Fuel 150 (2015) 512–518

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Liquefaction of dried distiller's grains with solubles (DDGS) followed by hydroprocessing to produce liquid hydrocarbons

Sathish K. Tanneru, Philip H. Steele *

Department of Sustainable Bioproducts, Mississippi State University, Mississippi State, Starkville, MS 39762, United States

HIGHLIGHTS

- Conversion of DDGS to value-added liquid hydrocarbons was performed successfully.
- Hydroprocessing of HTL product was more successful compared to the pyrolysis oil.
- The HHV of hydrocarbons produced increased by 127.2% as compared to DDGS.

ARTICLE INFO

Article history:
Received 3 November 2014
Received in revised form 9 January 2015
Accepted 29 January 2015
Available online 20 February 2015

Keywords:
Liquefaction
DDGS
Hydroprocessing
DHA
FTIR
GC–MS

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.

1. Introduction

Renewable, environmentally friendly, clean-burning and CO_2 neutral energy resources have been developed in recent years to replace conventional fuels [18] 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 [9–11,18]. 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% (by volume) additive to gasoline [27]. 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 [26]. 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 [4]. 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 [15]. Therefore, it would be desirable to develop new methods to produce economically viable fuels from DDG.

* Corresponding author.
E-mail address: psteele@cfr.msstate.edu (P.H. Steele).

http://dx.doi.org/10.1016/j.fuel.2015.01.105
0016-2361/

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 [13,21]. 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 [2,14,20].

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 [14].

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 [24]. 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. [2].

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 [12]. The shelf life of WDG prior to deterioration is 3–4 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 lb) of corn feedstock produces 18 lb (2.72 gallons) of ethanol, approximately 17.5 lb of distiller's grains and 18 lb of carbon dioxide (CO_2) [27,26]. 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 Fig. 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 [26,16].

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 [23]. The liquefaction process has some unique features. Liquefaction

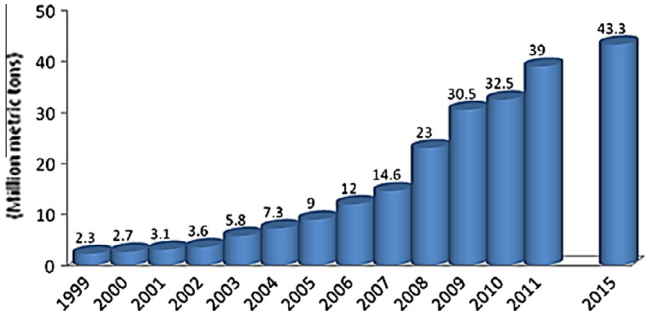

Fig. 1. Historic DDG production from U.S ethanol biorefineries [26,16].

does not require that the feedstock be dried. Drying is an expensive step and usually takes a large amount of energy and time [28,1]. 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. [27] 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. [7] 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 3:1–5:1. 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. [12] 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 to 50.3 wt% while yields of biochar ranged from 23.5 to 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. [25] also studied the pyrolysis of DDGS by using spouted-entrained bed and fixed bed reactors. The pyrolysis of