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Compositional Analysis of Defatted Syrup from a Corn Ethanol Dry-Grind Process as a Feedstock for Biobased Products

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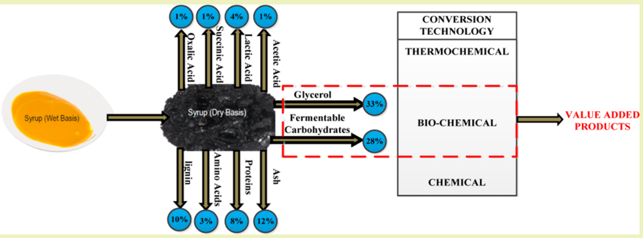
Ⓢ *Supporting Information*



ABSTRACT: A characterization study was conducted on defatted corn syrup (DCS) from an ethanol dry-grind process and its potential as feedstock for biobased products and biofuel is evaluated. Analyses included total solids, ash content, total protein, amino acids, inorganic elements, starch, total carbohydrates, lignin, organic acids, glycerol, and presence of functional groups. Total solids content was 37.4% (±0.4%) by weight, and the mass balance closure was 101 (±0.5%). Total carbohydrates [27% (±5%) wt of dry solids] were composed of starch (6.3%), soluble monomer carbohydrates (12%), and nonstarch carbohydrates (9.3%). Hemicellulose components (structural and nonstructural) were xylan (6%), xylose (1%), mannan (1%), mannose (0.4%), arabinan (1%), arabinose (0.4%), galatactan (3%), and galactose (0.4%). On the basis of measured physical and chemical components, a biochemical conversion route and subsequent fermentation to value-added products is a good possibility. Though less promising as a feedstock for liquid transportation fuels, DCS has the potential to meet current United States demand (20−30 million kg per year) for succinic acid. Finally, even without any form of hydrolysis, DCS could also potentially meet global demand for histidine (360,000 kg per year).

KEYWORDS: *Carbohydrate, Dry mill, Glucan, Succinic acid, Defatted corn syrup*

■ INTRODUCTION

Depletion of nonrenewable fossil fuels and increasing greenhouse gas (GHG) emissions continue to raise economic and environmental concerns. As a result, research on biobased fuels and chemicals has gained worldwide momentum. Lignocellulosic biomass and processing residues[1,2] are two types of feedstocks that could be used to produce biobased fuels and chemicals, while not competing with the production of food.

The USDA-DOE billion ton update report[3] identified forest and agricultural resources as major sources of biomass with the potential of sustainably displacing about 1/3 of present United States petroleum consumption. The potential of feedstock such as switchgrass, willow, and hybrid poplar have been extensively studied.[4,5] However, recent studies focused less on the potential of industry-processed residues. Investigations of process residues such as municipal solid waste, sewage sludge, defatted corn syrup (DCS) from a dry-grind process, dried distillers grains with solubles (DDGS), and food-processing wastes from dairy and sugar industries as potential feedstocks for biobased products have received less attention.

Biomass characterization is an important first step in evaluating the feasibility of biomass as a potential feedstock for conversion to biofuels and biobased products. Apart from informing us of the choice of conversion platform such as thermochemical, chemical, or biochemical, it is vital for other reasons.[6] For example, quantification of cellulose, hemicellulose, and lignin is crucial as it affects the overall economics of biorefining, especially for wet biomass conversion processes. Inorganic elements (macro and micronutrients) analyses provide useful information on nutrient depletion of soil,[4] while lignin can be incinerated and used as process heat energy.[7]

DCS received from the dry-grind mill facility was assumed to be produced according to Figure 1; more details are reported in another study.[8] Thin stillage (TS), which is the parent stream of syrup [referred to as DCS in this article (Figure 1)], is the feedstock in our study. DCS stream results from dewatering of TS through multiple effect evaporators. DCS is golden brown in color with a slightly fermented aroma, and it is also viscous compared to water. Due to its high fiber, carbohydrate, and protein content, DCS is usually added to DDGS for drying and used as a feed additive.[8]

A literature review on prior work done on DCS identified a number of studies to be relevant.[9−16] One study[9] characterized the elemental compositions of primary process streams from dry-grind ethanol plants with a focus on tolerable levels of these elements as a source of animal feed. In another study,[12] the authors investigated the fuel and emission characteristics of

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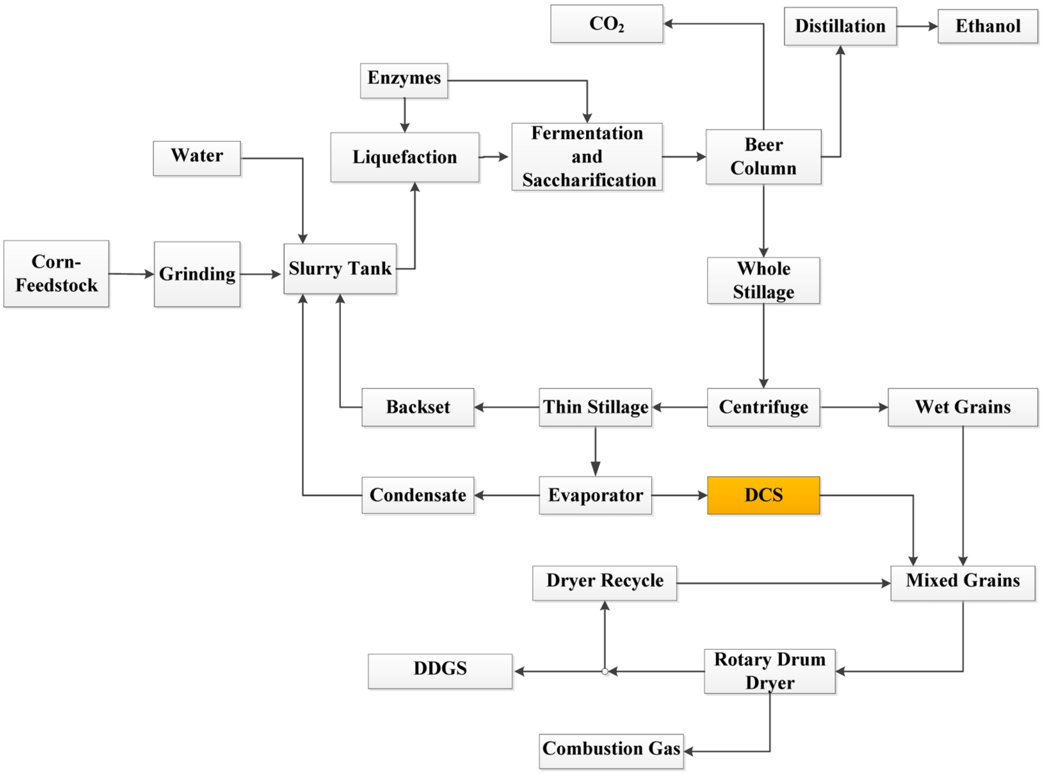

Figure 1. Schematic diagram of the dry-grind corn mill facility.[15]

coproducts such as distillers wet grains (DWG), condensed distillers solubles (referred to as "syrup" or "DCS" in this study), DDGS, and corn stover. Technical evaluation of stillage treatment and byproduct recovery in the ethanol industry focusing on the viability of anaerobic digestion for stillage treatment was another relevant study identified.[16] Reported studies on DCS have focused less on its potential as a feedstock for biobased chemicals. This study contributes to the knowledge of the potential utilization of DCS as a renewable feedstock by presenting a thorough analysis of DCS accompanied by a material balance. Results from this study are of relevance to commercial dry-grind facilities and the chemical industry. The results from our analysis would enable more robust analysis on the potential economic value of DCS as a feedstock for biobased chemicals.

Three key objectives were identified in this study: (1) conduct a detailed composition analyses on DCS (i.e., total solids, ash content, protein, amino acids, inorganic elements, starch, structural and soluble carbohydrates, lignin, organic acids, glycerol, and functional group analysis), (2) recommend the most suitable conversion technology, i.e., thermochemical, chemical, or biochemical for DCS, and (3) conduct an analysis of the potential market for which DCS can serve as a feedstock for the production of biofuels and biobased products.

■ MATERIALS AND METHODS

Six different samples of DCS each in a 500 mL centrifuge flasks labeled "A" through "F" were received from a dry-grind corn processing facility and stored in a refrigerator at 5 °C prior to any analyses. In our analysis, DCS received from the dry-grind facility was assumed to contain minimal amount of fat and as a result was not included in our analysis. All equations adopted for these analyses are summarized in Table S.1 of the Supporting Information.

Total Solids Analysis. DCS samples "A" through "F" were analyzed (Table S.1, eq S.1, Supporting Information) for total solid percentage by drying in a convection-drying oven (Precision Scientific, Chicago, IL) at 105 °C following National Renewable Energy Laboratory (NREL) protocol. Solid residues were sealed in Ziploc bags and stored in a desiccator for ash content analysis. All experiments were conducted in duplicates.

Ash Content Analysis. The NREL protocol for ash analysis[17] was used to estimate the total ash content of DCS using a Thermolyene 2000 muffle furnace (Thermo Scientific, West Palm Beach, FL). The percentage compositions of ash for samples labeled "A" through "F" were estimated (Table S.1, eq S.2, Supporting Information) by conducting duplicate trials at 575 °C.

Inorganic Element Profile. In each 10 mL of 1% HNO_3 (v/v) solution, 1 g of oven-dried DCS (ground to powder using a Norpro 696 round porcelain mortar and pestle, 1/4 cup) was digested.[18] The solution was heated to 90 °C for 45 min and subsequently increased to 140 °C with occasional swirling until approximately 1 mL of the solution was remaining. After cooling, 20 mL of 1N nitric acid was added; the solution was further diluted with deionized water (~30−60× dilution) for analysis using the inductively coupled plasma spectrometry (PerkinElmer Optima 7000DV ICP-OES, Waltham, MA). DCS samples "D" and "E" were analyzed for the following elements: Ca, Fe, Mg, Na, K, P, Al, Cu, Zn, Mn, and S. All experiments were conducted in duplicates.

Protein Content Analysis. A Bradford reagent (St. Louis, MO) was used for this analysis. A detailed experimental procedure was reported in the product's technical bulletin.[19] Using bovine serum albumin (BSA) as the reference protein, standards were prepared, and absorbance of standards and syrup solutions were measured at 595 nm using a Milton Roy Spectronic 21D spectrophotometer (Champaign, IL).

Amino Acid Analysis of Syrup. Amino acid analysis (AAA) technique by Agilent Technologies[20] was used to analyze DCS. Briefly, 0.5 mL of DCS was transferred into 1.5 mL centrifuge vial using a micropipet and diluted three-fold with distilled water. Ensuring uniform solution mixture by shaking with hands, the vials were then subsequently centrifuged using VWR Galaxy 16 Microcentrifuge (Batavia, IL) at 10,000 rpm for 25 min. A 0.2 μm membrane (Whatman) was used to filter the supernatant into high-performance

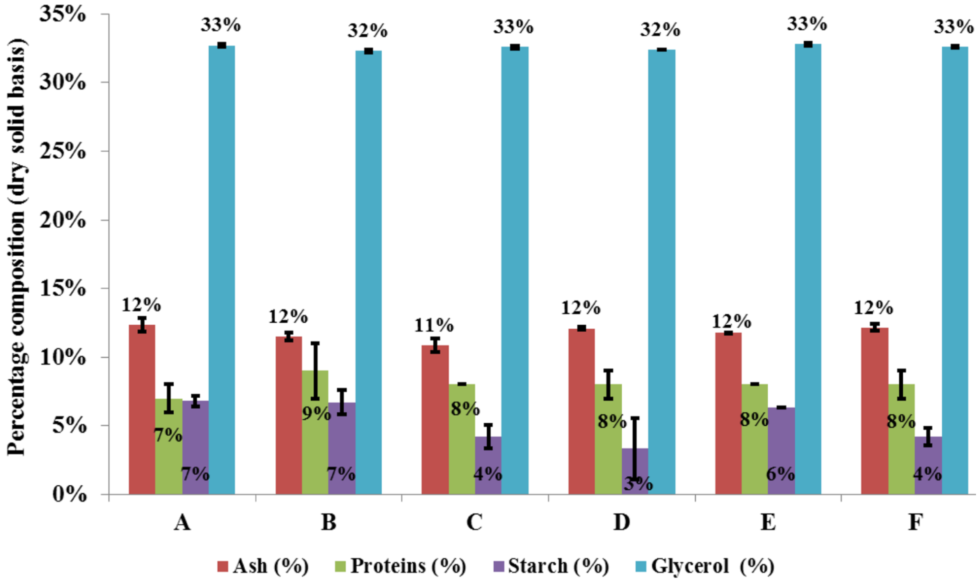

Figure 2. Percentage composition on a dry syrup solids basis of total ash, protein, starch, and glycerol for samples "A" through "F".

liquid chromatography (HPLC) vials. Samples were analyzed using HPLC (Agilent 1200 series) equipped with Zorbax Eclipse column (4.6 $\mu \times 150\ \mu \times 5\ \mu$m) at an operating temperature of 40 °C.

Total Carbohydrate Analysis. The total carbohydrate analysis (not including lignin) of DCS was composed of three major components: (i) starch assay, (ii) soluble carbohydrate analysis, and (iii) nonstarch carbohydrate analysis. Duplicate samples of vials "A" and "E" were analyzed, and their results were averaged to represent DCS.

Starch Assay. This assay focused on glucose generated from the starch hydrolysis enzyme taking into account the initial glucose present.

Soluble Carbohydrate Analysis. Water-soluble C_5 and C_6 sugars (nonpolymeric carbohydrates) in DCS were included in our analysis

Nonstarch Carbohydrate Analysis. Polymeric carbohydrates such as cellulose and hemicelluloses and any other oligomers in the DCS were also analyzed

Starch Assay. The detailed experimental method for the starch assay adopted for DCS was reported in a NREL report.[21] Briefly, 0.1 g of oven-dried DCS was hydrolyzed using α-amylase (St. Louis, MO) and amyloglucosidase (St. Louis, MO). Hydrolysate was centrifuged, filtered (0.2 μm), and analyzed for glucose using Aminex HPX-87P column (Bio-Rad Life Sciences, Hercules, CA) in the HPLC (Agilent 1200 series). A starch recovery standard was run under the same conditions simultaneously to account for unhydrolyzed starch using pure potato-extracted starch (St. Louis, MO). Equations S.3 and S.4 in Table S.1 of the Supporting Information were used to estimate the starch recovery standards (%R_{starch}) and the percentage of starch (% Starch) in DCS, respectively.

Soluble Carbohydrate Analysis. The concentrations of soluble carbohydrates (cellobiose, xylose, glucose, galactose, mannose, and arabinose) and fermentation inhibitors [furfural and hydroxymethylfurfural (HMF)] in DCS were determined by HPLC (Agilent 1200, Santa Clara, CA), using Aminex HPX-87P column (Bio-Rad Life Sciences, Hercules, CA). Both refractive index detection (RID) and diode array detection (DAD) were used. A 10× dilution of DCS was prepared using distilled water and mixed and then filtered (VWR, polycarbonate membrane filter, 25 mm dia., 0.2 μm pore size) into HPLC vials. Standards for both sugars and inhibitors were analyzed to generate four-point calibration curves. Duplicate samples were analyzed.

Nonstarch Carbohydrate Analyses. A detailed experimental procedure for this analysis was reported by NREL.[22] This analysis was conducted by measuring the total polymeric carbohydrate sugars[22] and then subtracting from this the starch carbohydrate and soluble monomer sugars. Briefly, oven-dried DCS was taken through a two-step pretreatment procedure using H_2SO_4. To 0.3 g of oven-dried DCS, 3 mL of 72 wt % H_2SO_4 was added and incubated in a water bath (30 °C) for 60 min for the first stage pretreatment step. Hydrolysate was subsequently brought to 4 wt % H_2SO_4 acid using distilled water and autoclaved (New Brunswick Scientific AC-48) at 121 °C for 60 min. For sugar recovery standards (SRS), monomer sugars of known concentration were run through the second step of the two-step procedure to account for sugar degradation and percent sugar recovered (%R_{sugar}) using HPLC. Equations S.5 and S.6 in Table S.1 of the Supporting Information were adopted for this analysis.

Lignin Analyses. The acid soluble lignin (ASL) and acid insoluble lignin (AIL) analysis protocols by NREL[22] were adopted for this study. Similar to the total carbohydrate analysis previously described, the oven-dried DCS biomass was run through a two-step pretreatment stage. The hydrolyzate was separated by filtration using a membrane filter (VWR, polycarbonate membrane filter, 25 mm dia., 0.2 μm pore size) into two fractions: a liquid fraction and an insoluble fraction. The liquid fraction containing the soluble lignin was analyzed using a UV—vis spectrophotometer (Genensys 10, Thermo Electron Corp., West Palm Beach, FL) at a wavelength of 240 nm. AIL concentrations were corrected for protein by subtracting protein concentrations estimated under protein content analysis of DCS. The insoluble fraction was ashed at 575 °C until a constant weight, and the final weights of the residues were measured. Both AIL and ASL were estimated using eqs S.7 and S.8 in Table S.1 of the Supporting Information, respectively. Absorptivity (55 L/g/cm) was used in eq S.8 of the Supporting Information.

Glycerol Analysis. DCS samples "A" through "F" were diluted five-fold using distilled water. The diluted samples were filtered into HPLC vials (0.2 μm membrane) and analyzed using HPLC with an Aminex HPX-87P column and a refractive index detector. Calibration standards were run with known concentrations of glycerol (Macron Fine Chemicals., Batavia, IL). Duplicate samples were analyzed.

Total Organic Acid Analysis. DCS samples (2 mL each) were transferred into a 10 mL vial. Each sample was diluted two-fold by adding 2 mL distilled water. The syrup solution was vortexed to ensure uniform mixture. A 0.2 μm membrane was used to filter the solution into an HPLC vial for organic acid analysis using HPLC. The Rezex ROA-organic H+ (8%) column (Phenomenex., Torrance, CA) was used for this analysis. The mobile phase was 0.005N H_2SO_4 with a flow rate of 0.6 mL/min and an operating temperature of 80 °C. Both standards and diluted syrup were analyzed using the RI detector. The following standards were analyzed: oxalic acid, citric acid, succinic acid, acetic acid, and lactic acid. Assuming that acetic acid in the sample was from acetate, a 0.983 conversion factor of acetic acid to acetate[22] was used to estimate the acetate content of DCS.

Functional Group Analysis Using FTIR-ATR. A Fourier transform infrared attenuated total reflectance (FTIR ATR-PerkinElmer, Waltham, MA) spectrophotometer equipped with a clean diamond ATR crystal was used to investigate the functional group components of the syrup. Oven-dried DCS (at 105 °C) was grounded into fine powder using Norpro 696 round porcelain mortar and pestle, 1/4 cup. Using a detection resolution of 4 cm^{-1} and 32 scans per sample, oven-dried DCS was analyzed for their spectra. Duplicate samples of "A", "B", and "C" were analyzed for their functional groups. Using Speckwin32 software,[23] observed spectra for all samples analyzed were averaged and used to represent DCS.

■ RESULTS AND DISCUSSION

Apart from amino acid analysis where samples received in the years 2010 and 2011 were averaged to represent DCS, all other reported results were for samples received in 2011. The following results will be accompanied by discussions of potential DCS conversion processing challenges and opportunities for biorenewable chemical or fuels production.

Total Solids and Ash Content. The total solid concentration of DCS was consistent in all samples ranging between 37 and 38% wt, 37.4% (±0.4%) wt of total solids [i.e., 62.6% (±0.4%) wt of moisture content]. Ash percentage composition in DCS on a dry solid basis ranged from 11 to 12% wt. For both analyses, the average of samples (Figure 2) "A" through "F" was used to represent DCS. Other studies reported 60−70% of moisture and approximately 30−40% wt of total solids[12,13] and 15% wt of ash in DCS[12] on dry solid basis.

Thermochemical (pyrolysis or gasification) conversion requires low moisture content feedstock (typically <50%) while bioconvention technology can utilize higher moisture content feedstock[6] making the latter more suitable for DCS. Dilute acid and enzymatic hydrolysis followed by fermentation to produce biofuels, biochemicals, or other bioproducts may be more suitable. Another possible implication during biochemical conversion processes such as acid pretreatment is higher consumption of acid due to the alkaline nature of ash. Finally, high ash content will likely influence the overall cost of handling and processing solid residues from nonbiodegradable carbon in DCS in the downstream processing and should be considered during the biorefinery concept stage.

Inorganic Element Profile. Table S.2 of the Supporting Information summarizes the elemental composition of DCS for duplicate samples. Final concentrations accounted for any dilutions made prior to analysis on the ICP, and variability between samples "E" and "F" was insignificant based on the reported standard deviation. From Table S.2 of the Supporting Information, S, K, and P are the dominant elements in DCS, while another study[13] reported Na, K, and P as dominant.

The reactive nature of alkali metals with silica in biomass results in the formation of "slag" during thermal conversion process, which blocks airways in furnace and boiler plants.[6] This may be an issue during processing of high-throughput DCS via thermal conversion route.

Protein Content Analysis. Protein concentrations in DCS ranged from 5 to 7 mg/mL representing 7−9% wt of syrup on a dry basis (Figure 2). Duplicate samples were analyzed for sample "A" through "F" and averaged. Average protein concentration was 6.06 (±0.85) mg/mL of proteins representing 8% (±0.6%) wt of DCS on a dry basis. In a separate study,[13] the authors reported relatively higher protein concentration [29.8 g/100 g on dry matter (DM) basis] in the syrup stream, while the crude protein content of DDGS and wet distiller's grain (Figure 1, wet grains) were reported to be 30.1 (±1.4%) and 33.1 (±3.2%),[10] respectively. The higher protein concentration in DDGS and wet distillers' grains as opposed to DCS is expected. After centrifugation of the whole stillage (Figure 1), the solid fraction (containing most of the proteins) goes into making the DDGS and wet distiller's grain, while the supernatant goes into making the TS (parent stream of DCS).

Few studies on integrated biorefinery scenarios have considered the technical feasibility, cost, and environmental impact of protein recovery[24,25] using biomass feedstock. DCS is yet to be subjected to such analyses, and any attempt to extract protein from DCS makes the use of thermochemical technologies unsuitable.

Glycerol Analysis. By averaging all glycerol results (Figure 2), it was estimated that DCS contained approximately 122 mg/mL (±0.25) of glycerol, representing 33% (±0.2%) wt in DCS on a dry solids basis. Glycerol percentage compositions were significant and consistent in all samples analyzed as displayed in Figure 2. Glycerol, which is a three carbon component of triglycerides, comes from the oil fraction of corn, and it is usually not freely available. We suspect the high percentage composition [33% (±0.2%) DM] measured in DCS is a result of glycerol byproduct formation due to sugar fermentation by yeast. The centrifugation step prior to the production of thin stillage (Figure 1) further increases the glycerol concentration in the syrup.[26]

Approximately 21 million tons of biodiesel were produced worldwide in 2011, and this generated 2.1 million tons of crude glycerol.[27] A glycerol glut in the market has stimulated research into its potential use as a feedstock for the production of value-added products. The production of co-products such as 1,3-propanediol, acetic acid, butanol, acetone, etc. through anaerobic fermentation of glycerol by *Clostridia* have been reported.[28] Also, the production of succinic acid, a value-added chemical,[29] using glycerol as a feedstock has been successfully demonstrated,[30] and this is another potential use of the glycerol component in DCS to improve processing plant profitability. Future conversion routes for DCS should explore the optimization of the sugar platform via acid hydrolysis and enzymatic saccharification to serve as fermentation media for the biobased platform chemicals.

Total Carbohydrate Content Analysis of DCS (Starch Assay Results). The starch content of DCS dry solids ranged from 3 to 8% wt, and by averaging the results obtained from samples "A" through "F", it was estimated that DCS contained 5.6% (±2%) wt of starch (Figure 2).

Total Carbohydrate Content Analysis of DCS (Soluble Monomer Carbohydrate Analysis Results). Glucose monomer concentration was highest in DCS being 36.9 mg/mL (±1.95) followed by cellobiose at 23.7 mg/mL (±1.95). Relatively smaller concentrations of xylose (3.55 ± 0.17), galactose (1.40 ± 0.09), and arabinose/mannose (2.76 ± 0.14) mg/mL were detected. Fermentation inhibitors in DCS were measured to be 0.27 (±0.02) and 0.26 (±0.01) mg/mL of furfural and HMF, respectively. These levels are not inhibitory given the reported inhibitory levels for both furfural (2−3.5 mg/mL) and HMF (4−5 mg/mL) depending on fermentative organisms (*Pichia stipitis* and *Escherichai coli* KO11).[31,32]

Total Carbohydrate Content Analysis of DCS [Nonstarch Carbohydrates (NSC) Results]. NSC components are composed of the following: cellulose and structurally bound hemicellulose components (xylan, galactan, arabinan, and mannan). Cellulose was a small fraction of DCS, with the highest estimated value of 1% wt (±0.01%) on a dry solid basis. Overall, hemicellulose components were approximately 9% wt, specifically with xylan 5% wt (±1%), galactan, 2% wt (±0.6%), arabinan 0.65 wt (±0.3%), and mannan 1 wt (±0.5%). The total carbohydrates (starch + soluble monomer carbohydrates + NSC) content of DCS averaged 28% (±5%) wt on a dry weight basis.

Acid Soluble and Acid Insoluble Lignin Analysis. AIL ranged from 6 to 9% wt on a dry solids basis, while ASL varied from 1 to 3% wt, (Figure S.1, Supporting Information). Averaging all samples analyzed, it was estimated that DCS contained 8% (±2%) wt and 2% (±1%) wt of AIL and ASL, respectively. As previously stated, lignin can further be incinerated for use as process heat[7] and should be considered in this regard for future biorefinery scale-up operations. Another option would be to use the lignin and ash components as soil-enhancing agents to sequester some carbon in the lignin.

Amino Acid Analysis. A summary of the amino acid profile of DCS is displayed in Figure S.2 in of the Supporting Information. Total amino acid concentrations were measured to be 3.51 (±0.24) and 3.38 (±0.35) mg/mL for DCS analyzed in the years 2011 and 2010, respectively. The amino acid profile was composed of the following primary amino acids: aspartic acid, glutamic acid, asparagine, serine, histidine, glycine, threonine, arginine, alanine, tyrosine, valine, methionine, phenylalanine, isoleucine, leucine, and lysine. No secondary amino acids were detected. Averaging all the samples (2010 and 2011) analyzed, it was estimated that free amino acids in DCS were approximately 3.45% (±0.3%) wt on a dry basis.

The total amino acids of TS on a dry solid basis were reported to be 1.1%.[11] We expected the amino acid profile for TS to be comparable to DCS because it is the parent stream. Table S.3 of the Supporting Information compares the amino acid profile for DCS analyzed in this study to TS reported in another study.[11] In both samples, tryptophan was not identified, while histidine, methionine, tyrosine, and asparagine were identified in DCS, but these were missing in TS. A possible explanation could be that these amino acid residues detected in the DCS were below the detection limit in the TS given its extremely high moisture content of 92.3%.[11] The presence of proteins in DCS presents an opportunity to produce more amino acids through hydrolysis reactions. Future research should explore the potential of amino acid production by hydrolysis of DCS.

Organic Acid Analysis. All sample vials "A" through "F" were analyzed in duplicate, and final results were averaged to represent DCS. All organic acids identified (oxalic acid, citric acid, succinic acid, acetic acid, and lactic acid) have boiling points above 105 °C,[33] which is the temperature at which drying was conducted (total solids analysis),[34] and these compounds were considered as part of the dry solids of DCS (not lost to evaporation during drying). Oxalic acid, succinic acid, lactic acid, and acetic acid were estimated to be 1% (±0.3%) wt, 1% (±0.3%) wt, 4% (±0.1%) wt, and 1% (±0.04%) wt, respectively.

FTIR-ATR Analysis. Spectra for all samples were averaged using Speckwin32 software,[23] and the blue colored spectra represents DCS (Figure S.3, Supporting Information). Twelve major peaks were identified and labeled "A" through "L". Table S.4 of the Supporting Information presents the various peaks identified and relates them to the expected functional groups as identified in the literature.[35−41]

Generally, FTIR as a semi-quantitative tool was useful in confirming most of the chemical components previously identified using other methods based on functional group absorbance. For example, peak "F" indicated the presence of proteins and strong bands of amide I and amide II. Functional group analysis results presented in Figure S.3 and Table S.4 of the Supporting Information strongly confirms the presence of chemical components measured using other analytical wet chemistry techniques in this study. FTIR is also useful to follow changes in functional groups in solid samples as a result of conversion reactions, although we deemed this beyond the scope of this characterization study.

Mass Balance Closure of DCS. The overall mass closure (101%) was calculated by summing the results reported in this section for components analyzed on a dry solid basis. This included the following: ash (12%), protein (8%), amino acids (3%), glycerol (33%), lignin (ASL and AIL-10%), oxalic acid (1%), succinic acid (1%), lactic acid (4%) acetate (1%), and total carbohydrates (28%). Figure S.4 of the Supporting Information summarizes these results showing the various components.

Results from our characterization studies are summarized in Table 1 and compared to TS and condensed distillers soluble (evaporated and fat-containing TS). Two important biobased feedstock components are carbohydrate sugars and glycerol. DCS showed the highest concentration on a dry basis for both components: sugars and glycerol. Readers should note that although DCS received from the dry-grind mill facility was

Table 1. Summary of Component Analysis for Thin Stillage, Condensed Distillers Solubles (Fat-Containing Syrup), and DCS[a]

components	thin stillage[43] (%)	condensed distillers soubles[43] (%)	defatted corn syrup (%)
Total Moisture	90	71	63
Total Solids	10	29	37
Total Carbohydrates	18	22	28
glucan	13	16	16
xylan and xylose	3	4	6
arabinan and arabinose	1	2	1
galactan and galactose	NR	NR	3
manann and mannose	NR	NR	1.5
Lignin	NR	NR	10
ASL	NR	NR	2
AIL	NR	NR	8
Organic Acids	9	9	7
oxalic acid	NR	NR	1
succinic acid	1	2	1
lactic acid	4	3	4
acetic acid	3	4	1
Other Solids	60	66	56
ash	9	10	12
proteins	13	16	8
fat	18	18	NR
glycerol	19	22	33
free amino acids	NR	NR	3
Mass Balance Closure	87	97	101

[a] Percent is based on dry matter content. Glucan = soluble glucose + starch + cellulose. NR: none reported.

Table 2. Potential Yields of Biobased Chemicals Using DCS as a Feedstock[a]

TBC	DCS component	current demand	potential with utilization of DCS	yield (X)
succinic acid	fermentable carbohydrates	20−30 M kg[49]	51 M kg	0.71[47]
ethanol	fermentable carbohydrates	14 billion gal[50]	51 T m^3(13M gal)	172.83[b] and 176.86[c46]
acetone butanol ethanol (ABE)	fermentable carbohydrates	25 M gal (butanol)[51,52]	9 T m^3 (2.3M gal)	0.31[53]
			17 T m^3(4.5M gal)	0.31[53]
			3 T m^3 (0.8M gal)	0.31[53]
succinic acid	glycerol	20−30 M kg[49]	110 M kg	1.23[30]
threonine	amino acid	3.6 M kg[48]	0.30 M kg	1.0
tyrosine	amino acid	110 T kg[48]	10 T kg	1.0
histidine	amino acid	360 T kg[48]	370 T kg	1.0
protein	protein	5 trillion kg[24]	21 M kg	1.0

[a] M: million. T: thousand. [b] 172. 83 gallons per dry ton of C_6 sugar (7.21×10^{-4} m^3 of ethanol/kg C_6 sugar). [c] 176. 86 gallons per dry ton of C_5 sugar (7.38×10^{-4} m^3 of ethanol/kg C_5 sugar).

reported as defatted there may be some residual fat that can potentially increase the mass balance closure of DCS in our study. Also worth noting is the relatively low concentration of the proteins in DCS. AAA via reverse-phase HPLC though time-consuming is the most reliable method for protein content analysis. Protein concentration (8−12%) of DCS on a dry weight basis has been confirmed in the lead author's dissertation[42] using this method (AAA).

Process conditions such as elevated temperature and the presence of acids are capable of rendering hemicellulose and cellulose soluble.[44] Acid pretreatment should be investigated as a potential conversion route for producing sugars using DCS as the feedstock. Apart from the fact that a significant amount of soluble sugars in DCS is in solution already (∼40 wt % of the total carbohydrates), dilute acid pretreatment may be advantageous given the prevalence of starch as compared to cellulose. In addition to dilute acid hydrolysis, future work could also investigate milder process conditions through the use of cellulases and starch hydrolyzing enzymes. Ultimately, the cost and quantity of available feedstock (DCS), usable fermentable sugars, concentration of fermentation inhibitors, and conversion yields will influence any intended use toward biobased specialty chemical production. The next section elaborates on the potential of DCS as a feedstock for some biobased chemicals.

Potential Yields from Biorefining Using Syrup as a Feedstock. In this section, by using the characterization results from this study, we estimate the potential quantity of target chemical products that can be produced using DCS as a feedstock. Production of DCS averaged 59 million kg per month (∼708 million kg per year) in the United States.[45] A summary of our analysis is displayed in Table 2. Apart from ethanol, which was estimated using the theoretical yield calculator (DOE),[46] all other target biobased chemicals (TBC) yields using fermentable carbohydrates were estimated using the equation below, where X represents yield of TBC on carbohydrate

$$\text{TBC (kg)} = 708 \times 10^6 \frac{\text{kg syrup}}{\text{year}} \times \frac{37.4}{100} \frac{\text{kg syrup DM}}{\text{kg syrup}} \times \frac{27 \text{ kg carbohydrate}}{100 \text{ kg syrup DM}} \times X$$

In the case of glycerol as a potential feedstock, the necessary adjustment was made by applying the ratio of 33/100 in the place of 27/100 in the equation. The key highlight from this analysis is that DCS has a potential to meet current United States demand for succinic acid, and future research should investigate the feasibility of utilizing both fermentable sugars as well as glycerol for the production of succinic acid. *Escherichia coli* and *Actinobacillus succinogenes* strains have been successfully used for succinic acid production using glucose and glycerol separately as feedstock.[30,47] It was also interesting to note that even without any form of hydrolysis and based only on the concentration in DCS, histidine could be recovered (a potential of 370,000 kg) and could meet global demand of 360,000 kg.[48] From our analysis, DCS seem less promising to displace significant amounts of liquid transportation fuels through production of ethanol and ABE (acetone butanol ethanol). We recommend future research to investigate the feasibility of using DCS in a sugar platform approach as a feedstock for biobased high-value chemicals production. If the biochemical pathway (hydrolysis and fermentation) is adopted, prior separation of sugars will not be necessary given that this approach is suitable for high moisture content feedstock (typically >50%).

Ultimately, detailed economic analyses considering feedstock cost, plant capacity, technology maturity, etc. will be required to analyze the economic feasibility of using DCS as a biobased feedstock. Potential yields as presented here would represent maximum production levels, and actual production levels from DCS would depend on costs and other process factors such as reaction selectivity and ease of biochemicals separation. Furthermore, additional processing challenges such as toxicity/inhibitory levels of hydrolysate components that influence fermentation yields, product separation and recovery costs, scale up, and system integration issues should be considered.

DCS is a co-product of the dry-grind corn ethanol process, and no previous studies have investigated the potential utilization of DCS as a renewable feedstock for biobased chemicals. In this study, we analyzed DCS for its physical and chemical characteristics and provided a detailed mass balance. With total solids of 37.4% wt, a mass balance closure on all components of DCS was 101%. Total carbohydrates (28% of dry wt) were composed of starch components (6%), soluble carbohydrates (12%), and nonstarch polymeric carbohydrates (10%). Structural and nonstructural bound hemicellulose components included xylan (6%), mannan (1%), arabinan (1%), and galatactan (3%). The ash content was composed of 12% wt on a DM basis, while protein, glycerol, and amino acids were 8% wt, 33% wt, and 3% wt on a DM basis, respectively. Though less promising as a feedstock for liquid transportation fuels, DCS has the potential to meet current United States demand (20−30 million kg per year) for succinic acid and global demand for histidine (360,000 kg per year). Syrup has good potential as a renewable feedstock for biochemical production through the biochemical pathway (hydrolysis and fermentation)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experiment results, such as inorganic elements, amino acids profile, functional groups, and SEM micrographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AAA - amino acid analysis
ABE - acetone butanol ethanol
ASL - acid soluble lignin
AIL - acid insoluble lignin
BSA - bovine serum albumin
DOE - Department of Energy
DCS - defatted corn syrup
DDGS - dried distillers grains with solubles
DM - dry matter
DWG - distillers wet grains
GHG - greenhouse gas
HPLC - high-performance liquid chromatography
HMF - hydroxymethylfurfural
M - million
ND - none detected
NREL - National Renewable Energy Lab
NSC - nonstarch carbohydrates
SRS - sugar recovery standards
%Starch - percentage of starch
$\%R_{starch}$ - starch recovery standards
T - thousand
TBC - target biobased chemical
TS - thin stillage
X - yield

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