Liquefaction of Dried Distiller's Grains with Solubles (DDGS) Followed by Hydroprocessing to
Produce Liquid Hydrocarbons

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Abstract

Dried distiller's grains with solubles (DDGS) is a byproduct of corn ethanol production in distillery industries. Presently the main use of DDGS is as livestock feed due to its high protein content. The demands for production of transportation fuel ethanol are increasing due to the increased Renewable Fuels Standard 2 (RFS2) mandate for higher ethanol production. Simultaneously DDGS supply as a co-product is also necessarily markedly increasing. There is a potential for DDGS supply to outgrow the demand for livestock feed or the increased supply has the potential to drive prices down. Therefore, it is highly desirable to find alternative uses of DDGS as a renewable source in the production of fuels or value-added chemicals.

The objective of this study was to produce transportation fuel range hydrocarbons from DDGS feedstock. In this study, DDGS was liquefied followed by hydroprocessing of the liquefied DDGS product to produce a hydrocarbon mixture. In the first step, liquefaction of DDGS was performed in a liquid media in the presence of a base catalyst at a temperature in the range of 400 °C. In the second step, the liquefied DDGS product was hydroprocessed in the presence of a heterogeneous catalyst at a temperature of 425 °C under pressurized hydrogen at 1500 psig. The physical and chemical properties of the liquefied DDGS product and the hydrocarbon mixture were measured by using American Society of Testing Methods. The

hydrocarbons produced were analyzed by gas chromatography-mass spectroscopy, detailed hydrocarbon analysis, Fourier transform infrared spectroscopy, simulated distillation analysis and elemental analysis.

Keywords: Liquefaction, DDGS, hydroprocessing, DHA, FTIR and GC-MS

Introduction:

Renewable, environmentally friendly, clean-burning and CO₂ neutral energy resources have been developed in recent years to replace conventional fuels [Mckendry 2002] that improve the greenhouse gas carbon balance. The biomass-derived bio-fuels such as ethanol from corn, and biodiesel, bio-butanol and ethanol from cellulosic biomass have been under development as promising replacements for fossil fuels [Mckendry 2002, Klass 2004, Gnansounou et al. 2005, Pimentel et al. 2005]. Ethanol has become an essential component of the U.S. motor fuel market. Ethanol as a renewable transportation fuel has been widely used to partially replace gasoline in the U.S. and many other nations. In the U.S. a number of states have mandated use of ethanol as a 10 percent (by volume) additive to gasoline [Xu et al. 2008]. In North America, 7 billion gallons of ethanol were consumed in 2006 and an increase in the production to 15 billion gallons of ethanol is mandated to be blended with gasoline by 2015 [Wang et al. 2013]. The Energy Independence and Security Act (EISA) of 2007 increased the volume of renewable fuel required to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022 [EPA 2013a]. Distillers dried grains (DDG) are an important revenue-producing byproduct of the ethanol process and the supply will increase with the increase in ethanol production. Adding value to DDG will increase the viability of the ethanol industry [RFA 2013a]. Therefore, it would be desirable to develop new methods to produce economically viable fuels from DDG.

Corn is the primary feedstock for ethanol production in the United States because of the high starch content amounting to approximately two-thirds of the corn. In the production of ethanol process a mass unit of corn yields ethanol, distillers grains, and carbon dioxide [Loy et al. 2008, Saunders et al. 2009]. Generally, there are two techniques for producing fuel ethanol using corn grain. They are: 1) the wet milling process and 2) the dry-grind (dry milling) process [Davis 2001, Ramirez et al. 2008, Rosentrater et al. 2009].

The corn wet milling process is very complex and has relatively high capital cost. This process produces a variety of products and co-products. Usually the wet milling process requires high quality corn. In wet milling, corn is first cleaned to separate foreign material such as sand, weeds, pieces of cob, and other cereal grains from corn kernels. The cleaned corn is then steeped to soften the corn kernel to assist in pure starch recovery. Following the steeping process, the wet milling corn process utilizes fermentation to obtain corn oil, germ meal, gluten meal, gluten feed, DDG and ethanol [Ramirez et al. 2008].

The corn dry-grind process is commonly referred to as the dry milling process. This method is the most widely used in the U.S. for ethanol production with an annual production capacity of 14.7 billion gallons [Urbanchuk 2013]. The advantages of this processing technique include low capital and energy investment costs using a relatively simple production process. In dry milling, corn is cleaned of foreign materials and hammer milled to a medium-coarse to fine grind meal. This corn meal is then mixed with fresh and recycled water in known ratios to form slurry. Hydrolysis of the corn starch to dextrin is then performed with an alpha amylase enzyme at a pH of 5-6 and temperature of 180-195 °F in a step referred to as liquefaction. After complete liquefaction of the starch the mash is cooked and then cooled to 90 °F and sent to a fermentation vessel to metabolically convert the dextrose to ethanol by *Saccharomyces crevisiae* yeast. In a

dry-grind mill, the resultant feed co-products are distiller's grains, distiller's grains with solubles and carbon dioxide [Davis et al. 2001].

Corn distiller's grains may be wet distiller's grains (WDG) or, following drying, distiller's dried grains with solubles (DDGS). Distiller's grains, wet or dry, are a byproduct of ethanol production from corn feedstock by distillery industries. The high protein content of distiller's grains has made its primary use as a livestock feed. DDGS is currently fed to livestock by most users [Lei et al. 2011]. The shelf life of WDG prior to deterioration is 3 to 4 days. Therefore, WDG is only utilized within a short haul distance of the ethanol plant even though the price of WDG is lower than DDGS. The production of fuel ethanol is increasing and simultaneously the distiller's grains co-product is also increasing. The success of the dry-mill ethanol production process in the near future could produce more DDGS than the domestic livestock feed market demands. In the production of ethanol by the dry-milling process, one bushel (56 pounds) of corn feedstock produces 18 pounds (2.72 gallons) of ethanol, approximately 17.5 pounds of distiller's grains and 18 pounds of carbon dioxide (CO₂) [Xu et al. 2008, Wang et al. 2013]. Therefore, the production of one gallon of ethanol yields 6.6 lb of DDGS.

According to the Renewable Fuels Association (RFA) the production of DDG from U.S ethanol biorefineries increased annually as shown in Figure 1. In 2011, ethanol biorefineries produced nearly 39 million metric tons of DDG. The ethanol industry is projected to produce 43.3 million metric tons of distiller's grains by the Food and Agricultural Policy Research Institute (FAPRI) at Iowa State University when producing 15 billion gallons of ethanol by 2015 from corn feedstock [Wang et al. 2013, RFA 2013b].

Liquefaction is a thermochemical conversion process by which biomass such as agricultural, forest, waste materials, coal and crop feedstocks can be converted into liquid products by reacting the material at temperatures usually below or equal to 400 °C [Toor et al. 2011]. The liquefaction process has some unique features. Liquefaction does not require that the feedstock be dried. Drying is an expensive step and usually takes a large amount of energy and time [Zhang 2010, Das et al. 2011]. Therefore, the cost of drying WDG to produce the more costly DDGS is not required to perform liquefaction. However, the advantage of being able to store and transport DDGS long distances is likely to make it the choice as a commercial feedstock for value added chemicals and fuels. The advantage of utilizing WDG would be initial lower cost the benefit of bypassing drying expenses and the fact that water present in the biomass works as a solvent and improves the efficiency of the process. The disadvantage is the short shelf life (less than 4 days) of the wet product.

Xu et al. (2008) performed the liquefaction of DDGS with hot compressed phenol to produce liquid products as a potential substitute for petroleum-derived phenol or an additive in the manufacturing of phenolic resins. Researchers studied the effect of liquefaction temperature, phenol/DDGS ratio, residence time, and catalysts on the yield of liquefaction products. Xu et al. performed the liquefaction of DDGS with hot-compressed phenol at 200-450 °C adopting a best temperature of 300 °C for 5 min at a phenol/DDGS ratio of 2/1 in the presence of K_2CO_3 . The researchers produced a liquefied DDGS product that was comprised of over 70% of phenols in the mixture.

Yu et al. (2008) studied the liquefaction of DDG in acidic conditions to produce polyurethane foams from the liquefied DDG. In this study, the researchers also investigated various parameters such as temperature, time, catalyst concentration and liquefaction solvent to

DDG ratio to optimizing the DDG liquefaction reaction. Researchers tested reaction conditions including liquefaction time of 1-3 h, temperature of 150-170 °C, sulfuric acid as a catalyst with concentration of 1-3 wt%, and liquefaction solvent (ethylene carbonate) to DDG ratio of 3:1 to 5:1. Researchers concluded that the optimum conditions for liquefaction of DDG were solvent to DDG ratio of 4:1 at a temperature of 160 °C with 3 wt% of sulfuric acid for 2 h of reaction time. At these optimized conditions bio-polyols rich in hydroxyl groups were produced with a yield of 94.4%. These bio-polyols were further treated with methylene diphenyl diisocyanate to prepare flexible and/or rigid polyurethane foams. Yu et al. also studied the biodegradability of polyurethane foams and found that they degraded about 12.6% in 10 months.

Lei et al. (2011) investigated the microwave pyrolysis of DDGS to determine the effects of pyrolytic conditions on the yields of bio-oil, syngas, and biochar. Practitioners studied the effect of various pyrolysis process variables such as reaction temperature, time and power input. A Sineo MAS-II batch microwave oven with a rated power of 1000 W was used at the 300-1000 W power setting. Yields of bio-oil ranged from 26.5-50.3 wt% while yields of biochar ranged from 23.5-62.2 wt%. The best bio-oil yield from this process had a HHV of 28 MJ/kg produced at a temperature of 650 °C for 8 min of reaction time.

Wang et al. (2012) also studied the pyrolysis of DDGS by using spouted-entrained bed and fixed bed reactors. The pyrolysis of DDGS by the spouted-entrained bed reactor was conducted at temperatures of 490-570 °C and by the fixed bed at temperatures of 490-610 °C. The spouted-entrained bed easily clogged. However, liquid was successfully obtained by the fixed bed. Researchers analyzed the pyrolytic liquids obtained from the fixed bed reactor by GC-MS. It was comprised mainly of phenol derivatives, fatty acids and their esters. They also found that when

pyrolyzed at 570 °C and catalyzed in-situ by CaO aliphatic and aromatic hydrocarbons were produced. Liquid yields were not reported by researchers.

The hydroprocessing step reduces oxygen in oxygenated compounds via hydrodeoxygenation (HDO), nitrogen via hydrodenitrogenation (HDN) and converts long-chain high molecular weight compounds to a lower molecular weight hydrocarbon mixture [Furimsky 2005, Elliott et al. 2012, Wang et al. 2013]. McCall et al. (2012) have performed hydroprocessing in two stages. It has become traditional to hydroprocess liquid intermediates (particularly fast pyrolysis oil) by an initial 1st stage hydrotreating step at a mild temperature to prevent polymerization often caused by application of hydrocracking which applies a more severe temperature. In a two-step process the hydrotreating step is performed at mild temperatures (200-400 °C) at a hydrogen pressure of 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. The hydrocracking step is performed at more severe temperatures (300-500 °C) but at the same general pressure of 4 to 10 MPa in the presence of a heterogeneous hydrocracking catalyst [Elliott 2007, Elliott et al. 2012, Tanneru et al. 2014]. McCall et al. have patented a method to upgrade the pyrolysis oil that depends on removing the water from the mild hydrotreating step prior to application of hydrocracking [McCall et al. 2012].

The promise of an abundant supply of distiller's grains has stimulated researchers to convert this material into a feedstock to produce value-added products. Researchers have developed methods to use DDGS in the production of value-added chemicals and bio products. As of now, no researcher has reported hydroprocessing of a liquefied DDGS product to produce transportation range hydrocarbon fuels. In this study, we have developed a method to produce hydrocarbons suitable for transportation range fuels from the DDGS feedstock. The first stage of

our method includes liquefaction of the DDGS. In the second stage, a subsequent hydroprocessing of the liquefied product is performed to produce a hydrocarbon mixture.

Research materials and methods

The DDGS for this study was provided by the Agricultural Utilization Research Institute (Waseca, MN, USA). KOH, ethylene glycol, CoMo/Al₂O₃, NiMo/Al₂O₃, CuO/Al₂O₃, Ni/SiO₂-Al₂O₃, Pt/C, Ru/C, Pt/Al₂O₃ and zeolites were purchased from Sigma Aldrich. Hydrogen gas was obtained from nexAir.

Reactor setup:

Liquefaction of DDGS and hydroprocessing of the liquefied product were performed in a stainless steel high-pressure batch autoclave Parr reactor as shown in Figure 2. The Parr reactor autoclave is equipped with an overhead magnetic stirrer, a pressure indicator (0-5000 psig) and a thermocouple for temperature monitoring (0-500 °C). It is also equipped with an electrical heating and cooling system to control the reactor temperature. Two gas supply valves are connected to supply hydrogen or helium or any gases. Unlike continuous packed bed reactors here desired hydrogen pressure will be pumped in to the reactor vessel at room temperature via gas valve. Exit gas valves are also present to evacuate the reaction gases when the reaction is complete. As shown in Figure 2, a temperature controller monitors reaction temperature, pressure and stirrer rotation speed per minute.

Experimental Procedures

Liquefaction and hydroprocessing experiments were performed in the above mentioned Parr autoclave. In our thermal liquefaction process we have used a well-known effective and inexpensive base catalyst, KOH and a mixture of water plus ethylene glycol as a solvent medium. The ratio of DDGS to aqueous alcohol was 1:2 (dry weight biomass basis) to convert

DDGS to a liquefied intermediate product. In an example of the application of this liquefaction process, we have performed a liquefaction treatment using 5 wt% (dry weight biomass basis) of KOH as a catalyst. The aqueous ethylene glycol solvent was comprised of 1:1 water and ethylene glycol was used as a solvent. Therefore, a 300 g quantity of material plus solvent and water to be liquefied would contain 100 g DDGS, 100g water and 100g of ethylene glycol. The 300 g of mixed ingredients were added to a Parr stirred batch reactor and thermally treated for 15 min without pressure or gas addition. After attaining a reaction temperature in the range of 400 °C the reaction was completed and the liquefied product removed. These all reaction conditions such as reaction temperature, solvent ratio and KOH weight percentages were selected based on the best results (high liquid product yield and HHV) obtained in our liquefaction process optimization reactions. The organic fraction yields were calculated by Equation 1.

$$\text{Organic liquid yield (wt\%)} = (P \text{ (g)} \times 100) / \text{dry DDGS weight (g)} \quad \text{Eq. 1}$$

Where: P= Organic products obtained (water/aqueous fraction was not included)

The liquefied product was hydroprocessed to produce a hydrocarbon mixture. This hydroprocessing was performed in a single stage to produce transportation fuel range hydrocarbons. Various commercial heterogeneous catalysts such as CoMo/Al₂O₃, NiMo/Al₂O₃, CuO/Al₂O₃, Ni/SiO₂-Al₂O₃, Pt/C, Ru/C, Pt/Al₂O₃, zeolites, and MSU-developed catalysts were screened in the hydroprocessing step. The hydroprocessing step was performed in the presence of 5 wt% of each heterogeneous catalyst at a temperature of 425 °C and under pressurized hydrogen of 1500 psig (desired hydrogen pressure was pumped in to the reaction vessel at room temperature) for a reaction time of 150 min to determine the best performing catalyst. Reaction parameters were selected based on high organic liquid and HHV obtained in hydroprocessing reaction optimization reactions.

Once the reaction was complete the liquid products were cooled in the reactor. The mixture was collected in centrifuge test tubes and centrifuged for 2-4 h to separate the resulting aqueous and organic phases. Both phases were separated and weighed for mass balance computation. The byproducts produced in this process include water and off-gas. Yields were calculated by Equation 2 [Nkafamiya et al. 2010].

$$\text{Organic liquid yield (wt\%)} = (P \text{ (g)} \times 100) / \text{bio-oil weight (g)} \quad \text{Eq. 2}$$

Where: P= Organic products obtained (aqueous fraction was not included)

Data analysis

The liquefied DDGS product and hydrocarbon mixture produced were characterized by ASTM methods. The densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052. Viscosities were determined by Ubbelohde capillary viscometer at 40 °C water bath temperature by ASTM D445. HHV was determined by Ika-5000 bomb calorimeter by ASTM D240. The acid value was determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution by ASTM D664. The pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture. The pH value was determined by ASTM E70 method. Elemental carbon, hydrogen, and nitrogen was determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. Water content was determined by Karl-Fisher titration by ASTM E203. The GC-MS analysis of the fuels was performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. The chemical component data obtained from GC-MS machines were analyzed using chem. Integration program together with NIST mass spectral search library (NIST 2005). FTIR spectra

were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software.

Results and discussion

Feedstock and Analysis:

As shown in Table 1, the dry DDGS feedstock properties such as HHV, moisture content and elemental composition were analyzed before performing the liquefaction step. The moisture content was determined using the Ohaus MB moisture analyzer. The C, H, N and O contents of the solid DDGS were also analyzed by EAI CE-440 elemental analyzer by ASTM D5291. The calorific value of the solid dry DDGS was determined with Ika-5000 bomb calorimeter by ASTM D240.

Liquefaction of DDGS

The liquefied mixture was separated into an aqueous phase and an oil phase. The aqueous phase settled to the bottom of the container and the oil fraction floats on this aqueous layer. The organic fraction was obtained with a yield of 62 wt% (aqueous fraction was not included) based on dry DDGS feedstock and had an HHV of 37.5 MJ/Kg. The yields of aqueous fraction (bottom water), char and gas were 28.4 wt%, 2.3 wt% and 7.3%, respectively.

Table 2 compares the properties of raw DDGS and liquefied DDGS product. The raw DDGS had a HHV of 19.1 MJ/kg and moisture content of 7.8 wt%. The liquefied DDGS product HHV increased to 37.5 MJ/kg, a percentage increase of 93.8%. The carbon content was increased by 73.9%. The large decrease in oxygen content reduced oxygen by 514.0%. Table 1 also shows that the liquefied DDGS product total acid value was 11.5 mg KOH/g, rather low for a bio-oil. Water content of the liquid DDGS product was 5.1%; pH was 5.2 indicating slight acidity for the liquid bio-oil intermediate; viscosity was 42.5 cSt.

Table 3 gives the chemical composition of liquefied DDGS product analyzed by GC-MS. Forty-three chemical compounds comprised of the liquefied DDGS product were identified by GC-MS. The chemical compound name and their area percentages with retention time (RT) are shown in Table 3. The total area percentage of these forty-three compounds was 67.3%.

Hydroprocessing of the liquefied DDGS product

The hydroprocessed products were clearly separated into two layers comprised of a bottom aqueous fraction with the hydrocarbon mixture floating on the aqueous fraction. The hydrocarbon mixture produced from this process had an HHV of 43.5 MJ/kg. The HHV of this undistilled mixture is just below the HHV of refined diesel (HHV value of 45.7 MJ/kg). The yield of the hydrocarbon mixture was high at 70.1 wt%. The yield of the hydrocarbon mixture was high at 70.1 wt%. This yield is much higher than the 42% reported by a hydrocarbon mixture produced from fast pyrolysis bio-oil produced from pine wood [Elliott et al. 2012].

Table 4 compares some properties of liquefied DDGS and the hydrocarbon mixture resulting from our hydroprocessing treatment. Hydrocarbon mixture properties were greatly improved from the liquefied DDGS bio-oil intermediate. HHV increased by 6.0 to 43.5 MJ/kg just below to the HHV of petroleum transportation fuels. The pH increased by 48.0% to 10.6, which made it slightly basic compared to fuels from fast pyrolysis oils that are acidic. The high pH may be due to the presence of high percentages of polycyclic aromatic hydrocarbons (PAH) and nitrogen contained compounds present in the produced hydrocarbons mixture. This eliminates any concern for acid corrosion for this hydrocarbon mixture that is always a concern with converted fast pyrolysis bio-oils. The total acid value was decreased to zero from 11.5 mg KOH/g. Water content was reduced from 5.1 to 1.1 vol%. Viscosity was reduced greatly to 3.2 from 42.5 cSt. This value is very close to the value for petroleum transportation fuels.

Table 5 shows the chemical composition of the hydrocarbon mixture produced via hydroprocessing of liquefied DDGS analyzed by GC-MS. Approximately 50 chemical compounds comparing the hydrocarbon mixture were identified. The chemical compound name and area percentage with RT are given in Table 5. The total area percentage of these compounds was approximately 100%. The hydrocarbon mixture was comprised of approximately 98.5% of hydrocarbons area% as shown in Table 5. These results are in good agreement with the DHA analysis of the hydrocarbon mixture as shown in Figure 3.

A detailed hydrocarbon analysis (DHA) was performed by the ASTM D6730-01 method. DHA classified the types of hydrocarbons and their mass percentages present in the hydrocarbon mixture produced from hydroprocessing of liquefied DDGS. The results of the DHA are given in Figure 3 and show that the hydrocarbon mixture contained n-paraffins of 6.8 mass%, iso-paraffins of 14.2 mass%, olefins of 30.0 mass%, naphthenes of 9.5 mass%, aromatics of 5.0 mass%, total C14+ of 20.4 mass% and unknown compounds of 10.9 mass%.

Figure 4 shows, simulated distillation analysis of the petroleum fuel equivalent hydrocarbons of the hydrocarbon mixture produced. Simulated distillation of hydrocarbon mixture was performed by the ASTM D2887 method for boiling range distribution of petroleum fractions by gas chromatography. These boiling temperatures are given below the named petroleum equivalents in the figure. The petroleum equivalents hydrocarbons boiling temperatures ranges are overlaps due to the presence of various complex hydrocarbon types. These petroleum equivalents were of the molecular weights of gasoline (40%), jet fuel (22%) and diesel (30%). Not shown in Figure 4 is the 7% of heavy fuel produced at temperatures above 350 °C.

The elemental analysis results of raw DDGS, liquefied DDGS product and hydrocarbon mixture are shown in Figure 5. The carbon and hydrogen content of liquefied DDGS compared to untreated DDGS increased to 77.2 and 10.6 wt% from 44.4 wt% and 7.2 wt%, respectively. The nitrogen and oxygen content decreased to 4.3 and 8.4 wt% from 5.3 wt% and 43.0 wt%, respectively. The large decrease in oxygen content reduced oxygen by 514.0%. The carbon and hydrogen content of the hydrocarbon mixture compared to liquefied DDGS increased from 77.2 to 82.7 and from 10.6 to 11.4 wt%, respectively. The nitrogen and oxygen content decreased to 3.8 from 4.3 and from 8.4 to 1.6 wt%, respectively.

Figure 6 compares the yields, HHVs, water content, acid values, and oxygen and nitrogen contents of hydrocarbon mixtures produced from hydroprocessing liquefied DDGS by using various commercial and MSU developed catalysts. Hydroprocessing of liquefied DDGS in the presence of heterogeneous catalysts such as CoMo/Al₂O₃, Pt/C, Ru/C, Ni/SiO₂-Al₂O₃, MSU 1 and MSU 2 results are shown in Figure 6. Based on our preliminary results MSU 1 and Ni/SiO₂-Al₂O₃ catalysts produced hydrocarbon mixtures with both high yield and HHV.

Figure 7 compares the FTIR spectra of liquefied DDGS product produced by liquefaction of DDGS feedstock and hydrocarbon mixture produced from hydroprocessing of liquefied DDGS. These spectra identified the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm⁻¹ (OH stretch), 2800-3100 cm⁻¹ (CH aliphatic stretch), 1600-1750 cm⁻¹ (C=O stretch) and 1350-1470 cm⁻¹ (CH bending). As shown in Figure 7, the CH (alkane functional group) aliphatic stretch and CH bending stretch absorption bands of hydrocarbons were considerably increased compared to the liquefied DDGS product. It was also

found that the C=O (carbonyl compounds) stretch absorption band was decreased in the hydrocarbons FTIR spectra compared to the liquefied DDGS. This change in absorption bands indicates that the carboxylic acids, aldehydes and other oxygenated chemical compounds were converted into hydrocarbons. The findings of the FTIR spectra were in good agreement with the physical and chemical properties described in Table 5, GC-MS chemical analysis described in Table 6 and DHA results.

Conclusions

The conversion of DDGS to value-added liquid hydrocarbon was performed successfully. The liquefaction of DDGS followed by single-stage hydroprocessing produced high energy liquid hydrocarbons of transportation fuel quality. The liquefied DDGS product was obtained with a yield of 62 wt% and had a HHV of 37.5 MJ/Kg. The energy density of liquefied DDGS produced increased by 95.6% as compared to DDGS. The hydrocarbon mixture produced from this process had an HHV of 43.5 MJ/kg. The yield of the hydrocarbon mixture was high at 70.1 wt%. The oxygen content of the hydrocarbons produced was reduced by 265.7%. The acid value of the hydrocarbons produced was decreased by 100%.

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Figure 1. Historic DDG production from U.S ethanol biorefineries. [Wang et al. 2013, RFA 2013b].

Figure 2. Schematic representation of the batch reactor setup for liquefaction and hydroprocessing reactions [Duan et al. 2011].

Figure 3. Hydrocarbon types and total mass percentages identified by DHA in the hydrocarbon mixture produced from hydroprocessing the liquefied DDGS product.

Figure 4. Gasoline, jet fuel and diesel fuels weight percentages present in hydrocarbon mixture results from simulated distillation analysis by the ASTM D2887.

Figure 5. Comparison of DDGS, liquefied DDGS product and hydrocarbon mixture elemental analysis.

Figure 6. Comparison of hydrocarbon mixture's hydrocarbons yields, HHVs, acid values, water content and oxygen and nitrogen contents produced from various catalysts.

Figure 7. Liquefied DDGS product and hydrocarbons produced samples FTIR spectra comparison.

Table 1. Tested chemical and physical properties of untreated dry DDGS.

Properties	DDGS
HHV, MJ/kg	19.1
Moisture content wt%	7.8
C %	44.4
H %	7.2
N %	5.3
O %	43.0

Table 2. Comparison of physical and chemical properties of raw DDGS and liquefied DDGS.

Properties	Raw DDGS	Liquefied DDGS
HHV, MJ/kg	19.1	37.4
Total acid number, mg KOH/g	-	11.5
pH	-	5.8
Water content, vol%	7.8	5.1
Kinematic viscosity, 40 °C, cSt	-	42.5
C %	44.4	77.2
H %	7.2	10.6
N %	5.3	4.3
O %	43.0	8.4

Table 3. Liquefied DDGS product chemical composition analysis by GC-MS with retention times and area percentages.

#	Compound names	RT	Area %
1	1H-Pyrrole, 1-methyl-	6.2	2.4
2	2,4-Hexadienal, (E,E)-	6.6	0.9

3	Toluene	7.3	1.0
4	1H-Pyrrole, 1-ethyl-	9.1	2.1
5	1H-Pyrrole, 2,5-dimethyl-	10.1	1.1
6	Cyclopentanone, 2-methyl-	10.4	1.2
7	Ethylbenzene	11.3	1.2
8	Nicotinyl Alcohol	13.2	1.1
9	1H-Pyrrole, 2-ethyl-3,5-dimethyl-	17.1	1.0
10	2-Cyclopenten-1-one, 2,3-dimethyl-	18.8	1.4
11	2-Cyclopenten-1-one, 2,3,4-trimethyl	19.8	1.4
12	1H-Pyrrole, 3-ethyl-2,4-dimethyl-	20.4	1.2
13	2-Cyclopenten-1-one, 2,3,4-trimethyl	20.9	1.7
14	1H-Pyrrole, 2-ethyl-3,5-dimethyl-	21.3	1.1
15	1H-Pyrrole, 2,3,4,5-tetramethyl-	22.4	1.0
16	Cyclopent-2-ene-1-one, 2,3,4-trimethyl-	22.5	1.1
17	Phenol, 3-ethyl-	22.8	1.1
18	1,4-Benzenediol, 2,6-dimethyl-	23.3	1.2
19	1H-Pyrrole, 3,4-diethyl-2-methyl-	23.4	3.5
20	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	23.8	1.1
21	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	24.1	3.1
22	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	24.7	4.0
23	N-Ethyl-3-methoxyaniline	26.1	0.9
24	1,3-Benzenediamine, 4-methyl-	26.2	1.6
25	2,4,6-Octatriene, 2,6-dimethyl-	26.6	2.5
26	Benzyl alcohol, 3-ethylamino-	26.8	1.5

27	Phenol, 3-(ethylamino)-4-methyl-	26.9	1.5
28	Tropidine, 2-acetyl-8-demethyl-	27.4	1.1
29	Phenol, 2,3,5,6-tetramethyl-	28.2	1.1
30	Phenol, 4-amino-3,5-diethyl	28.6	1.3
31	2-Methoxy-3-propyl-phenylamine	31.1	1.5
32	1,4-Benzenediamine, N,N-diethyl-	31.5	1.0
33	1H-Indole, 4-methyl-	32.0	1.3
34	2-Benzothiazolamine, 5,6-dimethyl-	32.9	1.8
35	1H-Indole, 1,3-dimethyl-	33.5	1.1
36	4-Oxatricyclo[4.3.1.1(3,8)]undecane	33.8	3.2
37	1H-Indole, 5,6,7-trimethyl-	37.3	1.3
38	3,5-Dichlorobenzaldehyde	38.3	1.2
39	1H-Indole, 2,3-dihydro-1,3,3-trimethyl-	39.1	1.1
40	Dodecane, 3-methyl-	41.4	2.7
41	Tridecanoic acid	48.2	1.9
42	Ethyl tridecanoate	49.0	1.0
43	Octadecanoic acid	53.0	1.9
	Total		67.3

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488 Table 4. Some physical and chemical properties of liquefied DDGS and hydroprocessed product.

489

Properties	Liquefied DDGS	Hydrocarbon mixture
HHV, MJ/kg	37.5	43.5
O, wt%	8.4	1.6
Total acid number, mg KOH/g	11.5	0

pH	5.8	10.6
Water content, vol%	5.1	1.1
Kinematic viscosity, 40°C, cSt	42.5	3.2

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491 Table 5. Hydrocarbon mixture chemical composition, RTs and area percentages as determined
 492 by GC-MS.

493

#	Compound name	RT	Area%
1	Cyclohexane	3.8	1.6
2	Cyclopropane, 1,2-dimethyl-, trans	4.5	1.8
3	1-Propene, 2-methyl-	4.8	1.7
4	Cyclohexane, methyl-	5.7	1.7
5	2-Hexene, 3-methyl-, (Z)-	6.1	1.4
6	Toluene	7.3	1.9
7	Cyclopentane, 1-ethyl-3-methyl-, t	8.3	2.5
8	Hexane, 3-ethyl-	8.6	1.6
9	Cyclohexane, ethyl-	10.2	1.6
10	Ethylbenzene	11.3	1.4
11	1-Butene, 2-ethyl-3-methyl-	11.8	0.6
12	Cyclooctanone	12.5	0.9
13	Cyclohexane, 1,2-dimethyl-	12.8	1.1
14	1-Hexene, 4-methyl-	13.1	1.4
15	Cyclohexane, 1-ethyl-2-methyl-	13.5	0.7
16	3,4-Octadiene, 7-methyl-	14.0	0.7
17	Cyclohexane, propyl-	14.5	1.1
18	Benzene, 1-ethyl-3-methyl-	15.7	0.8

19	Benzene, 1-ethyl-3-methyl-	16.5	0.7
20	Cyclohexane, 1,2-dimethyl-, cis-	16.8	0.8
21	Decane	17.4	1.5
22	Cyclohexane, butyl-	18.8	1.2
23	Cyclohexene, 1-methyl-	19.3	0.7
24	Benzene, butyl-	19.8	0.7
25	Undecane	21.5	2.1
26	Benzene, 1-methoxy-2-methyl-	23.5	1.2
27	1H-Pyrrole, 3,4-diethyl-2-methyl-	24.2	0.6
28	1-Methyl-2-tert-butylpyrrole	24.8	1.6
29	Benzene, (2-methyl-1-butenyl)-	25.0	0.7
30	25.01 0.65	25.3	1.3
31	Benzene, (methoxymethyl)-	26.3	0.9
32	Phenol, 2-ethyl-4-methyl-	26.7	0.6
33	4-Hydroxy-3-methylacetophenone	28.2	0.7
34	Undecane, 4,6-dimethyl-	29.0	0.9
35	Cyclooctene, 3-butoxy-	30.6	0.9
36	Naphthalene, 1,2,3,4-tetrahydro-1,	32.2	0.8
37	Tetradecane	32.3	1.7
38	4-Pyridinamine, N,N,2-trimethyl-	33.5	1.4
39	Pentadecane	35.6	9.8
40	Tridecane	38.6	4.4
41	3H-Indole, 3-ethyl-2,3-dimethyl-	40.3	0.6
42	1,6,10-Dodecatriene, 7,11-dimethyl	40.9	0.7

43	Heptadecane	41.5	26.6
44	Pentadecane	44.2	6.0
45	Tetradecane	44.7	1.6
46	Tridecane	46.8	2.1
47	Tridecane	49.2	1.3
48	Pentadecane	51.6	0.6
49	Cyclopentane, hexyl-	53.3	0.9
50	Tridecane	53.9	0.6
	Total		100.0

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Table 1. Tested chemical and physical properties of untreated dry DDGS.

Properties	DDGS
HHV, MJ/kg	19.1
Moisture content wt%	7.8
C %	44.4
H %	7.2
N %	5.3
O %	43.0

Table 2. Comparison of physical and chemical properties of raw DDGS and liquefied DDGS.

Properties	Raw DDGS	Liquefied DDGS
HHV, MJ/kg	19.1	37.4
Total acid number, mg KOH/g	-	11.5
pH	-	5.8
Water content, vol%	7.8	5.1
Kinematic viscosity, 40 °C, cSt	-	42.5
C %	44.4	77.2
H %	7.2	10.6
N %	5.3	4.3
O %	43.0	8.4

Table 3. Liquefied DDGS product chemical composition analysis by GC-MS with retention times and area percentages.

#	Compound names	RT	Area %
1	1H-Pyrrole, 1-methyl-	6.2	2.4
2	2,4-Hexadienal, (E,E)-	6.6	0.9

3	Toluene	7.3	1.0
4	1H-Pyrrole, 1-ethyl-	9.1	2.1
5	1H-Pyrrole, 2,5-dimethyl-	10.1	1.1
6	Cyclopentanone, 2-methyl-	10.4	1.2
7	Ethylbenzene	11.3	1.2
8	Nicotinyl Alcohol	13.2	1.1
9	1H-Pyrrole, 2-ethyl-3,5-dimethyl-	17.1	1.0
10	2-Cyclopenten-1-one, 2,3-dimethyl-	18.8	1.4
11	2-Cyclopenten-1-one, 2,3,4-trimethyl	19.8	1.4
12	1H-Pyrrole, 3-ethyl-2,4-dimethyl-	20.4	1.2
13	2-Cyclopenten-1-one, 2,3,4-trimethyl	20.9	1.7
14	1H-Pyrrole, 2-ethyl-3,5-dimethyl-	21.3	1.1
15	1H-Pyrrole, 2,3,4,5-tetramethyl-	22.4	1.0
16	Cyclopent-2-ene-1-one, 2,3,4-trimethyl-	22.5	1.1
17	Phenol, 3-ethyl-	22.8	1.1
18	1,4-Benzenediol, 2,6-dimethyl-	23.3	1.2
19	1H-Pyrrole, 3,4-diethyl-2-methyl-	23.4	3.5
20	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	23.8	1.1
21	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	24.1	3.1
22	1H-Pyrrole, 2-ethyl-3,4,5-trimethyl-	24.7	4.0
23	N-Ethyl-3-methoxyaniline	26.1	0.9
24	1,3-Benzenediamine, 4-methyl-	26.2	1.6
25	2,4,6-Octatriene, 2,6-dimethyl-	26.6	2.5
26	Benzyl alcohol, 3-ethylamino-	26.8	1.5

27	Phenol, 3-(ethylamino)-4-methyl-	26.9	1.5
28	Tropidine, 2-acetyl-8-demethyl-	27.4	1.1
29	Phenol, 2,3,5,6-tetramethyl-	28.2	1.1
30	Phenol, 4-amino-3,5-diethyl	28.6	1.3
31	2-Methoxy-3-propyl-phenylamine	31.1	1.5
32	1,4-Benzenediamine, N,N-diethyl-	31.5	1.0
33	1H-Indole, 4-methyl-	32.0	1.3
34	2-Benzothiazolamine, 5,6-dimethyl-	32.9	1.8
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36	4-Oxatricyclo[4.3.1.1(3,8)]undecane	33.8	3.2
37	1H-Indole, 5,6,7-trimethyl-	37.3	1.3
38	3,5-Dichlorobenzaldehyde	38.3	1.2
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42	Ethyl tridecanoate	49.0	1.0
43	Octadecanoic acid	53.0	1.9
	Total		67.3

Table 4. Some physical and chemical properties of liquefied DDGS and hydroprocessed product.

Properties	Liquefied DDGS	Hydrocarbon mixture
HHV, MJ/kg	37.5	43.5
O, wt%	8.4	1.6
Total acid number, mg KOH/g	11.5	0

pH	5.8	10.6
Water content, vol%	5.1	1.1
Kinematic viscosity, 40°C, cSt	42.5	3.2

Table 5. Hydrocarbon mixture chemical composition, RTs and area percentages as determined by GC-MS.

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9	Cyclohexane, ethyl-	10.2	1.6
10	Ethylbenzene	11.3	1.4
11	1-Butene, 2-ethyl-3-methyl-	11.8	0.6
12	Cyclooctanone	12.5	0.9
13	Cyclohexane, 1,2-dimethyl-	12.8	1.1
14	1-Hexene, 4-methyl-	13.1	1.4
15	Cyclohexane, 1-ethyl-2-methyl-	13.5	0.7
16	3,4-Octadiene, 7-methyl-	14.0	0.7
17	Cyclohexane, propyl-	14.5	1.1
18	Benzene, 1-ethyl-3-methyl-	15.7	0.8

19	Benzene, 1-ethyl-3-methyl-	16.5	0.7
20	Cyclohexane, 1,2-dimethyl-, cis-	16.8	0.8
21	Decane	17.4	1.5
22	Cyclohexane, butyl-	18.8	1.2
23	Cyclohexene, 1-methyl-	19.3	0.7
24	Benzene, butyl-	19.8	0.7
25	Undecane	21.5	2.1
26	Benzene, 1-methoxy-2-methyl-	23.5	1.2
27	1H-Pyrrole, 3,4-diethyl-2-methyl-	24.2	0.6
28	1-Methyl-2-tert-butylpyrrole	24.8	1.6
29	Benzene, (2-methyl-1-butenyl)-	25.0	0.7
30	25.01 0.65	25.3	1.3
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36	Naphthalene, 1,2,3,4-tetrahydro-1,	32.2	0.8
37	Tetradecane	32.3	1.7
38	4-Pyridinamine, N,N,2-trimethyl-	33.5	1.4
39	Pentadecane	35.6	9.8
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46	Tridecane	46.8	2.1
47	Tridecane	49.2	1.3
48	Pentadecane	51.6	0.6
49	Cyclopentane, hexyl-	53.3	0.9
50	Tridecane	53.9	0.6
	Total		100.0