Acetylation of corn distillers dried grains

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This paper shows that acidic conditions provide substantially higher % acetyl content, intrinsic viscosity and thermoplasticity even at low ratios of acetic anhydride and catalyst concentrations compared to using alkaline conditions for acetylation of oil-and-zein-free distillers dried grains with solubles (DDGS). Conventional methods of carbohydrate and protein acetylation are unsuitable for acetylating DDGS which is a mixture of carbohydrates and proteins. In this research, methods were developed to simultaneously acetylate the carbohydrates and proteins in DDGS using alkaline and acidic catalysts. The effect of various acetylation conditions on the % acetyl content and intrinsic viscosity of DDGS acetates was studied. Acetylation of DDGS was confirmed using FTIR and 1H NMR and thermal behavior of the DDGS acetates was studied using TGA and DSC. The highest % acetyl content obtained was 28.1% (Degree of substitution (DS) of 1.5) under alkaline conditions using an anhydride to DDGS ratio of 3:1 whereas a much higher % acetyl content of 36.1% (DS 2.1) was obtained under acidic conditions even with a lower anhydride to DDGS ratio of 2:1. DDGS acetates obtained using alkaline catalysts also had higher melting temperature and lower melting enthalpy and hence exhibit poor thermoplasticity compared to the DDGS acetates obtained using acid catalysts.

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1. Introduction

Distillers dried grains (DDG) are the major co-product of corn ethanol production [1]. About 30% DDG are generated as co-product when corn is processed for ethanol. Currently, more than 10 million tons of DDG are generated every year in the USA with a selling price of approximately $150 per ton [2]. The current selling price of DDG is much lower compared to common thermoplastic synthetic polymers such as high density polyethylene, polypropylene and polystyrene that sell at about $1400, $1500 and $2100 per ton, respectively. Even biopolymers such as starch acetate, cellulose acetate and poly (lactic acid) are considerably expensive at about $4800 per ton. Therefore, DDG is a co-product that is available in large quantities at low price. In addition, DDG is derived from a renewable resource, inevitably generated as a co-product without the need for additional land, energy or other resources and products made from DDG will be biodegradable. Using DDG to develop industrial products will also add value to DDG and help to reduce the cost of ethanol. Unfortunately, there is limited use of DDG for industrial applications and animal feed which has limited market and low value addition is currently the major use of DDG.

DDG is a mixture of oil (8–11%), proteins (25–30%) and carbohydrates (35–50%). We have shown that the oil, proteins (zein), cellulose and hemicellulose in DDG can be extracted for various applications [2,3]. Attempts have also been made to develop composites and other products from DDG. The potential of developing biodegradable thermoplastics by chemically modifying (carboxymethylation, glutaration, maleiation) DDG was studied by Schilling [4]. DDG was also used as reinforcement in composites by mixing DDG with phenolic resin and wood glue [5]. All of the above reports have used DDG in its native form to develop products. However, extracting the high value corn oil and zein in DDG and using the oil-and-zein-free DDG for industrial applications would be more economical than using native DDG.

Acetylation is one of the most common chemical modifications used to develop thermoplastics from biopolymers [6–10]. Acetylation is simple, provides products with good properties, uses green chemicals, is relatively inexpensive compared to other chemical modifications and acetylated products will be biodegradable and environmentally friendly. Cellulose and starch, two of the most common biopolymers have been acetylated and used to develop fibers, films, composites and many other products [8,11,12]. Similarly, proteins have also been acetylated to develop thermoplastics and other products [13,14]. The conditions of acetylation such as
concentration of chemicals and catalysts, time, temperature and pH of reaction play a crucial role in determining the efficiency (% acetylation, degree of polymerization) of acetylation and the properties of the products obtained. Conventional cellulose acetylation is performed under acidic conditions whereas starch acetylation is preferably performed under alkaline conditions since starch is reported to be hydrolyzed under acidic conditions [15]. Also, cellulose and starch acetylations are performed at relatively high temperatures (80–120 °C) using acetic anhydride with or without catalysts. It was shown that acetylated wheat straw had % weight gain of 7.8% and 20% when acetylated using acetic anhydride with and without amine catalysts, respectively [16]. However, protein acetylation is performed under mild alkaline (pH 8–8.5) conditions using acetic anhydride at room temperature [13,14]. Since DDGS is a mixture of carbohydrates and proteins, the conventional methods of acetylating carbohydrates and proteins are not suitable for acetylating DDGS. Carbohydrates in DDGS would have poor acetylation if protein acetylation conditions are used whereas proteins would be hydrolyzed if carbohydrate acetylation conditions reported in literature are used. Therefore, it is necessary to develop acetylation conditions that can provide optimum acetylation conditions for both the carbohydrates and proteins in DDGS.

In this research, oil-and-zein-free DDGS was acetylated using alkaline and acidic conditions and the effect of acetylation conditions on the % acetyl content and intrinsic viscosity was studied. The thermal behavior of the DDGS acetates obtained using alkaline catalysts was compared to the properties of DDGS acetates obtained using acidic catalysts. The thermoplasticity of the DDGS acetates was also evaluated.

2. Materials

DDGS was obtained from Abengoa BioEnergy Corporation, York, NE. Reagent grade sodium hydroxide, sulfuric acid, acetic acid, acetic anhydride (98% ACS grade) and other chemicals were purchased from VWR International, Bristol, CT.

2.1. Methods

2.1.1. Preparation of oil-and-zein-free DDGS

Oil and zein was extracted before acetylating the DDGS since the oil and zein are expensive chemicals and suitable for high value industrial applications. To remove oil, the DDGS was Soxhlet extracted using anhydrous ethanol until the DDGS was colorless. The oil-free DDGS was treated with 5:1 ratio of aqueous ethanol (70% w/w) to DDGS at 78 °C for 30 min in the presence of 0.25% (w/w) sodium sulfite as the reducing agent. pH of the mixture was adjusted to about 2 to facilitate the extraction of zein [2,3]. The oil-and-zein-free DDGS had approximate composition of 31.6% hemicellulose, 26.4% cellulose, 22.5% protein, 8.6% starch, ash and lignin accounted for the remaining constituents.

2.1.2. Acetylation of oil-and-zein-free DDGS

2.1.2.1. Acetylation under alkaline conditions. The oil-and-zein-free DDGS was acetylated using acetic anhydride and sodium hydroxide solution (50%, w/w) as the catalyst. Initially, acetic anhydride was added to oil-and-zein-free DDGS (3:1 ratio of anhydride to DDGS) and allowed to react for 60 min at room temperature. After the reaction, saturated sodium hydroxide (50% w/w in water) was added (10–100% w/w, based on weight of DDGS) as the catalyst maintaining the DDGS between –5 °C and +5 °C using an ice bath for 30 min. The acetylation reaction was then completed by heating the DDGS mixture for a specific time (10–120 min) at a specific temperature (90–130 °C). For temperatures above 100 °C, the reaction was performed in sealed high pressure canisters using an oil bath. After the reaction, cold water was added into the canister to precipitate the acetylated products. The products were later thoroughly washed until they were neutral.

2.1.2.2. Acetylation under acidic conditions. Acetylation under acidic conditions was performed using sulfuric acid as the catalyst and varying the ratio of anhydride to DDGS from 1:1 to 5:1, catalyst concentrations from 0% to 20% based on the weight of the DDGS, temperature from 50 to 120 °C and time from 10 to 120 min.

2.1.3. Acetyl content

The extent of acetylation of DDGS acetates obtained using alkaline and acidic catalysts were determined in terms of the % acetyl content by titration according to ASTM method D 871-96 with some minor modifications. The acetyl content is defined as the percentage of acetyl (CH\textsubscript{3}CO–) groups. Commercial cellulose triacetate with a degree of substitution (DS) of 2.91–2.96 corresponds to acetyl content of 44.0–44.4%. To determine the % acetyl content, the acetylated products were first hydrolyzed using 0.5 M NaOH. The NaOH that was not consumed during the hydrolysis was over-titrated using a known quantity of excess 0.5 M HCl. The solution was then back titrated using 0.5 M NaOH to eventually determine the amount of NaOH consumed to neutralize the acetic acid generated by the DDGS acetates.

The % acetyl content was calculated using the following equation:

\[
\text{% Acetyl content} = \left( \frac{A - B}{C} \right) \times M \times \left( \frac{F}{W} \right)
\]

where \(A\) was the amount (mL) of NaOH solution required for titration of the sample; \(B\) was the amount (mL) of NaOH solution required for titration of the blank; \(C\) was the amount (mL) of HCl solution required for titration of the sample; \(D\) was the amount (mL) of HCl solution required for titration of the blank; \(M\) is 0.5, the molar concentration of NaOH and HCl used for titration; \(F\) is 4.305 for acetyl, which was related to the molecular weight of the acetyl group (CH\textsubscript{3}CO), the unit conversion from liters to milliliters, and fraction to percentage,

\[
F = \frac{\text{Molecular Weight}}{1000 \text{mL/L}} \times 100 \times 43.05 = 4.305
\]

where \(W\) was the sample weight in grams.

2.1.4. Intrinsic viscosity

The intrinsic viscosity of the DDGS acetate was determined according to ASTM standard D 871-96 with some minor modifications. Briefly, the DDGS acetate was dissolved in DMSO/DMF (1:1, v/v). The DDGS solution was then centrifuged at 6000 rpm for 10 min and the supernatant formed was collected. The solution was evaporated to collect the DDGS acetates dissolved in the supernatant. The DDGS acetate obtained was redissolved in DMSO/DMF (1:1, v/v) at various known concentrations. The flow rate of the DDGS acetate solutions was measured in a viscometer maintained at 25 ± 0.1 °C. The solvent flow time \(t_0\) and the solution flow time \(t\) for different concentrations of DDG acetates were measured. For each concentration, the corresponding inherent viscosity was calculated. In solution viscosity measurements, inherent viscosity is the ratio of the natural logarithm of the relative viscosity to the concentration of the polymer. The intrinsic viscosity was obtained by extrapolating the curve of inherent viscosity to zero concentration. The intrinsic viscosity, (\(\eta_s\)), was calculated using Eq. (3).

\[
[\eta] = (\ln \eta_s) / C_{-0.5}, \text{mL/g}
\]

where \(\eta_s\) was the relative viscosity and \(C_{-0.5}\) was solution flow time, \(t_0\) was the solvent flow time, and \(C\) was the concentration of the DDGS acetate solution in grams per milliliter.
2.1.5. Fourier transform infrared (FTIR) spectrum analysis

The FTIR spectra of unmodified and acetylated DDGS were collected on an attenuated total reflectance ATR spectrophotometer (Nicolet 380; Thermo-Fisher, Waltham, MA). The samples were thoroughly washed in water to remove the solvent and catalysts. The washed samples were placed on a germanium plate and 64 scans were collected for each sample at a resolution of 32 cm\(^{-1}\).

2.1.6. Nuclear magnetic resonance studies

\(^1\)H NMR spectroscopy was used to confirm acetylation under alkaline and acidic catalysis conditions. The unmodified and acetylated DDGS were dissolved in DMSO and \(^1\)H NMR analysis was carried out using a Bruker Advance DRX-500 spectrometer operating at 500 MHz (Bruker, Billerica, MA).

2.1.7. Thermal analysis

Thermogravimetric analysis (TGA) was performed on the unmodified and acetylated DDGS with an instrument calibrated with nickel (Perkin Elmer STA 6000, Norwalk, CT). Samples (18–26 mg) were placed under nitrogen atmosphere and heated from 50 to 650 °C with a heating rate of 20 °C/min. A Mettler Toledo (Model: DSC822e) Differential Scanning Calorimeter (DSC) was used to study the thermal behavior of the unacetylated and acetylated DDGS. Samples (about 10 mg) were placed in the DSC and heated at a rate of 20 °C/min and were held at 50 °C for 10 min for the acetylated DDGS and for 20 min for the unmodified DDGS to remove moisture in the samples. The samples were then heated up to 180 °C at a rate of 20 °C/min.

2.1.8. Developing thermoplastics

The DDGS acetates obtained were compression molded in a carver hydraulic press to form thermoplastic films. After compression, samples were cooled by running cold water through the press. Digital pictures of the compression molded DDGS acetates and the unmodified DDGS were collected for comparison of the thermoplasticity.

2.1.9. Morphology of the modified and unmodified DDGS

The surface morphology of the modified and unmodified DDGS were observed using a variable pressure scanning electron microscope (VP-SEM) (Model: Hitachi S 3000 N, Hitachi High Technologies America, Inc., Schaumburg, IL). Samples were fixed using conductive adhesive tape and sputter coated with gold–platinum before observing in the SEM at a voltage of 20 kV.

3. Results and discussion

3.1. Effects of catalyst concentration on % acetyl content of DDGS acetates

Fig. 1 depicts the effect of changing the % of catalyst (sodium hydroxide) on the acetyl content of DDGS. Increasing catalyst concentration from 20% to 30% increased the % acetyl content by about 11%. Further increase in catalyst concentration from 30 to 40 and from 40% to 50% did not increase the % acetyl content significantly. However, the % acetyl content decreased substantially to 9.4% when the amount of catalyst used was equal to 100% of the weight of DDGS. The highest acetyl content obtained was 23% at a catalyst concentration of 30% and was used for the optimization of other acetylation parameters. The decrease in the % acetyl content at 100% catalyst was mainly due to the hydrolysis of the protein and carbohydrates under strong alkaline conditions and high temperatures. The catalyst (sodium hydroxide) was added into the reaction as a saturated solution (50% w/w) in water since sodium hydroxide does not dissolve in acetic anhydride. The addition of water and the presence of high amounts of alkali at high temperatures lead to the hydrolysis of the proteins in DDGS and hence the % acetyl content decreased [17].

3.2. Effects of temperature on % acetyl content and intrinsic viscosity of DDGS acetates

Fig. 2 shows the effect of increasing reaction temperature on the % acetyl content and intrinsic viscosity of the acetylated DDGS. Increasing reaction temperature from 90 to 130 °C increased the acetyl content by about 23%. A highest acetyl content of 28.5% was obtained when the reaction was carried out at 130 °C. As seen from Fig. 2, the intrinsic viscosity of the DDGS acetate obtained at 130 °C was significantly lower than the viscosity of the unmodified DDGS acetate obtained at 120 °C. Increasing reaction temperature increased the accessibility of the proteins and carbohydrates to chemicals and also increased the acetyl content and therefore the intrinsic viscosity. At high temperatures (130 °C) and in the presence of alkali and water, some of the proteins and carbohydrates in DDGS were hydrolyzed and therefore the intrinsic viscosity decreased [18,19]. Since the DDGS acetate obtained at 120 °C has similar acetyl content but higher viscosity compared to that obtained at 130 °C, a temperature of 120 °C was chosen to optimize the other acetylation conditions.
3.3. Effects of reaction time on % acetyl content of DDGS acetates

Increasing reaction time from 10 to 30 min and from 30 to 60 min increased the % acetyl content by 7.6% and 9.7%, respectively as seen from Fig. 3. Further increase in reaction time above 60 min did not change the % acetyl content. The initial increase in acetyl content with increase in temperature should be due to the better acetylation of DDGS. Higher number of carbohydrates and proteins are acetylated with increasing time and therefore the % acetyl content increases. However, the acetylation reaction reaches equilibrium at 60 min and therefore there was no increase in the % acetyl content when the reaction time was increased above 60 min under the reaction conditions studied.

3.4. Effects of ratio of acetic anhydride on % acetyl content of DDGS acetates

A relatively low ratio of acetic anhydride to DDGS (2:1) was sufficient to provide high acetyl content (26.5%) as seen from Fig. 4. Increasing the ratio of acetic anhydride above 2:1 marginally increased the acetyl content to 28.1% but the acetyl content remained the same at acetic anhydride ratios of 4:1 and 5:1 (28.1% and 28.2%, respectively). The number of accessible hydroxyl groups probably reached equilibrium at an anhydride ratio of 3:1 and we therefore do not see an increase in % acetyl content with increasing ratio of anhydride. Since acetic anhydride accounts for the major cost of acetylation and the % acetyl content obtained at 2:1 and 3:1 ratio of anhydride are similar, it is preferable to use 2:1 ratio to reduce the cost of acetylation.

3.4.1. $^1$H NMR spectra of DDGS acetates

The $^1$H NMR spectrums of the unmodified and acetylated DDGS are shown in Fig. 5. The presence of large number of peaks in the range of 1.9–2.2 ppm (absorbance of methyl protons from the acetyl groups) confirms the presence of carbohydrates esters formed due to acetylation [20–22]. The integral area of the curve between 1.9 and 2.2 ppm for the DDGS obtained using alkaline catalysts was 0.7 and 1.13 for the DDGS acetates formed under acidic catalysis. The higher peak area for the DDGS acetates formed under acidic catalysis confirmed the presence of higher number of acetyl groups and therefore higher degree of substitution than the DDGS acetates formed under alkaline conditions.

3.5. FTIR measurements

Fig. 6 shows the FTIR curves of the unmodified and acetylated DDGS. The presence of strong absorbance peaks between 1745 and 1754 cm$^{-1}$ belonging to the stretching of the ester carbonyl C=O group and the strengthening of the COC ester stretching peak at 1250 cm$^{-1}$ for the acetylated DDGS confirms acetylation. However, the heights of the peaks are different for the DDGS acetates obtained using alkaline and acidic catalysts. The length of the C=O stretching peak at 1750 cm$^{-1}$ is 3.4 cm for DDGS acetate formed under alkaline conditions and 2.9 cm for the DDGS acetate obtained under acidic conditions. Using the aromatic peak at 1510 cm$^{-1}$ as a reference, the ratio of height of the peaks at 1750 and 1510 cm$^{-1}$ for DDGS acetate formed under alkaline conditions was 2 and 2.9 for the DDGS acetates obtained under acidic conditions. This shows that the DDGS acetates obtained using acidic catalysts have higher acetyl content.

3.6. Thermal analysis

The thermal behavior of the acetylated DDGS obtained using acidic and alkaline catalysts are compared to the unmodified DDGS.
in Fig. 7. The unmodified and acetylated DDGS had similar thermal degradation up to about 220 °C. Above 220 °C, the degradation of the DDGS acetates formed under acidic catalysis was similar to that of unmodified DDGS whereas the DDGS acetates obtained under alkaline catalysis had lower thermal degradation. The better thermal stability of the DDGS acetates obtained under alkaline conditions was most likely due to less proteins in the alkaline DDGS acetates than DDGS acetates obtained using acidic catalysts. A large portion of proteins in DDGS acetates were probably hydrolyzed under strong aqueous alkaline and high temperature conditions used for alkaline catalysis. The hydrolyzed proteins were removed from the acetates resulting in carbohydrates and remaining proteins that had high thermal stability. However, both the DDGS acetates had higher final weight loss than the unmodified DDGS. The overall weight loss of the DDGS acetates was about 80% compared to 73% for the unmodified DDGS. The higher degradation of the DDGS acetates compared to the unmodified DDGS was mainly due to the presence of the acetyl groups that make the DDGS acetates unstable. Acetylated DDGS will be decomposed more readily and therefore has higher weight loss than that of the unmodified DDGS.

DSC thermograms in Fig. 8 shows that the DDGS obtained using alkaline catalysts had a melting peak at about 125 °C whereas the DDGS acetates catalyzed by alkali had a relatively small melting peak at a temperature of about 147 °C. The melting enthalpy for the DDGS acetates formed under acidic conditions was 4.2 J/g whereas DDGS acetates formed under alkaline conditions had a much lower melting enthalpy of 0.5 J/g. Under alkaline acetylation conditions, proteins will be hydrolyzed whereas the carbohydrates are relatively unaffected compared to acetylation under acidic conditions. Since most of the hydrolyzed proteins are removed during washing, the DDGS acetate obtained under alkaline conditions had better thermal stability and hence a higher melting point compared to the DDGS acetates formed under acidic conditions. However, the DDGS acetate obtained under alkaline conditions had much lower acetyl content (28.1% corresponding to a DS value to 1.5) compared to the DDGS acetates formed under acidic conditions which had an acetyl content of 36.1% (DS value of 2.1). Therefore, the DDGS acetate obtained under acidic conditions had higher melting enthalpy and can be expected to have better thermoplasticity than the DDGS acetates obtained using alkaline catalysts.

3.7. Comparison of alkaline and acid catalysis of carbohydrates and proteins in DDGS

Fig. 9 shows the comparison of the intrinsic viscosity and % acetyl content of the DDGS acetates obtained using alkaline and acidic catalysis at various acetylation conditions. As seen from the figure, the DDGS acetates obtained under alkaline conditions had much lower intrinsic viscosity than the DDGS acetates obtained using acidic catalysts at various acetylation conditions. The viscosity of the DDGS acetates obtained under alkaline conditions varied from 10.3 to 17.4 when the ratio of anhydride to DDGS was varied from 1.5:1 to as high as 3:1 (Curve C). Acidic conditions provided much higher intrinsic viscosity even at substantially lower ratios of anhydride to DDGS. The intrinsic viscosity of the DDGS acetates obtained using acidic catalysts varied from 10.6 to 31.8 when the ratio of anhydride to DDGS was varied from 0.5:1 to 1.5:1 (Curve B).

DDGS acetates obtained using acid catalysts also had considerably higher % acetyl content and therefore better thermoplasticity than DDGS acetates obtained using alkaline catalysts at similar ratios of acetic anhydride. The highest % acetyl content obtained for alkaline catalysis was 28.1% at an acetic anhydride to DDGS ratio of 3:1 whereas the % acetyl content for the acid DDGS at anhydride to DDGS ratio of 3:1 was 37.3%. Acid catalysis was able to provide a high acetyl content of 36.1% even at a low anhydride to DDGS ratio of 2:1. The lower intrinsic viscosity and % acetyl content of the
DDGS acetates obtained under alkaline conditions shows that alkaline catalysis is less favorable for acetylation of the carbohydrates and proteins in DDGS compared to acidic catalysis. The better acetylation of DDGS under acidic conditions than alkaline conditions should be due to the following reasons.

Alkaline catalysis required high temperatures (120 °C) under high concentrations of catalyst (30% w/w) for 60 min to achieve good acetylation, similar to the conditions used for acetylating starch [8]. Alkali (NaOH) used as catalyst did not dissolve in acetic anhydride and therefore high concentrations of alkali solution in water were used as the catalyst. Under these conditions, proteins and to some extent carbohydrates will be hydrolyzed [17,19,23]. In addition, carbohydrates are oxidized in the presence of strong alkali leading to a decrease in the molecular weight [18]. Alkaline media also causes isomerization of the carbonyl groups in the carbohydrates resulting in depolymerization [24]. Therefore, the intrinsic viscosity of the DDGS acetates obtained using alkaline catalysts was low. Acid catalysis was performed under relatively mild conditions and without the presence of water. Therefore, there was limited hydrolysis and decrease in molecular weight of the proteins and carbohydrates [18]. The amount of catalyst required for acid catalysis was also low at about 10% compared to 30% for the alkaline catalysis. In fact, acid concentration of 5% provided the highest intrinsic viscosity and acetyl content but with an anhydride to DDGS ratio of 2:1 as seen from Fig. 9.

The better thermoplasticity of the DDGS acetates obtained using acid catalysts was also evident from the thermoplastic DDGS acetates films shown in Fig. 10. As seen from the figure, DDGS acetate obtained using alkaline catalyst are less thermoplastic and did not melt. The acid DDGS acetates were made into films by
compression molding at 138 °C for 2 min whereas the alkaline DDGS acetates required much higher temperature (170 °C) and longer times (5 min) to form films also indicating the relatively poor thermoplasticity (low % acetyl content) of the DDGS acetates obtained using alkaline catalysts. SEM images in Fig. 11 also show that the DDGS alkaline acetates (A) and acid acetates (B) melt and have a smooth and non-particulate surface whereas the unmodified DDGS (C) did not melt and had many particles on the surface.

4. Conclusions

This research showed that acetylation using acidic catalysts provides substantially higher acetyl content and intrinsic viscosity at low ratios of anhydride and catalyst concentrations compared to alkaline catalysis of the carbohydrates and proteins in DDGS. Alkaline catalysis required high temperatures (120 °C) and catalyst concentrations (30%) which hydrolyzed the proteins and the carbohydrates to some extent resulting in DDGS acetates with low % acetyl content and intrinsic viscosity. DDGS acetates with highest acetyl content of 28.1% and intrinsic viscosity of 17.4 were obtained using an anhydride to DDG ratio of 3:1 and 30% catalyst for alkaline catalysis whereas similar acetyl content (27.8%) but higher intrinsic viscosity (22.7) can be obtained under acidic conditions using a much lower anhydride to DDGS ratio of 1:1 and 10% catalyst or anhydride ratio of 2:1 and catalyst concentration of 4%. Both FTIR and $^1$H NMR confirmed acetylation and the higher % acetyl content in DDGS acetates obtained using acidic catalysts. DDGS acetates obtained using acid catalyst also had lower melting temperature and higher melting enthalpy resulting in more transparent thermoplastics than the DDGS acetates obtained using alkaline catalysts. The DDGS acetates developed in this research were thermoplastic and could be used to develop various thermoplastic products.

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