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Production and Use of Evolving Corn-Based Fuel Ethanol Coproducts in the U.S.

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Additional information is available at the end of the chapter

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1. Introduction

We face many challenges in our society, due especially to growing population pressures and increased economic mobility. These can result in increased demands for food, clothing, housing, and consumer goods. Additionally, there has been a growing need for energy during the last several decades, which historically has been met primarily by use of fossil fuels. In the U.S., transportation fuels generally account for about 1/3 of all energy consumed. Of this, about 90% comes from fossil sources. Between 1/2 and 2/3 of the total U.S. demand for petroleum has been met by imports during the last 30 years [1]. Many argue that this scenario is not sustainable in the long run, and other energy alternatives are needed. During 2005-2010, the U.S. experienced some of the highest growth rates ever seen in the domestic biofuels industry.

The U.S. biofuels industry has recently grown as a response to increasing energy needs and energy prices. Bio-based fuels can theoretically be manufactured from many biological materials. Biochemical conversion of carbohydrates into ethanol and lipids into biodiesel are the two most common routes at this point in time. This includes most cereal grains (e.g., corn, barley, wheat, sorghum, rice, etc.), oilseeds (e.g., soybeans, sunflowers, flax, rapeseed, and others), native prairie grasses (including miscanthus, switchgrass, prairie cord grass, reed canary grass, and other grasses), agricultural residues (including corn stover, rice husks, wheat straw, and other crop residues), algae, municipal solid wastes, food processing wastes, and other biological wastes and substrates [2, 3, 4, 5, 6, 7, 8, 9, 10]. Right now, however, the most heavily used feedstock for biofuel production in the U.S. is corn grain. Industrial-scale alcohol manufacturing from corn starch is readily accomplished, and at a low cost (generally about \$1/gal), which is considerably lower than other biological material conversions in the U.S.

In recent years, the corn-based fuel ethanol industry in the U.S. has reached a scale which can impact the nation's supply of transportation fuels. Only during the last decade, however, has



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this industry become visible to the average citizen. This has been due, in part, to the growing demand for domestic transportation fuels for national security, escalating prices at the fuel pump, positive economic effects throughout rural America, as well as questions and controversies surrounding the production and use of corn ethanol. While fuel is the main aim of the ethanol industry, nonfermentable coproducts are also generated during manufacturing. The primary coproduct is distillers dried grains with solubles (DDGS) (Figure 1), which is the focus of this chapter.



Figure 1. Corn-based Distillers Dried Grains with Solubles (DDGS) is currently the most common coproduct available from U.S. fuel ethanol plants (Photo courtesy of Rosentrater).

To help meet the increasing demand for transportation fuels, and to meet federal U.S. mandates, the number of ethanol plants has rapidly increased in recent years, as has the quantity of fuel ethanol and coproducts produced (Figure 2). As of 2015, the RFS (Renewable Fuel Standard) mandates the use of 15 billion gal/y (56.8 billion L/y) of corn-based ethanol in the U.S. [13]. At the beginning of 2015, there were 213 fuel ethanol plants in the U.S., which produced nearly 56.8 billion L/y (15.0 billion gal/y) [12, 15]. As the biofuels industry continues to evolve, cellulosic and other bio-based fuels will gain prevalence in coming years.

Most new ethanol plants have been dry-grind facilities (Figure 3), which will be discussed subsequently. As production volume has increased, the processing residues, known collectively as "distillers grains" – have increased concomitantly (Figure 2). Between 35 and 40 million metric tonnes (t) of distillers grains (both wet and dry) will be produced each year by the U.S. fuel ethanol industry over the next several years. In recent years there has actually been a slight decline in distillers grains production, due to evolving processes which now extract oil from the coproduct streams. This will be discussed at a later point in the chapter.

As the industry has grown over the last few decades, the consumption of corn has grown as well (Figure 4). In recent years, over 30% of the U.S. corn crop is used to produce fuel ethanol.

When examining these data, however, it is important to note several key points: most corn in the U.S. is not human food-grade corn, exports have been relatively constant over time, there has only been a slight decline in the corn used for animal feed, but the overall quantity of corn which is produced by U.S. farmers has been greatly increasing over time. The corn used to manufacture fuel ethanol has arisen from the growing U.S. supply of corn. Furthermore, and more importantly, the corn which has been used to produce ethanol (instead of animal feed) is generally replaced by DDGS and other ethanol coproducts in these animal feeds. Ethanol coproducts (primarily DDGS and DWG) are key to the long-term viability of the fuel ethanol industry as well as the various livestock industries. Thus feed and fuel can be produced simultaneously, contrary to what may be discussed in the media.

2. Objectives

The aims of this chapter are multiple: 1) to review fuel ethanol and coproduct manufacturing in the U.S.; 2) to discuss the importance of distillers coproducts to both the biofuel and the livestock industries; and 3) to illustrate how coproducts are changing and potential uses are expanding as the ethanol industry evolves.

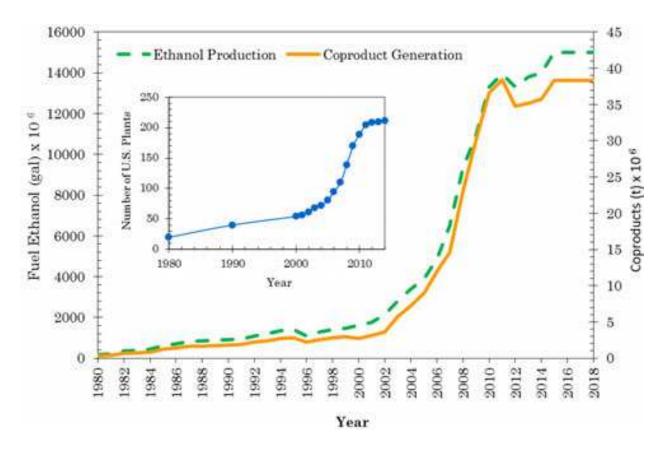
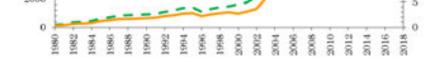


Figure 2. U.S. fuel ethanol (gal) and DDGS (t) production over time; RFS denotes levels mandated by the Renewable Fuel Standard. Inset shows number of U.S. ethanol plants over time [12, 13, 14, 15].



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Year

Fig. 2. U.S. fuel ethanol (gal) and DDGS (t) production over time; RFS denotes levels mandated by the Renewable Fuel Standard. Inset shows number of U.S. ethanol plants over time [12, 13, 14, 15].



Fig. 3. U.S. dry grind corn-to-ethanol manufacturing plants. A. 450 x 10⁶ L/y plant. B. 80 x 10⁶ L/y plant (Photos courtes of Rosentrater)

courtesy of Rosentrater). **Figure 3.** U.S. dry grind corn-to-ethanol manufacturing plants. A. 450 x 10⁶ L/y plant. B. 80 x 10⁶ L/y plant (Photos courtesy of Rosentrater).



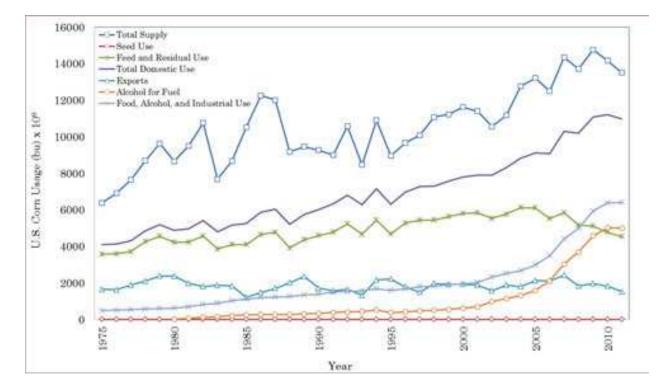


Figure 4. U.S. corn production (bu) and consumption according to major categories of use (adapted from [16]).

3. Manufacturing Processes

Corn ethanol is produced by two main commercial approaches. These include dry grind processing and wet milling. Over the last 20 years, many new fuel ethanol plants have been constructed in the U.S. (Figure 2). During this time, the industry has grown, evolved, and matured. Dry grind processing has become the most popular method for ethanol manufacturing for a variety of reasons, including lower capital and operational costs, lower energy use, and lower water consumption. In fact, most new ethanol plants in recent years have been dry grind facilities, and comprise approximately 80% of ethanol facilities in the U.S. [13].

Dry grind processing (Figure 5) consists of multiple unit operations. Primary steps include grain receiving, cleaning, storage, grinding, cooking, liquefaction, saccharification and fermentation, solids separation, distillation, ethanol storage and loadout, whole stillage centrifugation, coproduct drying, coproduct storage, and loadout. Additionally, ethanol plants entail heat recovery, waste management, CO₂ extraction, dust control, and facility instrumentation systems. Specific details will vary, though, as each ethanol plant is somewhat unique in design and operation. Oil extraction is a relatively new technology for creating additional coproduct streams, and will be discussed later.

Grinding, cooking, and liquefying increase surface area and allow the corn starch to be broken down into dextrins by enzymes (e.g., alpha-amylase) during saccharification, and subsequently into glucose molecules (using gluco-amylase), which are then consumed during fermentation by yeast (Saccharomyces cerevisiae). After fermentation, ethanol is removed from water and nonfermentable materials (e.g., proteins, fibres, oils, minerals) by separation and distillation. Dewatering results in wet cake (e.g., suspended solids) and soluble solid-laden water, evaporation of the soluble solids in the water stream, mixing the condensed solubles with the wet cake, and then drying this mixture can result in a variety of coproducts. These are known as "distillers grains", and can be wet or dry, and may or may not have condensed soluble materials added into the mix. Distillers Dried Grains with Solubles (DDGS) is the most common coproduct. It is typically dried to about 10% moisture content or less, to ensure proper shelf life and reduce flowability problems. Distillers grains are generally sold to local livestock producers. It is also transported by truck and rail to livestock producers throughout the nation. DDGS has increasingly been exported to overseas markets in recent years. Distillers Wet Grains (or DWG) is popular with beef and dairy producers near ethanol plants, due to better digestibility and lower price (because it is not dried). In fact, it has been estimated that, nationwide, approximately 25% to 30% of distillers grains sales are for DWG. But, because the moisture contents are generally greater than 50 to 60%, their shelf life is very limited (less than one week, generally), especially in summer months, and shipping large quantities of water is expensive. DDGS is still the most prevalent type of distillers coproduct in the marketplace.

Dry grind ethanol manufacturing generally results in three key products. These include fuel ethanol, the primary end product; residual nonfermentable corn kernel components, which are further processed and then sold as distillers grains (or coproducts); and carbon dioxide. A rule of thumb used in industry is that each 1 kg of corn processed will produce approximately 1/3 kg of each of the products. Another general rule is that each bushel of corn processed (about

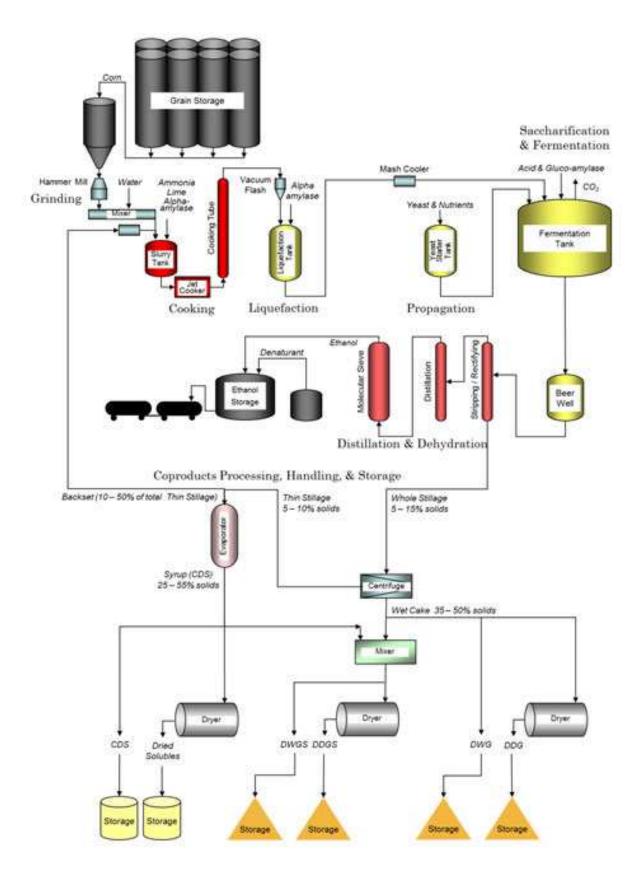


Figure 5. Flow chart of typical corn dry grind fuel ethanol and coproducts processing operations.

56 lb; 25.4 kg) will yield almost 2.9 gal (11.0 L) of ethanol (in reality, it will range from about 2.7 to 2.8 gal/bu, depending on the efficiency of the plant), 18 lb (8.2 kg) of distillers grains, and 18 lb (8.2 kg) of carbon dioxide (which is a byproduct of the yeast metabolism). These will vary from plant to plant due to production practices, equipment used, residence times, process temperatures, concentrations, maintenance schedules, equipment cleanliness, environmental conditions, as well as the composition and quality of the raw corn, the location where the corn was grown, and the growing season that produced that corn.

During fermentation the yeast's metabolic processes which convert glucose into ethanol result in carbon dioxide as a byproduct. This can be captured, compressed, and sold to gas markets such as beverage or dry ice manufacturers. This is especially attractive to ethanol plants near metropolitan areas. Most of the time it is just released to the atmosphere because logistics make CO_2 sales impractical. Additional detailed information on ethanol and DDGS manufacturing can be found in [17, 18].

4. Importance of Coproducts

Coproducts are important to the ethanol industry for a number of reasons. First and foremost, coproducts are additional sources of revenue to ethanol plants. Since these coproducts are primarily used as animal feed ingredients, monitoring and maintaining the consistency of coproduct compositions is critical to sales and utilization. DDGS from most modern U.S. fuel ethanol plants typically contains about 30% protein, 10% fat, at least 40% neutral detergent fibre, and up to 12% starch (of course, the lower the starch the better, as this is indicative of conversion efficiency) [19, 20]. DDGS composition can vary somewhat between plants. Within a single plant over time, however, DDGS is much less variable than amongst plants. Table 1 illustrates composition of DDGS from five ethanol plants in South Dakota, USA. Protein levels ranged from 28.3 to 31.8%, fat ranged between 9.4 and 11.0%, and ash ranged from 4.1 to 13.3%.

Plant	Crude Protein (%)	Crude Lipid (%)	NDF (%)	ADF (%)	Starch (%)	Ash (%)
1	28.33	10.76	31.84	15.56	11.82	13.27
2	30.65	9.75	39.90	15.21	9.81	12.84
3	28.70	10.98	38.46	17.89	11.59	11.52
4	30.65	9.40	36.73	15.28	9.05	4.13
5	31.78	9.50	38.88	17.24	10.05	4.48

 Table 1. Composition (% db) of DDGS from ethanol plants in South Dakota [21].

It is instructive to examine composition differences in DDGS from plants throughout the U.S. For example, DDGS from 49 plants from 12 states were analysed for proximate composition (Table 2) and amino acid profiles (Table 3) [22]. On average, dry matter ranged from 87.9% to

90.6%, protein ranged from 29.4% to 32.6%, fat ranged from 9.6% to 12.8%, crude fibre ranged from 6.7% to 9.3%, and ash ranged from 4.2% to 6.6%. It appeared that geographic location of the ethanol plants didn't really play a role for any of the nutrients, as no nutrients seemed to be significantly affected by location.

Some ethanol plants are implementing new fractionation systems to produce new coproduct streams [13], and this is beginning to alter the nutrient composition of the distillers coproducts in the market place. More will be discussed later in this chapter.

State	Plants Sampled	Dry Matter (%)	Crude Protein (%)	Crude Lipid (%)	Crude Fibre (%)	Ash (%)
Minnesota	12	89.03	30.70	11.73	6.96	6.63
Illinois	6	89.72	29.98	11.48	7.26	5.60
Indiana	2	90.55	29.40	12.80	8.07	5.86
Iowa	7	88.92	31.23	10.27	7.57	5.76
Kentucky	3	90.57	29.43	9.77	9.28	4.47
Michigan	1	89.60	32.60	11.00	7.37	6.06
Missouri	2	87.90	30.45	10.25	7.17	5.39
Nebraska	4	89.02	30.40	11.35	8.13	4.23
New York	1	88.21	30.00	9.60	7.87	4.55
North Dakota	4	89.21	31.75	11.70	6.89	6.32
South Dakota	4	88.61	31.80	11.53	6.65	4.78
Wisconsin	3	89.68	31.70	11.63	7.59	5.77
Overall Average	49 (Total)	89.25	30.79	11.09	7.57	5.45

Table 2. Typical proximate composition (% db) of DDGS (averages of samples from 49 ethanol plants) [22].

State	Plants Sampled	Arginine (%)	Histidine (%)	Isoleucine (%)	Leucine (%)	Lysine (%)	Methionine (%)
Minnesota	12	1.39	0.84	1.20	3.63	0.99	0.61
Illinois	6	1.37	0.82	1.15	3.45	0.94	0.63
Indiana	2	1.19	0.79	1.08	3.28	0.85	0.60
Iowa	7	1.34	0.86	1.20	3.63	0.95	0.61
Kentucky	3	1.35	0.79	1.09	3.33	0.89	0.66
Michigan	1	1.28	0.86	1.18	3.67	0.87	0.71
Missouri	2	1.35	0.83	1.18	3.68	0.89	0.73
Nebraska	4	1.46	0.88	1.18	3.61	1.05	0.65
New York	1	1.46	0.85	1.21	3.64	1.04	0.61
North Dakota	4	1.37	0.88	1.24	3.76	0.97	0.65

State	Plants Sampled	Arginine (%)	Histidine (%)	Isoleucine (%)	Leucine (%)	Lysine (%)	Methionine (%)
South Dakota	4	1.47	0.87	1.22	3.70	1.08	0.62
Wisconsin	3	1.45	0.86	1.24	3.75	1.07	0.59
Overall Average	49	1.37	0.84	1.18	3.59	0.96	0.64
State	Plants Sampled	Phenylalanine (%)	Threonine (%)	Tryptop (%)		Valine (%)	Tyrosine (%)
Minnesota	12	1.59	1.17	0.24		1.62	1.20
Illinois	6	1.51	1.11	0.22	<u>,</u>	1.52	1.22
Indiana	2	1.45	1.04	0.21	_	1.44	-
Iowa	7	1.57	1.14	0.25	5	1.60	-
Kentucky	3	1.48	1.09	0.26)	1.43	-
Michigan	1	1.52	1.15	0.25	5	1.57	-
Missouri	2	1.53	1.15	0.24	Ł	1.58	-
Nebraska	4	1.58	1.15	0.26)	1.58	1.14
New York	1	1.63	1.11	0.20)	1.59	1.19
North Dakota	4	1.62	1.19	0.25	5	1.67	-
South Dakota	4	1.67	1.19	0.23	3	1.63	1.35
Wisconsin	3	1.65	1.14	0.22	2	1.64	1.25
Overall Average	49	1.56	1.13	0.24	ŀ	1.57	1.22

Table 3. Typical amino acid levels (% db) of DDGS (averages of samples from 49 ethanol plants) [22].

The U.S. ethanol industry's primary market for distillers grains has historically been as a commodity livestock feed ingredient. Most often this has been in the form of DDGS, and in recent years in the form of DWG. All other ethanol coproducts have historically been sold at much lower levels; some of these other coproducts are not produced at some ethanol plants). Using ethanol coproducts for livestock feed or feed supplements have become effective methods for using these materials. Coproducts contain appropriate nutrients and they are highly digestible (depending on the species). Furthermore, use of coproducts in animal feeds (in place of corn grain) will actually help offset corn which has been used for ethanol production (the so-called food vs. fuel debate). In fact, it has been shown that DDGS can replace corn in livestock diets on a 1:1 up to a 1:1.2 level, depending on the species. The majority (over 80%) of U.S. distillers coproducts are used in beef and dairy feeds, because ruminants can use high levels of fibre. As feed ingredient prices have increased in recent years, coupled with increasing knowledge about how to effectively use these feed ingredients, ethanol coproduct use in swine and poultry diets have increased in recent years [22]. Many feeding trials have been conducted on coproducts in livestock diets over the years, for both monogastric and ruminant feeds (many of these studies are fully described in Liu and Rosentrater, 2011). Depending on the diet

composition used, all livestock species have been shown to thrive at 10% DDGS inclusion, and most can tolerate levels up to and even greater than 20%.

DDGS use in livestock diets has continued to increase over the years. Various predictions of peak potential DDGS use in domestic U.S. beef, dairy, swine, and poultry markets have estimated that between 40 and 60 million t could be used in the U.S. each year, depending upon inclusion rates, age, etc., for each species [23, 24, 25]. Around the world, the need for protein-based animal feeds continues to grow, and DDGS has become a global commodity. Of the 23 million t of DDGS produced in 2008 [13], 4.5 million t were exported to international markets [26]; this accounted for nearly 20% of U.S. DDGS production that year (Figure 6). And the potential for global exports is projected to increase for the foreseeable future, and will likely hover near about 25% of all DDGS production in coming years [25, 27]. In recent years, China has become the dominant global importer of DDGS. Extensive information about the use of DDGS in livestock diets can be found in [18] as well as [28].

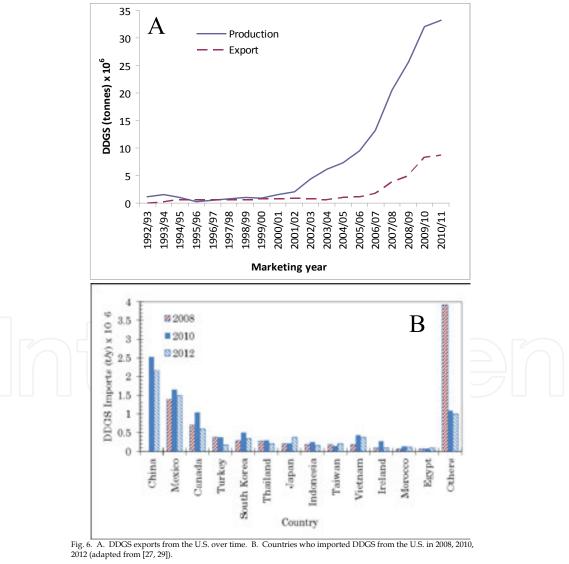


Figure 6. A. DDGS exports from the U.S. over time. B. Countries who imported DDGS from the U.S. in 2008, 2010, 2012 (adapted from [27, 29]).

The sale of nonfermentable coproducts is critical to the fuel ethanol industry as a source of revenue; and these materials have also become important feed ingredients to the livestock industry over the last decade. Sales of dry and wet distillers coproducts generally translates into 10 to 20% of an ethanol plant's total revenues, and can even be as high as 40% (depending on the economics). These materials really are "coproducts", not "byproducts" or "waste materials". In fact, many plants recognize this and promote their simultaneous production of animal feed and biofuel.

In recent years, the market price of DDGS has ranged from approximately \$50/t (in the early 2000s) to more than \$300/t (2012-2013) (Figure 7). The prices of corn and DDGS have generally paralleled each other fairly well over the years (Figure 8A). This trend occurs due, in large part, to the fact that DDGS is often used to replace corn in livestock diets. In the last decade, DDGS has increasingly been used as a soybean meal replacement also. Because soybean meal has a higher protein content, DDGS is often sold at a lower price compared to either corn or soybean meal (Figure 8A). This has been true volumetrically as well as per unit protein (Figure 8B). In the last few years DDGS has actually been sold at more than 100% the value of corn. This is frequently due to external impacts on the marketplace, including international exports.

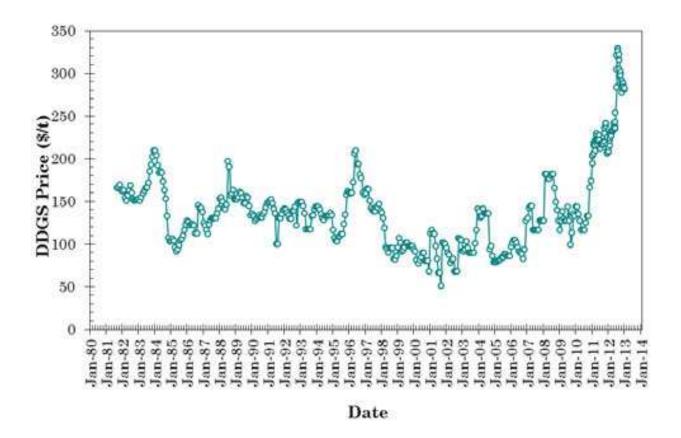


Figure 7. DDGS sales price over time (monthly averages) (adapted from [16, 30]).

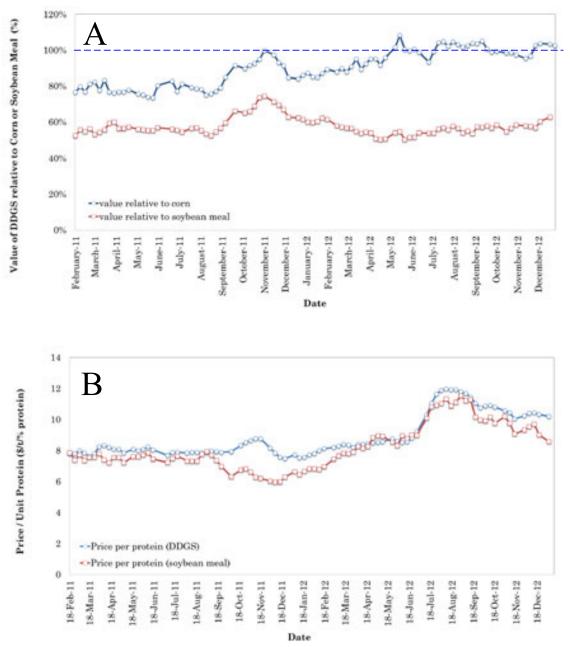


Fig. 8. A. Example comparisons of DDGS, soybean meal (SBM), and corn sales prices and their relative comparisons. Figure Sost comparison approximate processing and their relative comparisons. B. Cost comparisons on a per unit protein basis (adapted from [30]).

5. Coproduct Evolution

Even though the corn ethanol industry is maturing, there continue to be efforts to develop new, valued-added materials from the corn kernels as well as from the coproduct materials. When these research efforts are commercialised, they will result in more products from the corn kernel itself (an approach known as upstream fractionation) and the distillers grains (known as downstream fractionation). These types of fractionation approaches can result in

the separation of components of high, medium, and low value (Figure 9). For example, several mechanical and chemical approaches have been developed to remove protein, fibre, or oil components from the endosperm (which contains the starch). This type of separation will allow a highly-concentrated starch substrate to be introduced to the fermentation process, and will allow the other corn kernel components to be used for human food or other high-value applications. [31] provided an extensive discussion regarding various pre-fermentation fractionation approaches. On the other hand, post-fermentation fractionation techniques have also been examined. For example, [32] used a combination of air classification and sieving to separate fibre particles from DDGS. All of these approaches, if implemented commercially, will alter the chemical composition and digestibility of the resulting DDGS.

Many plants have recently begun adding capabilities to concentrate nutrient streams such as oil, protein, and fibre into specific fractions, which can then be used for targeted markets and specific uses. For example, one company in Iowa is now separating fibre from the DDGS and using it as a feedstock for cellulosic ethanol production. Additionally, many companies have begun removing oil from the whole stillage and/or CDS streams (Figure 10). This oil, which is officially known as Distillers Oil, Feed Grade (Figure 11), can readily be converted into biodiesel or animal feed ingredients, but they cannot be used for food grade corn oil, because they are too degraded. In fact, more than 85% of U.S. ethanol plants are now removing oil, because the economics are so favourable. Of note, in 2010 almost no ethanol plants were extracting oil...the rapid increase has solely been due to added value streams for the ethanol plants. On the horizon is concentrated corn proteins, which can be used for high-value animal feeds (such as aquaculture or pet foods), or other feed applications which require high protein levels (such as monogastrics or younger animals).



Figure 9. Fractionation of DDGS into individual chemical components (or at least concentrating them) offers the opportunity for new value-added uses and new revenue streams.

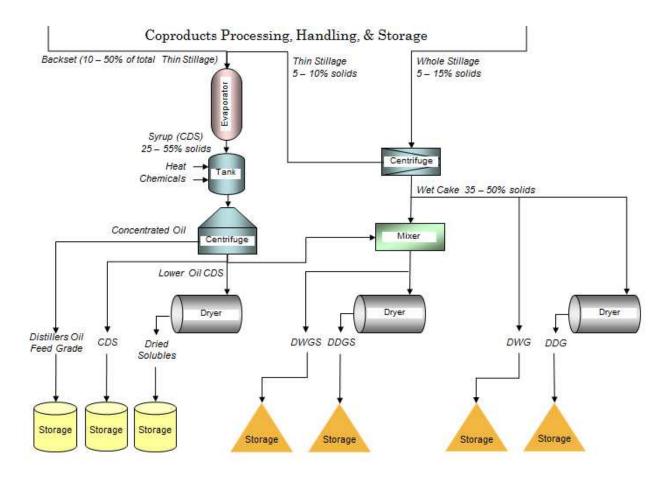


Figure 10. Oil is now removed at many ethanol plants via centrifugation of condensed distillers solubles, after a heating step and additional chemicals are added, which allow the oil to be removed without forming an emulsion.



Figure 11. Distillers Oil, Feed Grade, is being extracted from nearly 85% of all U.S. ethanol plants in 2014 (Photo courtesy of Rosentrater).

As these process modifications are developed, tested, and implemented at commercial facilities, improvements in coproducts will be realized and increasingly used in the market-

place. These new products will require extensive investigation in order to determine how to optimally use them and to quantify their values in the marketplace.

6. Conclusions

The fuel ethanol industry in the U.S. has grown exponentially during the last decade in response to government mandates and due to increased demand for alternative fuels. This has become especially pronounced as the price of gasoline has drastically fluctuated, and consumers have realized that fuel prices are problematic. Additionally, energy has become an issue of national security. Corn-based ethanol is not the entire solution to transportation fuel needs. But it is clearly a key component to addressing energy needs. Corn ethanol is seen by many as a transition to other bio-based fuels in the long run; but this industrial sector will continue to play a key role in the bioeconomy, as it is a proven approach to large-scale industrial bioprocessing. And as the industry grows, coproducts will become increasingly important for economic and environmental sustainability. One way to improve sustainability is to diversify coproducts as well as integrate systems (Figure 12, for example), where materials and energy cycle and recycle. For example, upstream outputs become downstream inputs for various components of a biorefinery factory, animal operation, energy production (i.e., heat, electricity, steam, etc.), feedstock operation, and other systems. A closed loop system would be the ultimate scenario. By integrating these various components, and developing a diversified portfolio (beyond just ethanol and distillers grains) the biorefinery will not only produce fuel, but also fertilizer, feed, food, industrial products, energy, and more importantly, can be selfsustaining.

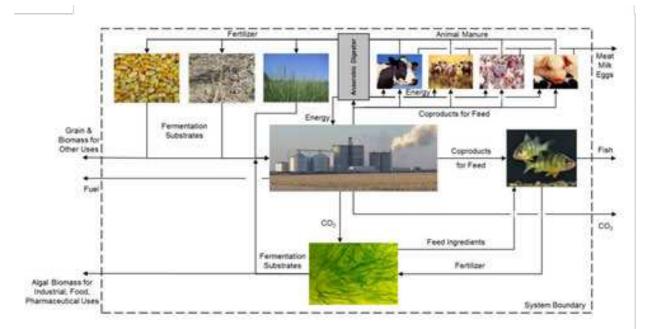


Figure 12. Coproducts will continue to play a key role as the biofuels industry evolves and becomes more fully integrated. This figure illustrates one concept of combining fuel production with animal and plant production systems.

List of Abbreviations

CDS: Condensed distillers solubles DDG: Distillers dried grains DDGS: Distillers dried grains with solubles DWG: Distillers wet grains DWGS: Distillers wet grains with solubles RFS: Renewable Fuel Standard SBM: Soybean meal

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