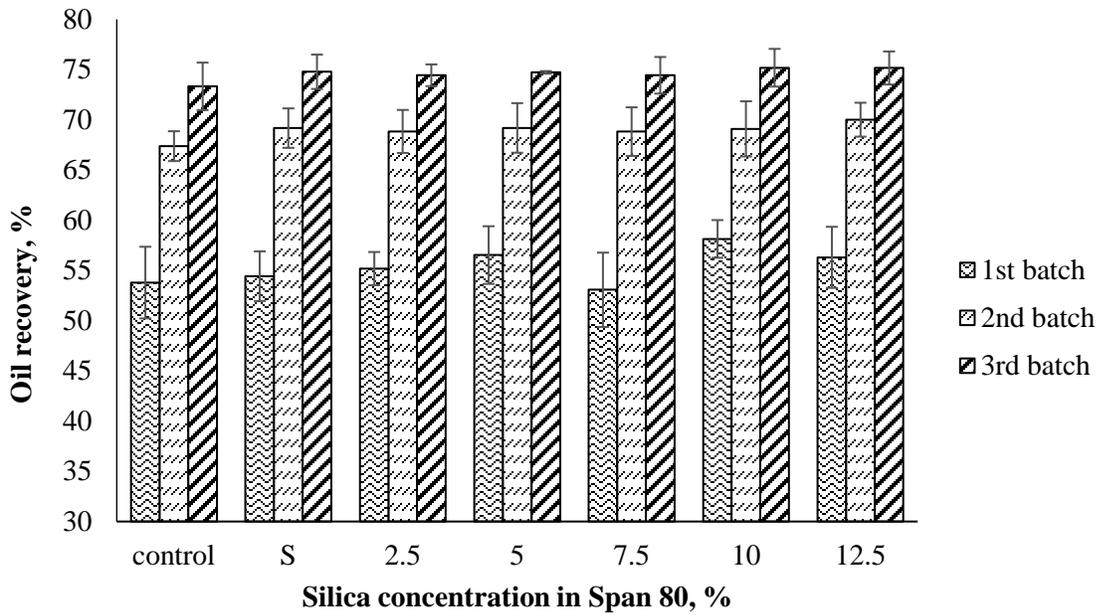


Figure 4. Synergistic effect of Span® 80/ hydrophilic silica (upper chart) and Span® 80/ hydrophobic silica (lower chart) on oil recovery from 3 batches of CCDS. S is Span® 80 alone. Data sharing the same letter in the same batch of CCDS did not have significant difference ($P > 0.05$).

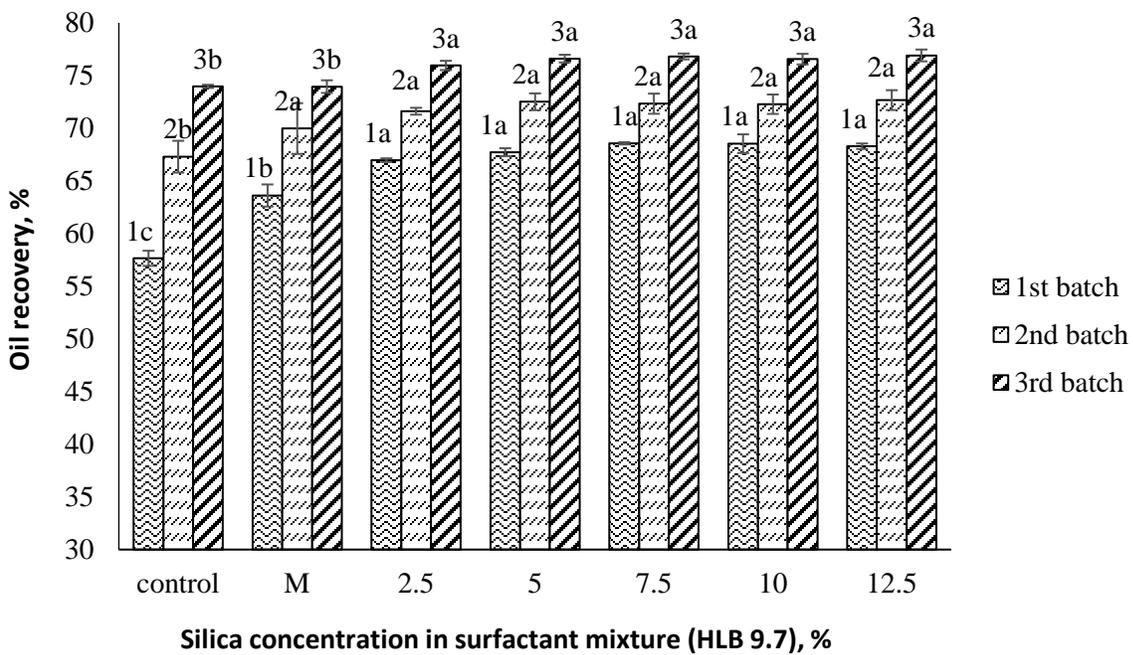
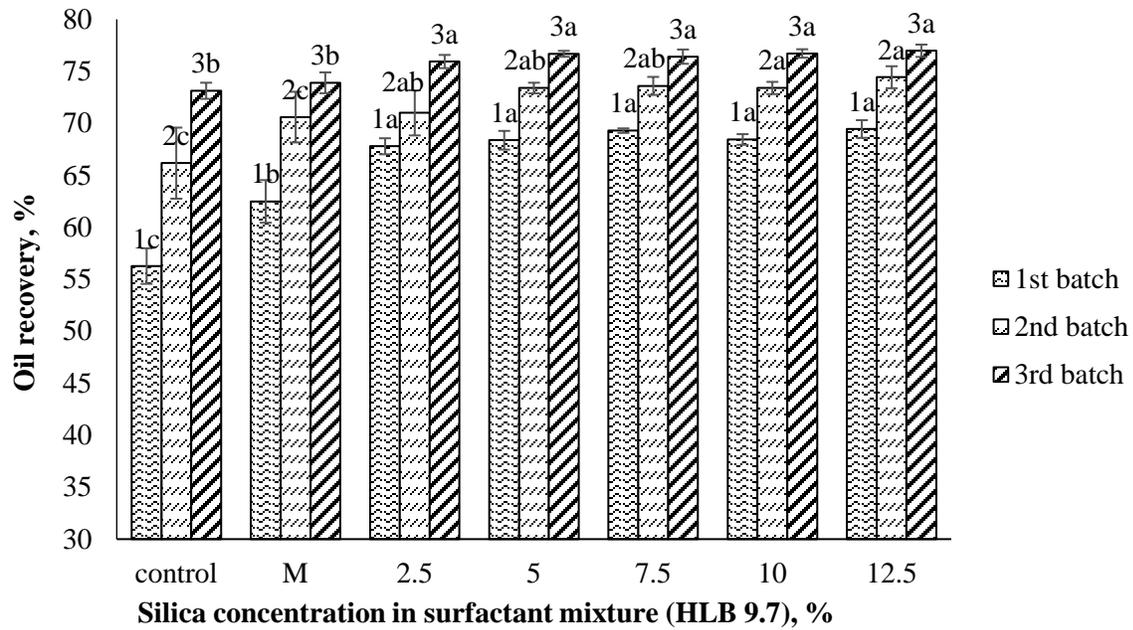


Figure 5. Synergistic effect between surfactant mixture (HLB 9.7)/ hydrophilic silica (upper chart) and surfactant mixture (HLB 9.7)/ hydrophobic silica (lower chart) on oil recovery from 3 batches of CCDS. M is surfactant mixture (HLB 9.7) alone. Data sharing the same letter in the same batch of CCDS did not have significant difference ($P > 0.05$).

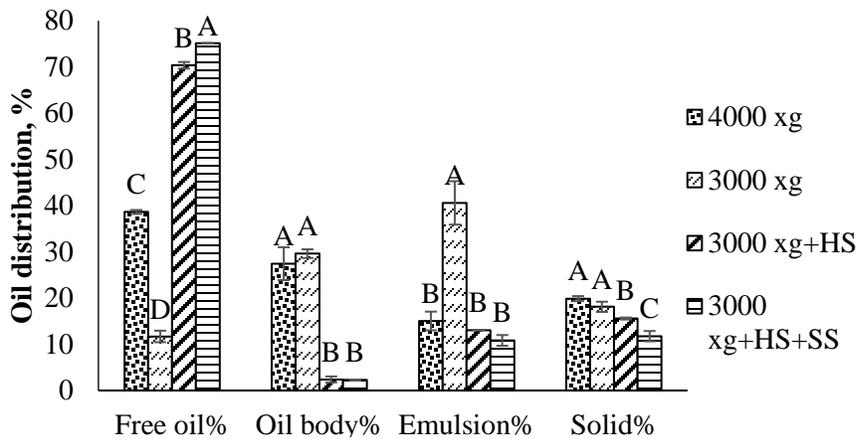
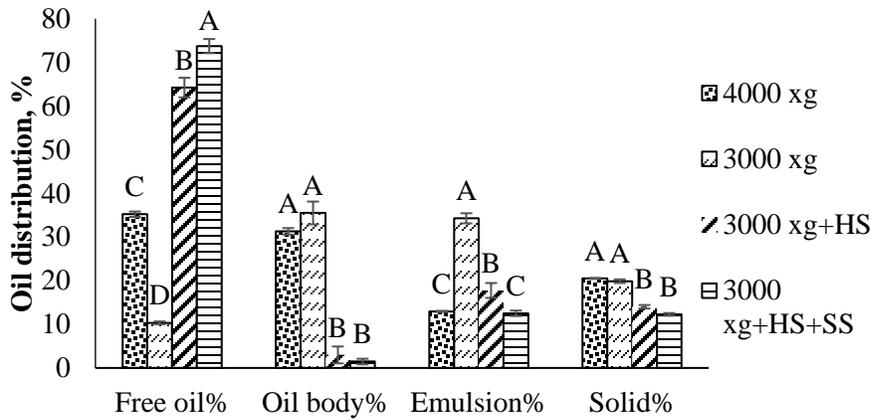
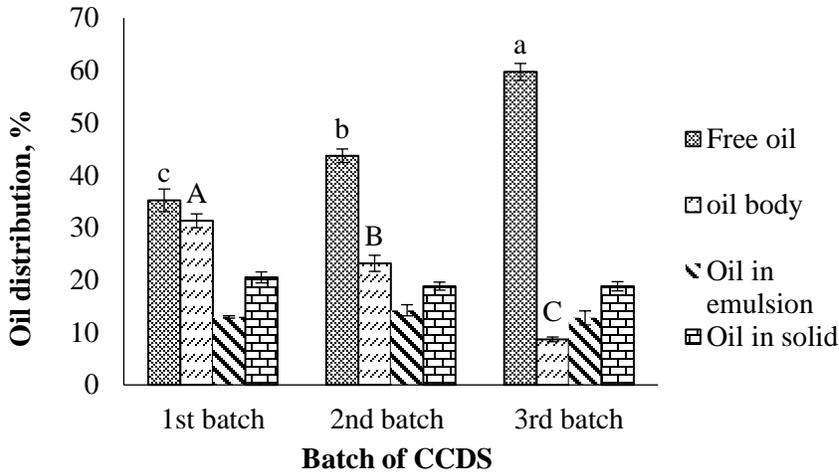


Figure 6. Oil distributions in the 3 batches of CCDS after 4000 xg, 30 min centrifugation (upper chart) and effect of treatments on distribution of difference types of oil in first (middle chart) and second batch (bottom chart) of CCDS. 4000 xg is centrifugation at 4000 xg for 30 min; 3000 xg is centrifugation at 3000 xg for 10 min; HS is heating and shaking; SS is Tween® 80/Span® 80 mixture at 1:1 ratio with 2.5% hydrophilic silica . Data sharing the same letter in the same oil type did not have significant difference ($P>0.05$).