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BIOADHESIVES FROM DISTILLER'S DRIED GRAINS WITH SOLUBLES (DDGS) AND STUDIES ON SUSTAINABILITY ISSUES OF CORN ETHANOL INDUSTRIES

presented by

ABHISHEK SINGH

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of the requirements for the

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Major Professor's Signature

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By

Abhishek Singh

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ABSTRACT

Bioadhesives from Distiller's Dried Grains with Solubles (DDGS) and Studies on Sustainability Issues of Corn Ethanol Industries

By

Abhishek Singh

Presently, the United States is the largest producer of bioethanol in the world. Currently, around 7 billion gallons of bioethanol is produced by more than 130 corn-milling facilities. Dry milling of corn produces ethanol, and coproducts like Distillers Dried Grains with Solubles (DDGS) and carbon dioxide in equal proportions. Based on experiments, it was observed that only 1/6th of the entire corn plant is converted to ethanol, the rest is underutilized or goes to waste. Recent research thrust is to produce ethanol from the lignocellulose biomass. Bioadhesives derived from DDGS would be one of the value-added approaches to increase the economic revenues. The DDGS-based adhesive developed here is intended to be an alternative to conventional starch adhesives. DDGS was hydrolyzed in an alkali medium, resulting in a brown, viscous and tacky liquid, referred to here as bioadhesive. One of the bioadhesive formulations had average lap-shear strength of 127 psi when used to bond paperboard. The mode of failure was cohesive in nature. The thermal stability of bioadhesive was above 200°C, suggesting suitability for use over a broad temperature range. The bioadhesive had good spreadability even at 50% solids content, where as in case of starch even a 10% solution is too viscous for use. In the present study, aspects such as environmental concerns, animal nutrition, toxicity were evaluated to find the reasons that limit the scope of its sustainability. In the context of mounting environmental concerns and due to the fact that the petroleum resources are fast depleting, it is important to grow the biobased economy.

I dedicate this thesis to my parents and my sister Alpana

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Chapter - Introduction

Crude oil and natural gas are the lifelines of any nation as it satiates domestic and commercial energy requirements. Fossil fuel dependencies are ever increasing and at this point of civilization, it would be irrational to expect energy consumption reduction. An estimate predicts that the world's energy needs will increase approximately three-fold by the end of this century [1]. World patterns of petroleum consumption are increasing at 2% growth rate which accounts to a production of 1000 barrels a second [2]. Historic trends of petroleum consumption are clear from Figure 1 [3]. Realizing energy crisis it is important to appreciate that energy is one of the most significant parameters to scale the development of a nation. As a general trend, the more developed a nation is, the more energy it consumes, estimated by energy consumed per capita.

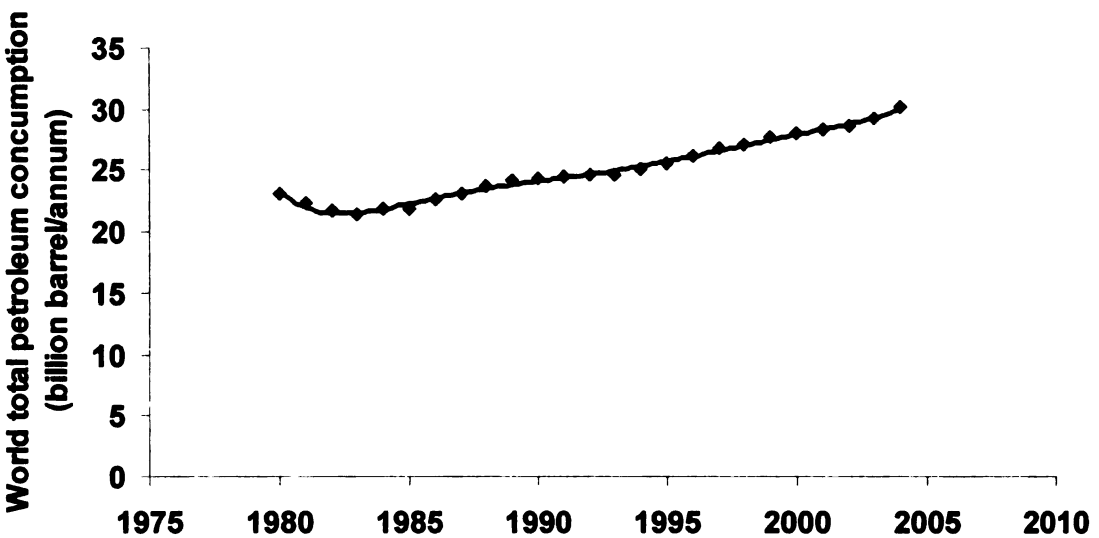

Figure 1: World petroleum consumption pattern (*after ref. 3)*

In analyzing energy consumption key sectors of consideration are transportation, industrial, commercial and public services, agriculture and residential. Sectoral consumption of energy suggests that there is huge difference between the developed and

developing nations. As per the International Energy Agency (IEA), it is estimated that biomass fulfils for on an average one-third of the energy requirements in developing nations from Africa and Asia. The poor countries have still higher dependencies on biomass as fuel for heat and cooking purposes [4]. Energy consumption patterns among various sectors of industrially developed nations, as compared to the developing nations, suggest that there is huge energy consumption contrast [5]. Typically, for a developed nation the energy consumptions are higher than developing nations by 10 times in the transportation sector, 2.7 times in agriculture sector, more than 13 times in commercial and public services, 5 times in industrial consumption and 3 times higher for residential energy needs. A striking disparity is observed in the energy consumption that residential sector energy requirement of developed countries is comparable to the developing nation's total energy demand [5]. Per capita energy consumption is a significant parameter to estimate degree of development. Comparing three classes of development also suggests contrast. In poor countries, an average person survives on less than one barrel (5.6 gigaJoules) of oil equivalent per year. A person in the developing nation utilizes the energy equivalent to 6 barrels of oil (34 gigaJoules) on annual basis. Whereas the average person in the developed world can afford to spend nearly 40 barrels of oil equivalent (220 gigaJoules) [5, 6].

On a broader perspective, energy consumption trend suggests that the more developed a nation is, the higher is the energy consumption. However, correlation of nation's wealth to its energy consumption does not always go hand in hand; the energy efficiency can add contrast to this relation. To exemplify, consider nations Japan and Norway, though Japan has slightly higher per capita income, USD 35,620, but due to

fewer local resources of energy generation, there is more efficient energy usage therefore lower per capita energy consumption (150 GJ). Whereas for Norway there is plenty of cheap hydroelectricity resources therefore, even with slightly lower per capita income of USD 34,530 the per capita energy consumption is 250 gigaJoules [7] . As regards to energy, petroleum is the most popular energy source, common to all nations. Again the industrial technologies prevalent in developing nations are more energy intensive than their developed competitors.

1.1 Renewable energy

Renewable energies are those that either are renewable natural resources or inexhaustible by source. The classification of renewable energy includes biomass energy, hydroelectric, solar, wind, and geothermal. Among all contributor to the world energy economy, biomass is the fourth largest after oil, natural gas and coal [8]. Biomass holds the potential to produce a variety of energy forms viz. electricity, fuels in solid, liquid, and gaseous states, and heat, as well as chemicals and biobased materials. In United States by 2004 about 100 quadrillion Btu of total energy was consumed and it is projected that the energy demand in the following two decades is likely to increase up to 131 Btu [9].

As per vision 25x25 the United States targeted to produce 25 percent of its energy from renewable resources by the year 2025 [10]. By 2004 the total share of renewable energy is little more than 6 % while fossil fuels account for 80 % of energy requirements. From Figure 2 and Appendix 1, it is clear that the contribution of renewable energy has been steady during the early half of this decade [11]. Among fossil fuels coal and natural

gas has contributed more or less by equal amount and petroleum accounts for about 50 % of fossil fuels. However, among renewable energy sources more than 90 percent is obtained from biomass and hydroelectricity as shown in Figure 3 [11]. Renewable fuels are blessed to be sustainable and environment friendly, however their commercialization has invariably struggled because the technology to harness the energy is expensive. Let us have the general understanding of various renewable modes of energy.

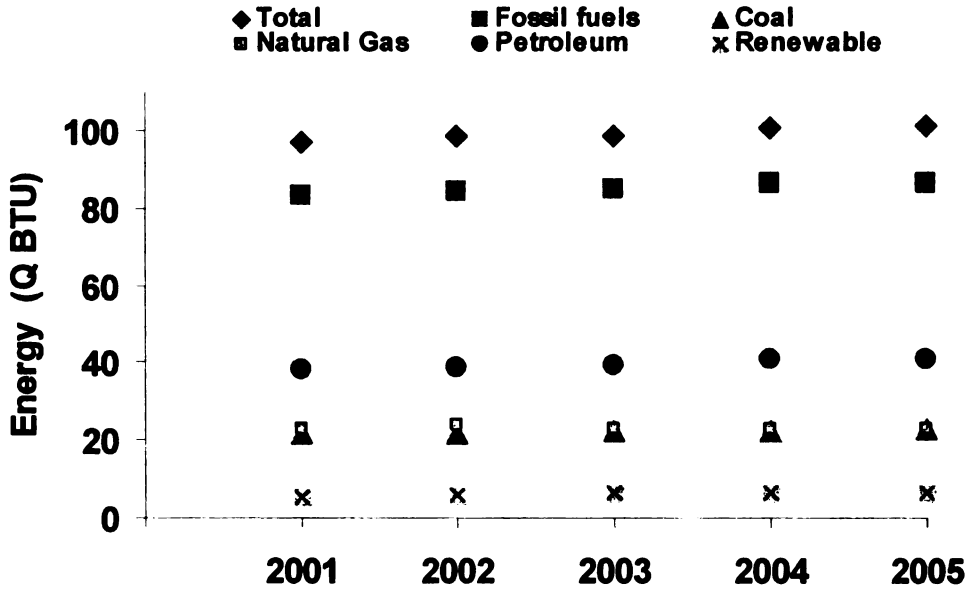

Figure 2: US Energy consumption pattern and trends (*after ref. 11*)

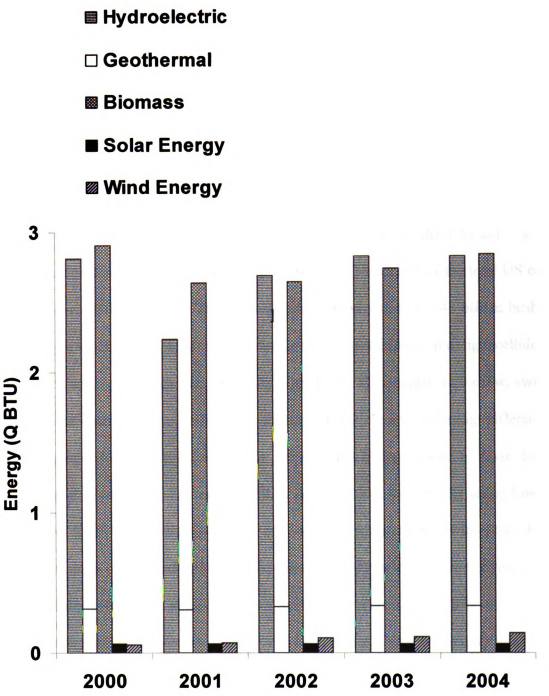

Figure 3: US Renewable energy consumption pattern and trend (*after ref. 11*)

Renewable resource based fuels such as corn-ethanol and biodiesel are required to develop as alternative resources to cater the energy need. Ethanol accounts for 99% of all biofuels in the United States (US) [12]. In 2004, 3.4 billion gallons ethanol was produced which grew to 4.4 billion gallons by February 2006 [13]. Nearly 5 billion gallons of ethanol as produced by end of 2006 could displace about 3.57 % of 140 billion barrels of consumed gasoline sold by volume and 2.38 % in terms of energy [14]. The predominant source for ethanol in the US is corn. Corn based ethanol is used as gasoline additive resulting in a cleaner-burning fuel with higher-octane value. In the US, corn is the primary feedstock for ethanol production. In 2006, about 18 percent of the total US corn crop was converted into ethanol. This corresponds to approximately 1.43 billion bushels [15]. Other potential sources of ethanol are grains like sorghum and lignocellulosic biomass such as crop residues viz. corn cobs, cornstalks, wheat straw, rice straw, switch grass, prairie grass and vegetable and forestry waste. Ever increasing differences between demand and supply led to serious amendments in regulations of fossil fuel's production and distribution. The energy bill in August 2005, which falls under Energy Policy Act of 2005 makes mandatory use of renewable fuels as blends in automobiles [16]. Repercussion of political and economic decisions in favor of adoption of renewable fuels, especially corn based ethanol, ensures steady and promising growth of the corn-ethanol industry which serves as catalyst to tackle nation's energy security challenge [17].

Depleting petroleum sources is not the only bias in attempts to replace gasoline, another critical factor of concern is environmental. Fossil fuels like gasoline and diesel do not burn as cleanly as ethanol or hydrogen. With prevailing technologies, we cannot

generate enough hydrogen fuel to meet energy needs. However, ethanol has emerged as an immediate rescue to the energy crisis. Biofuels like bioethanol and biodeisel helps reducing greenhouse gas emissions from vehicles. The need for higher-octane value, clean burning components and a substitute for methyl-tert-butyl ether (MTBE) in gasoline has created a niche market for ethanol as an inescapable constituent in automobile fuels. MTBE is added to gasoline as an oxygenate that increases its oxygen content and octane value. However, on the dark side, MTBE is known to pollute soil and water [18] ; therefore MTBE is gradually being phased out. In the United States, legislation to abolish MTBE has been enforced on an individual state basis. Since July 2005, 25 states in the USA have banned MTBE for being major ground water pollutant [19]. Incorporation of ethanol into gasoline as an oxygenate and octane value booster bears the limitation that the distribution and storage process invariably gets contaminated with water. The water contaminated ethanol blend of gasoline suffers from the phase separation of ethanol and gasoline due to the fact that ethanol finds preferential solubility in water and that water is immiscible to gasoline. The formation of these two phases results in improper burning of the fuel mixture. Petroleum hydrocarbons belong to the chemical category of alkanes, alkenes, aromatic compounds and their derivatives. Such hydrocarbons are chemically hydrophobic and exist in a phase separated from the water; since ethanol has hydroxyl functionality, it has substantial affinity for water. Therefore, ethanol segregates from the gasoline into the water. Consequently, ethanol is transported and stored separately until delivery to retail stations [20].

1.2 Environmental impact

Increasing energy demands drive higher consumption rates of fossil fuels. Emissions from burning fossil fuel increase the carbon dioxide concentration in the air. Carbon dioxide is a greenhouse gas that traps solar heat and contributes to global warming. Global warming not only makes polar ice liquescent, but also affects aquatic life. Thermally-limited oxygen delivery shows close match with environmental temperatures. Exceeding this temperature limits the growth, performance and abundance of marine species [21]. *Zoarces viviparus* is a bioindicator fish whose population declines due to temperature rise. This fish is used for monitoring the effect of global warming in the North and Baltic seas. The greenhouse effect is responsible for the rise in environmental temperature. Factors that contribute to global warming are population; sophisticated living standards, which demands extra electricity and equipment; increased growth in industrial output and increases in transportation and travel [22]. All such factors show ever increasing dependence on coal, gasoline and natural gas for electric power generation.

As regards the greenhouse emission considerations, it is critical to evaluate quantum of such air pollutants are present in the system and their relative proportions. Annual assessment of greenhouse gases and their sources help us understand and predict the impact of such activities and resources on the environment. Below are shown proportions of various greenhouse gases and their relative discharge to the atmosphere

In 2001, it was observed that in the US as a whole electrical power generation that produce most of the CO_2 emissions (39%) followed by the transportation sector (32%), industrial (18%) , the residential (6.4%)and the commercial sector (4.6%) [23].

Emissions data are expressed in CO_2 equivalents where the carbon dioxide equivalent refers to that weight of carbon dioxide that would produce equivalent radiation absorption i.e. equivalent trapped thermal energy. Carbon dioxide equivalent data can be converted to carbon equivalents by multiplying by a factor of 12/44. Equivalence for greenhouse gases like methane and nitrous oxide is expressed in CO_2 equivalent units by multiplying their emissions (in metric tons) by their global warming potentials (GWP). Global warming potential (GWP) is a measure of the absorptive power of heat of greenhouse gases in the atmosphere. GWP conversions of each gas are relative to that of carbon dioxide (CO_2), as well as the decay rate of each gas from the atmosphere. Thus, GWP helps in estimating various green house gases using a common scale [24]. The hunt for dependable sources of energy has culminated into valorous petroleum explorations and state of art refineries from downstream processing. However, it was myopic vision that sustainability factor was ignored since the crude oil became backbone of our energy needs. To meet our energy surge of modern civilization we must develop our alternate sources and most importantly renewable ones. Earnest efforts towards renewable fuel are reflected in the phenomenal growth of ethanol industries in the US and the exponential increase in ethanol production as shown in Figure 4 and Figure 5 respectively [25]. The production of ethanol has shown significant increase over past two decade for 1980 to 1989 growth rate was 83 % however early 90's showed slight decrease however gained momentum towards the later half of the decade and having over growth rate of 53% for

the decade. However, for the past 4 years there has been an exponential rise in with the growth rate having linear equivalence of 500%. Alarming global warming as set forth by automobile exhaust demands for greener fuels. Bioethanol has therefore emerged with commercial endeavors to meet environmental needs.

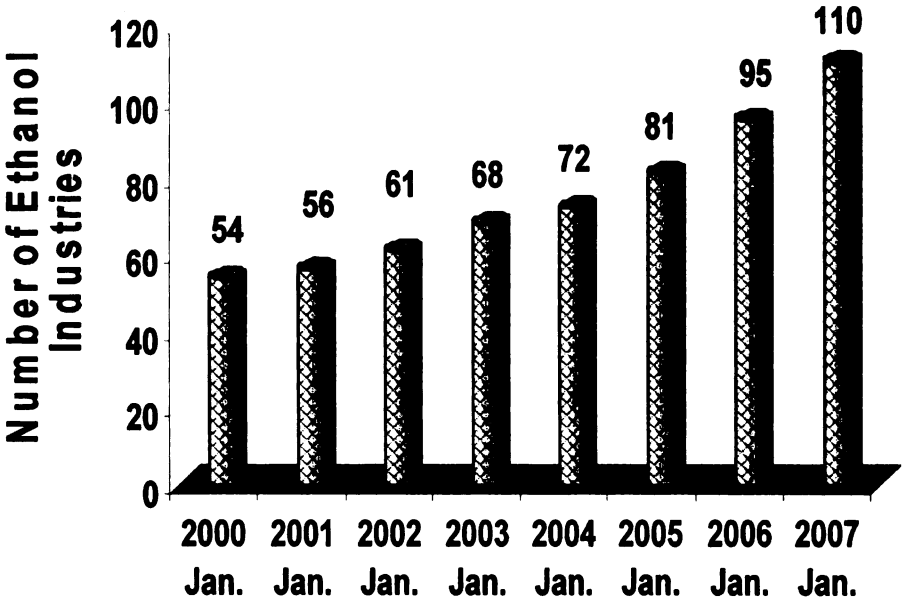

Figure 4: Recent Ethanol Industry Expansion (after *ref. 25)*

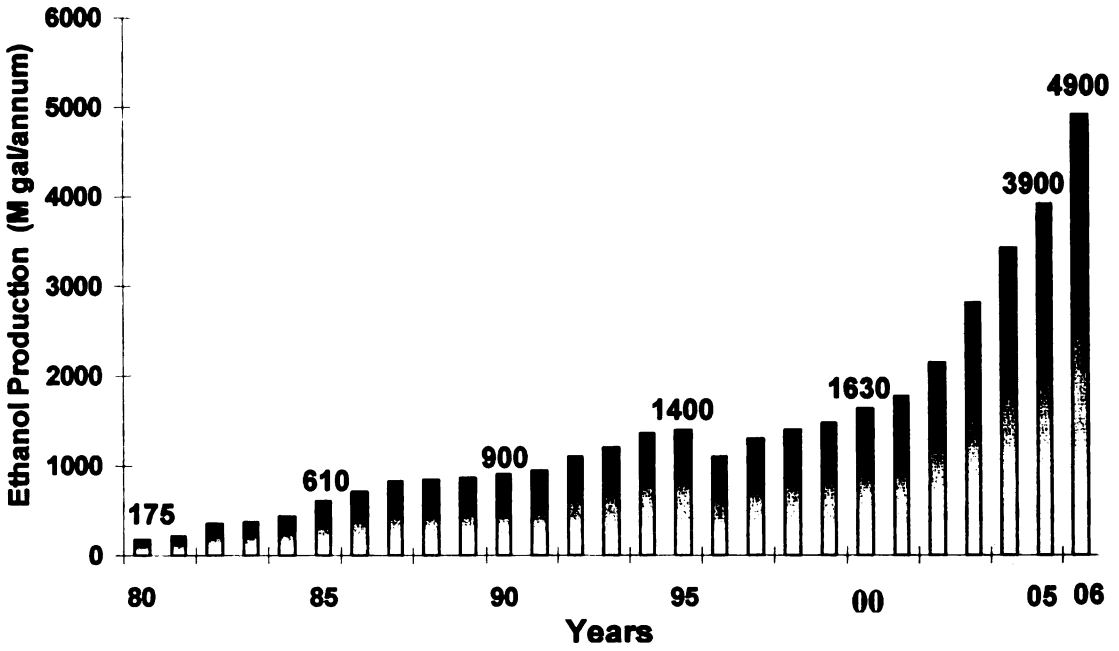

Figure 5: Historic ethanol production. In the x- axis of this figure, 80 means the year 1980 and similarly, 00 means the year 2000 (*after ref. 25)*

Ever depleting non-replenishable fossil fuel resources, we are not only facing glimpse of energy crisis but also leaving a bleak future for generations to come. Appreciating the need of an hour, it's wise to make hay while the sun shines. Shifting gears from petroleum refining to biomass refining will significantly reduce both greenhouse gas emissions and the extent of non-renewable resource depletion. By reducing U.S. dependence on foreign oil and the military investment associated with this dependence, large-scale biomass refining would ensure nation's energy security. Rural economy boost is realized by creating a large market for energy crops that could potentially balance demand for agricultural products with current production capacity [26].

1.3 Bioethanol giants

Market of bioethanol as fuel is dominated by Brazil and followed by the US. Together Brazil and the US produce about 80% of world's total ethanol. Like Brazil, the US produces fuel ethanol from agriculture crops. Brazil utilizes sugarcane while the US ferments ethanol fuel from corn. Comparative study of two bioethanol giants suggests that crop type and fraction of crop that goes for fuel production dictates the ethanol market share and market growth rate. Brazil cultivates sugarcane on 6.2 million hectares with a yield little more than 422 million tons. Over 50% of sugarcane produce is dedicated for ethanol production while remaining goes for sugar production to suffice domestic needs and export [27]. Brazil produces 4.45 billion gallons and ranks second to the US which produced 4.9 billion gallons of ethanol in year 2006. Brazil contributes 38 % while the US contribution is 41% of world ethanol production. In contrast to Brazil, the US, produced 273 million tons of corn of which 45.81 million tons were utilized for making ethanol. Fossil fuel prices hike and its depleting sources were the driving forces for Brazil and the US to adopt renewable fuels. Brazil faced the oil crisis in early 70's, and therefore, launched a national program of alcohol (PROALCOOL), in 1975 [28]. In the world context, Brazil is the first nation to adopt fuel ethanol as renewable automobile fuel. Presently in Brazil, 80% of non-diesel vehicles have flexible fuel internal combustion engines. In Brazil, bioethanol fuel is used in 40% of total non-diesel automobiles [29]. Brazil has been using ethanol in automobiles as early as 1930, the growth rate of sugarcane ethanol in Brazil had been phenomenal this decade, produced 192,000 barrels a day in 2001 which rose to 282,000 barrels a day in 2005. Brazil

government, ministry of agriculture is optimistic on ethanol production to reach 442,000 barrels a day by 2010 [29].

In Brazil there is an extensive ethanol distribution network having a record number 32,000 ethanol filling facilities. In contrast USA, has about 1166 gas stations that sell the E85 blended fuel [27, 30]. United states have more price fluctuation in corn and subsequent ethanol production. Such volatility in ethanol pricing has opportunities for Brazil to capitalize; one of the burning examples refers to the ethanol export from Brazil to US dated back October 2005, that time Brazil's ethanol production cost was $ 0.83 per gallon while that in US was $1.09 per gallon. Domestic market selling price for Brazil and US was $1.38 per gallon and $2.47 per gallon for the same month respectively. Brazilian ethanol on adding the import tariffs and freight cost $2.12 per gallon, which was $0.35 per gallon cheaper than the contemporary cost of ethanol in US. Such a huge price difference allowed Brazil to export 5.2 million gallons of ethanol to US [31]. In contrast, the US, owns a reputation of being world largest producer and consumer of corn. In the year 2006/07, by August, the US corn production was 278.797 million metric tons against world's total of 689.313 million metric tons. As regards consumption in 2006/07, US consumed about 245.503 million metric tons of corn against world's consumption of 723.476 million metric tons [32]. As regards world production and consumption, the deficit was met by previous year's stocks. In the US, corn-ethanol is derived from field corn which is cultivated as conventional corn and genetically modified (GM) corn. Conventional corn is easily attacked by pests and affected by weeds and thus its yield is limited. To overcome such cultivation issues, GM corn species were developed that had resistance to pests and weeds. In the US, major genetically modified

corn varieties cultivated are *Bacillus Thuringiensis* (BT), herbicide tolerant (HT) and stacked genes varieties [33]. These genetically modified corn accounts for more than half of the planted corn crop. Historic data for yield per acre of corn crop suggests that there is an increase in the corn yield per acre. Increment in the corn yield is due to the advent of hybrid varieties of corn. Agriculture technologies have evolved over a period of time resulting in an efficient recovery of harvested grain which otherwise goes in vain due to damage caused by insects and herbs along with harvesting losses.. Figure 6 shows historic growth trends of fermentation and corn yields [34]. In case of ethanol conversion the growth rate is not so contrasting as enzyme modification is limited. Growth in fermentation technologies has been sluggish with little improvement over a period. From the Figure 6 it can be seen that there is mere 17% growth rate in conversion efficiency. At this point it is important to understand the corn milling processes that has actuated the corn ethanol revolution.

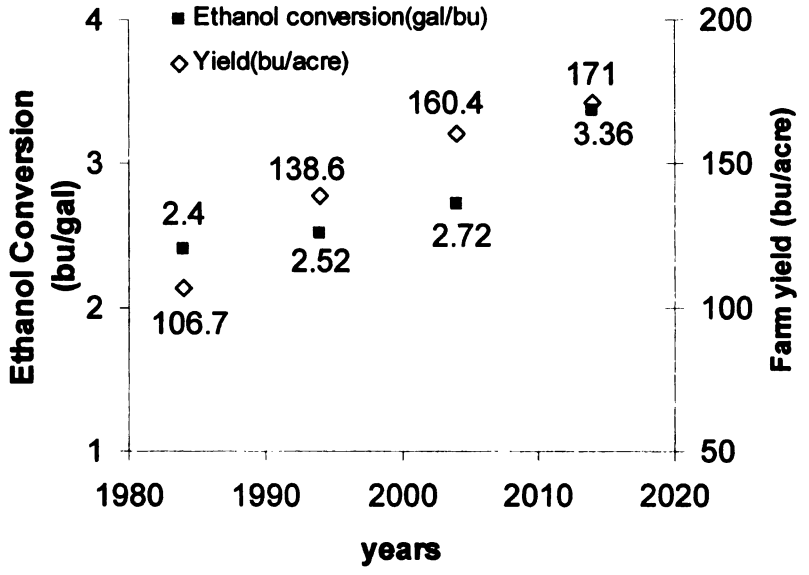

Figure 6: Trend of ethanol conversion and corn farm yield (*after ref. 34*)

1.4 Corn milling technology

In the US, presently, two main technologies are adopted in corn milling and subsequent fermentation into ethanol i.e., dry milling and wet milling. Both technologies differ in processing conditions and co-product yields. Ethanol and co-product distribution is discussed in Table 1 [35]. In US at present, around 82 % of ethanol production is done using dry milling of corn [36]. Dry milling process comprises of sequential steps of grinding, saccharification, fermentation and purification. The main product of dry milling is ethanol and associated co-products are distillers dried grains with solubles (DDGS) and carbon dioxide. The predominant choice of dry grinding is due to simpler processing and relatively cheap equipments. Wet milling is the process of separating the corn kernel into starch, protein gluten, germ, and fiber in an aqueous medium. Ethanol is the main product of wet milling while various co-products are corn gluten meal (CGM), corn gluten feed and mixtures of sugars. Various steps involved in this technology are shown in Figure 7 and Figure 8 respectively [37].

Table1: Ethanol and coproduct distribution of corn milling technologies (*after ref. 35*)

Process/Products	Dry Milling	Wet Milling
Ethanol (gal)	2.7	2.5
DDGS (lbs)	18	-
CGM (lbs)	-	2.5
CO_2 (lbs)	18	18

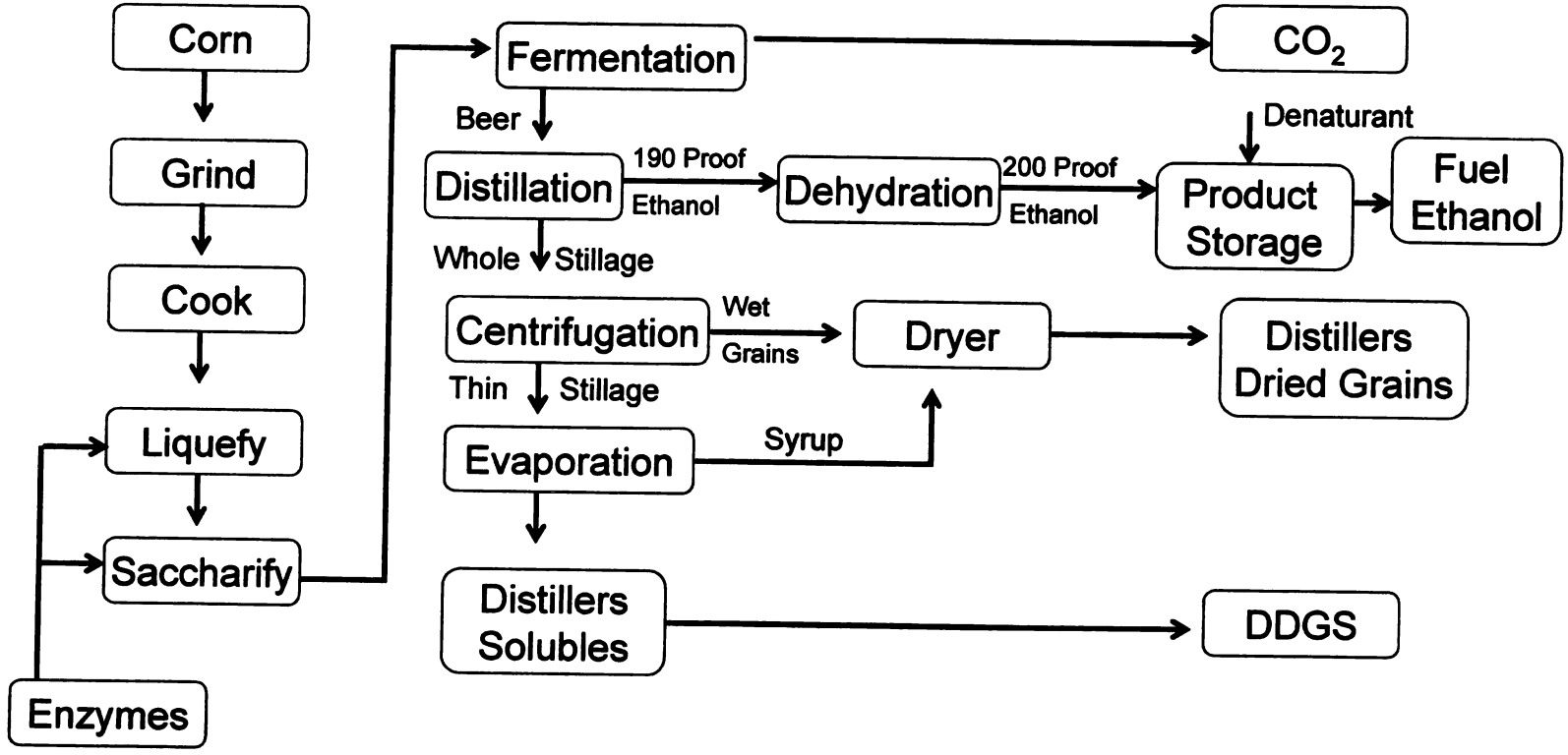

Figure 7: Corn dry milling process for ethanol production (*after ref. 36*)

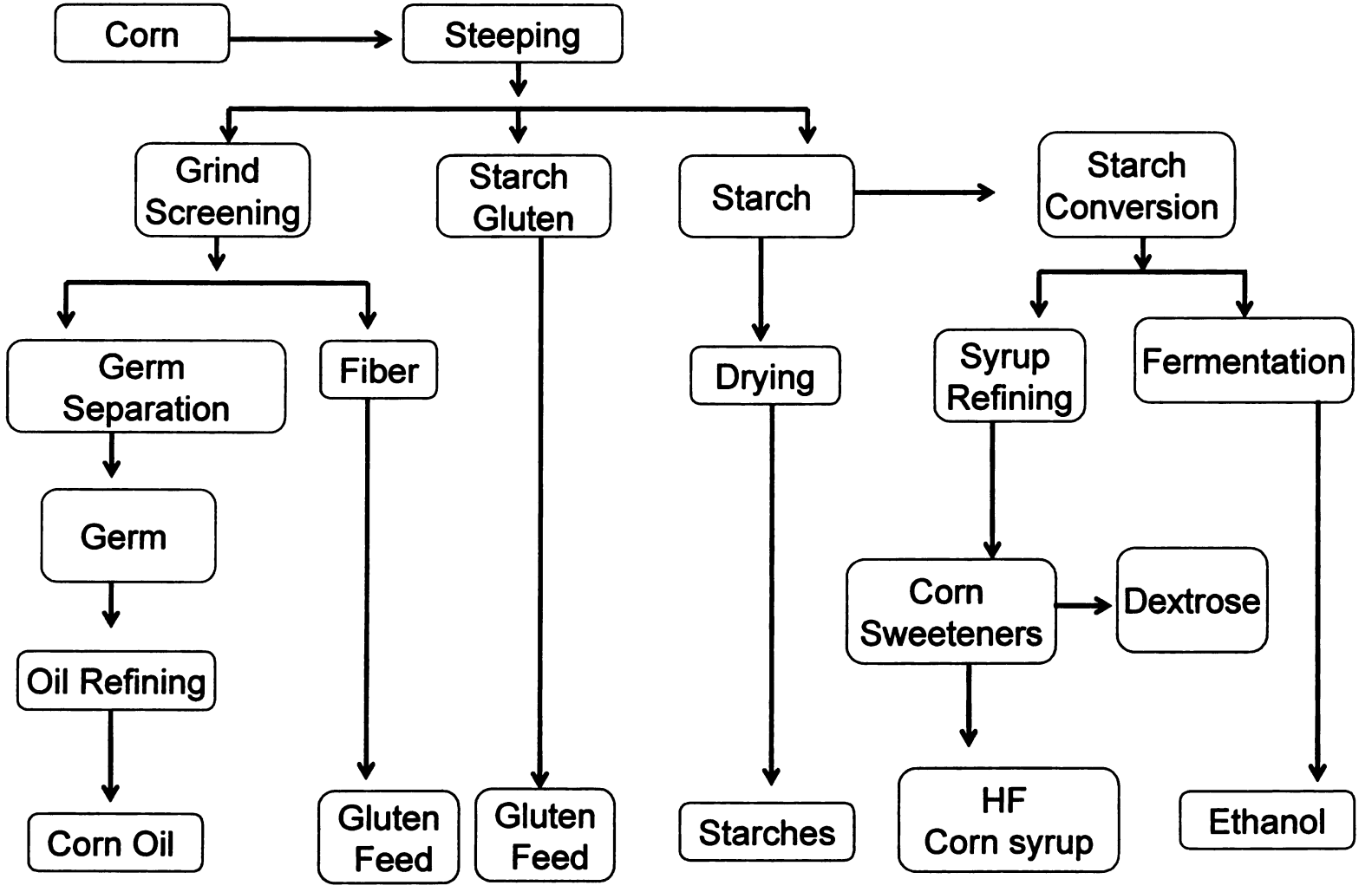

Figure 8: Corn wet milling process for ethanol production (*after ref. 36*)

1.5 Fermentation mechanism

Commercially, yeasts predominantly perform ethanol fermentation. *Saccharomyces cerevisiae*, an anaerobic microorganism, is the most important species that is used in making ethanol. In the fermentation industries, ethanol is obtained mainly by anaerobic breakdown of glucose using these organisms. The reaction pathway of glycolysis is named as the Embden-Meyerhof-Parnas pathway, as shown in Figure 9 [38]. The process of glucose fermentation by the yeasts is mainly the glycolysis process with additional steps of decarboxylating pyruvate to form acetaldehyde using pyruvate decarboxylase, then reducing acetaldehyde to ethanol using alcohol dehydrogenase. In the whole process, there are two moles of adenosine triphosphate (ATP) net gain per mole of glucose. The final steps are mainly carried out to recover the used nicotinamide adenine dinucleotide (NAD) in the previous step and thus produce ethanol [39, 40].

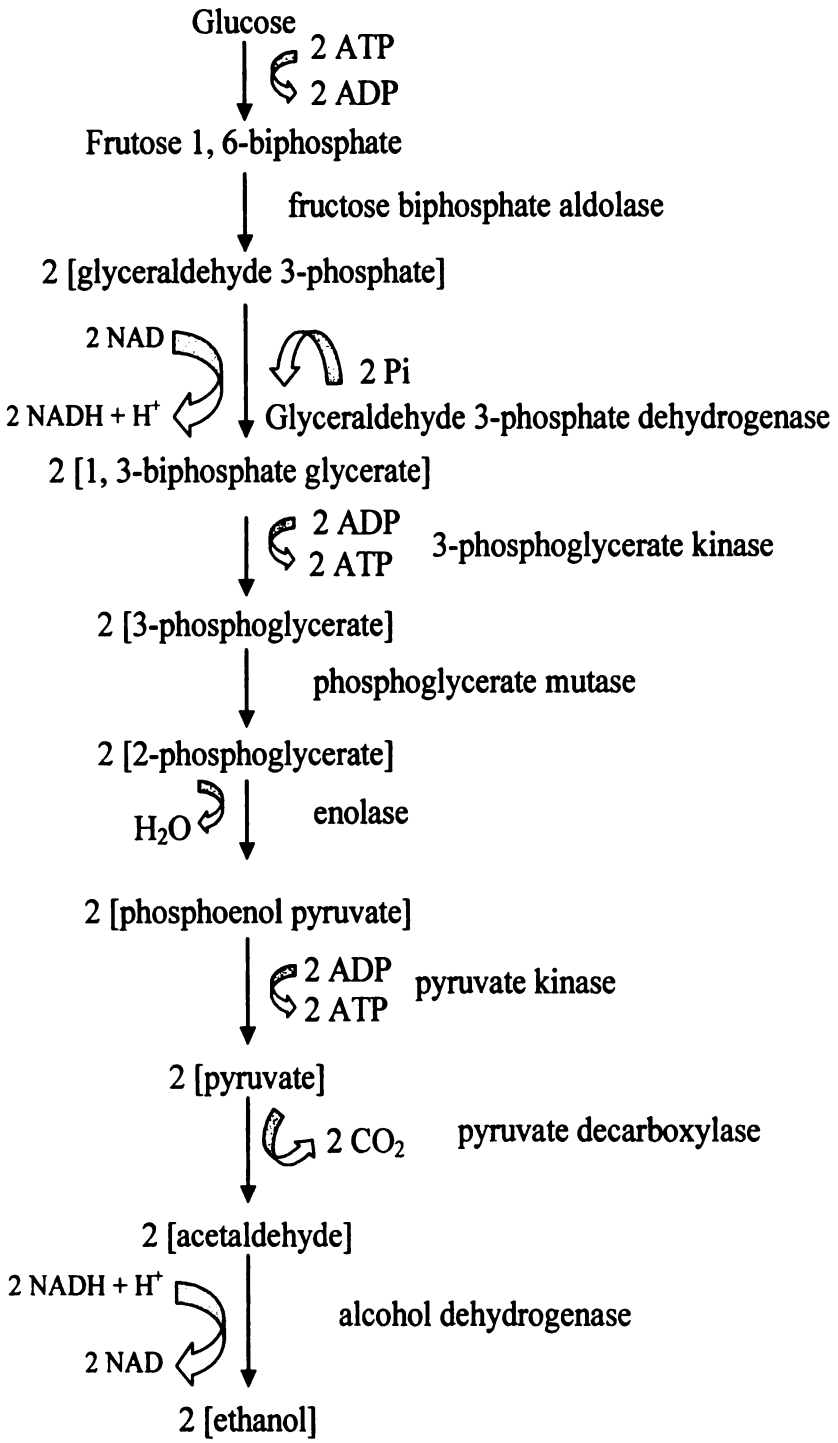

Figure 9: Fermentation of glucose to ethanol and CO_2 by yeasts (*after ref. 38*)

1.6 Corn milling co-products CGM and DDGS

In contrast to lignocellulosic biomass, easily fermentable sugars from corn have made it a niche feedstock for ethanol production; however, conversion of corn into ethanol is limited to 2.8 gal / bushel[34]. Presently bulk of DDGS produced is consumed for fauna feed as shown in Figure 10 [25]. DDGS as animal feed does not provide enough value addition, and the phenomenal growth of ethanol industry is generating tremendous amount of DDGS that will surplus of animal feed requirements. Presently revenues generated by DDGS priced for $ 80-$120 per ton as animal feed accounts for 15-20 % of total revenues of an ethanol plant[41]. Besides animal feed, value added application of DDGS, would lead to high economic returns. DDGS is a rich source of zein protein. Zein protein is used for encapsulating essential oils such as oregano, red thyme and cassia, these oils have antimicrobial properties. Extremely small zein-coated particles are designed for controlled delivery system. This minimizes the interactions of essential oils with other components in the food [42]. In many instances, in order to obtain the desired inhibition, an excess of oil is required which results in poor economics and a number of undesirable effects. As a neutraceutical application, a group of corn tripeptides present in DDGS, was reported to inhibit the angiotensin converting enzyme (ACE) and therefore helps lowering of blood pressure. Also, certain corn penta peptides have been reported to have herbicidal activity; as the penta peptides act as toxins to common weeds. Literature suggests that larger basic peptides, isolated by acid extraction from corn kernels that exhibit antimicrobial properties[43]. The development of new antimicrobial peptides is of practical importance as a result of increasing levels of bacterial resistance to antibiotics due to overuse in humans and livestock.

Another co-product of corn-wet milling is Corn Gluten Meal (CGM). Table 2 compares DDGS and CGM in terms of their relative nutrient composition[44]. Primary use of CGM is animal feed. Corn gluten meal is richer in protein content than DDGS. It is a potential natural herbicide. Corn gluten meal has a physical state of a non-volatile powder, in its granular state CGM retains its state of aggregation and does not spread away. Corn polypeptides due to their characteristics allow selective control and application of CGM as a pesticide and herbicide. CGM is effective in established lawns, where it hampers root growth in weed seedlings. CGM is targeted to control pests like crabgrass, redroot bigweed, creeping bentgrass, purslane, smart weed, bermuda grass, dandelions, lambs quarter, barnyard grass, and foxtail [45]. As regards the whole corn plant, we are able to convert only a small portion of total, rest is again a agricultural residue. In order that corn ethanol industry to flourish, there should be maximum use of corn plant.

Table 2: Comparison of various co-products in terms of composition (*after ref. 44*)

Nutrients	High Quality U.S. Corn DDGS	Corn Gluten Meal
Crude protein, %	30.6	66.9
Crude Fat	10.7	3.2
NDF (Neutral Detergent Fiber)	43.6	9.7
ADF (Acid-Detergent Fiber)	11.8	5.1
Lysine	0.83	1.13
Methionine	1.13	2.31
Tryptophan	0.24	0.34
Calcium	0.06	0.06
Phosphorus	0.89	0.44

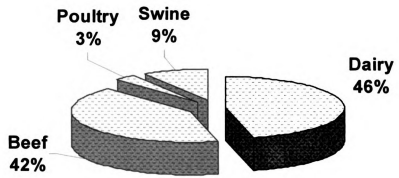

Figure 10: North American DDGS Consumption (*after ref. 25*)

It is noteworthy that utilization of grains and oils for energy generation or chemicals is commercially viable, however at a cost, which is their unavailability for use as food or feed. Remains of the crop plant after harvesting grains and oils such as stover and straw are promising sources of biomass and brighter side of the story is that their use does not compromise the supply of food. Corn ethanol faces criticism for kernels that are feeding automobiles can instead be food for more than 2 billion world malnutrition population [14]. Non food corn stover is the leading candidate as a biomass source to support a lignocellulosic biorefinery because of large quantities available. As per an estimate in year, 2003 in USA there is a potential supply of between 60 to 100 million tons of corn stover per year [46].

Summing up, Brazil and the US ethanol scenario, although the US is largest ethanol producer, yet its energy independence is a distant goal. Brazil enjoys energy independence is due to reasons such as nature of feedstock, cheaper production rates and energy efficient residue endues. As regards the feedstock considerations sugarcane scores far ahead than corn. On the energy grounds net energy returns are 1.3- 1.8 for corn whereas for sugarcane the energy returns is 8.3 [47] Such high values of energy returns are obtained due to the fact that bagaasse which is burned to produce electricity and meet energy demands of ethanol plant. Another factor of consideration is that sugarcane yields twice more volume of ethanol obtained per hectare than corn [48]. On a concluding note Brazil counts upon sugarcane coproduct energy returns this allows cheaper ethanol production rates. In the US, corn ethanol coproduct DDGS, has poor fuel value as it rich in proteins. However, biobased products derived from coproducts shall generate enough economic returns that help in lowering manufacture cost of ethanol.

Chapter - Sustainability

1.7 Is corn sustainable?

Sustainability is a comprehensive rating factor that decides the overall acceptability of a system. Sustainability can be understood as an ecological coherence with the associated technology and capital. Sustainability assessments are gaining popularity in estimating the system's impact on the environment, its commercial viability and future prospects. This study is a partial fulfillment in order to evaluate the sustainability of Distiller's Dried Grains with Solubles (DDGS). In the US, bioethanol is derived from corn. As a national pride, the US owns this reputation of being the world's largest producer of not only corn but also bioethanol derived from the same. Corn has faced criticism over the net energy returns in producing bioethanol. Technology advancement made upstream and downstream processing energy efficient thereby improving net energy returns. Again, in order to address the issue, *sustainable corn ethanol* demands further rigorous assessments in terms of environment friendliness and economy. Presently, ethanol derived form corn receives a subsidy of $0.51 per gallon to sustain its market [49]. The higher cost of ethanol is primarily due to the corn grain price followed by fossil fuels required to run the plant. Coproducts such as DDGS and carbon dioxide (collected by some ethanol plants), are produced by the dry milling of corn are sold cheap, resulting in little revenue returns. DDGS has a trade value of 3-5 cents a pound [41].

1.8 Need for sustainability

The necessity to evaluate the sustainability of coproducts is evident from the fact that in order for corn ethanol to be sustainable, every component associated should

individually be sustainable. It would be irrational if corn ethanol was sustainable while the coproducts were unsustainable. Therefore, the coproducts and their related processing should be modified to qualify there status as sustainable. This sustainability study of DDGS emphasizes upon defining the criteria for sustainability and identifying those factors that hampers the scope of DDGS as sustainable feedstock.

To our present consideration, system refers to the corn dry milling ethanol plant, ethanol as the main product, with DDGS and carbon dioxide as its co-products. Sustainability issues regarding the value addition of co-products (DDGS) of the corn ethanol industry can be best understood while considering the system in totality. To be sustainable, DDGS should contribute to the biobased economy, besides having its end use in harmony with the environment. DDGS is produced in plenty and is therefore a potential resources for food and new biobased materials. Apart from raw material support, the value addition of co-products provides an economic support that strengthens long-term commercialization prospects. The under utilization of co-products does not contribute to their full potential to the economy or even worse, can raise environmental hazards thereby weakening environmental friendliness and sustainability at large [50]. Value additions of DDGS in terms of biochemicals, biobased materials and energy will reinforce the economy of corn ethanol production. However, it is explicit that processes related to value addition should by themselves comply with the criteria of sustainability. Unmanaged DDGS is a potential environmental hazard; therefore it is an important factor that can limit the production of ethanol form corn and amount of corn to be cultivated. As long as the upstream compliments the downstream processing of corn to produce ethanol and does not harm the environment, the industry grows in a sustainable manner.

Moreover, crop cultivation requires huge machinery that runs on fossil fuels. Corn cultivation requires fertilizer and fuel to run machinery as nonrenwable inputs. A petrochemical such as urea is an inevitable nitrogen fertilizer; however its use can be optimized by crop rotation. Integrating the nutrient cycle including nitrogen fixation improves the efficiency of corn cultivation [51]. Moreover, the fuels that run the machines can be blended and eventually, replaced with renewable alternatives such as ethanol and biodiesel. Crop transportation also demands fossil fuel inputs; transportation fuel once being renewable shall raise the energy returns from corn ethanol. Among fertilizers, cultivation machinery and transportation vehicles, it is relatively easier to introduce renewable fuels in the transportation system. The value addition of co-products and the efficient bioethanol conversion process do extend the domain of corn sustainability, but in a limited manner. The bulk demand for ethanol can be met in a sustainable fashion only by lignocellulosic feedstocks. Resource utilization is related to the economic aspect of sustainability. With given material inputs it is important to have minimum waste generation. In this study, the focus is limited on the co-products DDGS and CO_2. From Figure 10, it can be seen that the limited consumption of DDGS as swine and poultry feed is indicative of DDGS related issues in animal feed. Before evaluating DDGS as feedstock on nutritional grounds, it is important to understand the composition of corn kernel. Typically, a mature corn kernel contains about 61 % starch, 19.2 % crude protein and fiber, and 3.8 % fat [52]. Such corn kernels lose starch after fermentation while protein, fat and fibers remain. The undigested part of the corn after dry milling is referred to as distiller's grain, this fermentation residue is mixed with the concentrate of the thin stillage to produce DDGS. The co-product DDGS is rich in protein and fat.

Typically, protein, fibers, fat and other nutrient concentrations are increased up to 3-4 times than that in original corn kernels. DDGS is typically rich in amino acids such as Lysine, Methionine, Cystine, Threonine, Tryptophan, Arginine, Isoleucine, Valine and Leucine [53]. DDGS also contains macro mineral content such as phosphorus, potassium, magnesium, sodium and calcium [54]. Unlike proteins, amino acid concentration in DDGS decreases than that present in corn. The reason for this decease is due to the thermal degradation during the drying cycle. The price of DDGS is governed by phosphorus levels, lysine content, and metabolizable energy content [55]. The issue associated with the color of DDGS is important as it is correlated to the amount of available amino acids in particular lysine. The lighter the color better it is in terms of amino acid concentration. Therefore, the drying of DDGS affects product acceptability.

1.9 DDGS sustainability: limiting parameters

DDGS goes as a nutrition supplement in animal feed. Issues that govern the scope of sustainability for DDGS as identified include high phosphorus content, energy returns, mycotoxin contamination, flowability issues, lack of standardized testing and inconsistent product.

1.9.1 High phosphorus

Among DDGS, corn and corn gluten meal, the former has highest concentration of available phosphorus. In a research study, formulations were prepared by varying the amount of DDGS in the feed ranging from 0 to 40 wt%. With 40 wt% of DDGS in the diet there was an increase of more than 55% in the phosphorus content [56]. As such, there is no commercial process to extract phosphorus from DDGS in a cost effective

manner. Therefore, the amount of DDGS in the animal feed has to be regulated. A DDGS rich diet results in a manure rich in nitrogen and phosphorus. However, the amount of such manure when applied based on nitrogen content leads to an excess of phosphorus concentration in the soil. This excess phosphorus gets carried away to water bodies (both surface and ground) this process is called eutrophication [57]. Higher levels of Phosphorus in water affect the aquatic life, therefore disturbing the ecological balance. If however, when manure is applied based on the amount of phosphorus, the required nitrogen levels are not met. Amount of Phosphorus that goes in the manure of non-ruminats can be controlled by making it more digestible in the diet. Phytase, an enzyme, which when added in the feed along with DDGS can increase digestibility of phosphates in pigs by maximum of 60-65 % [58].

1.9.2 Flowability aspects

One of the critical issues associated with the storage and handling of DDGS is its ability to flow. In 2005, about 52% of total DDGS exports were sold to Ireland, Spain, Mexico and Canada while the remaining was exported to countries such as Thailand, Germany and Indonesia. The exports of DDGS from the US is increasing, there was an observed 26% increase in exports from 2004 to 2005 [54]. The trade and transit of DDGS requires bulk storage and handling. DDGS upon storage tends to agglomerate and does not flow easily. DDGS has a bulk density range of 389 to 496 Kg/m^3 and has an angle of repose ranging from 26 ^{o} to 34 ^{o} that leads to arch formation inside bins and silos, which hampers its flow outward after storage. DDGS when stored in bins and silos have a tendency to form an interlock i.e. a bridge formation that prevents the free flowing of DDGS particles. DDGS particle size span a range of 127 micrometers to 1100

micrometers. The average particle size for DDGS falls below 600 micrometers [59]. Such small particle sizes are responsible for the characteristics of such hindered flow. Moreover, as the soluble content in DDGS is increased, the particle size increases and also affects pelletizability [60]. In the US, animal feed is palletized, and since DDGS does not easily palletize, this proposes obvious problem [61]. Together, the inability to palletize and the poor flowability of DDGS affect its transportation and trade at large. Several flow enhancers such as aluminum silicate, silica and calcium stearate have shown significant flow enhancement in sucrose, lactose and modified cornstarch. Such flow enhancers are likely to enhance the flowabilty of DDGS. The mechanism of flowing aid is that it sticks to the substrate by means of secondary forces and produces smooth boundaries. Also they fill the inter grain voids. However, these quantities are typically added up to 2% to 3 % [62]. Higher quantities may have antagonistic results. Results of decreased caking and flowability were observed in calcium carbonate [63], mango powder using tricalcium phosphate, maltodextrin and glycerol monostearate [62].

1.9.3 Energy value

DDGS by composition averages around 50% carbohydrates including starch, cellulose, simple sugars. This makes DDGS a potential boiler fuel. DDGS has 9860 BTU/lb of thermal energy. As compared to DDGS, propane has 2.5 times more calorific value. However, when compared to the cost of fuel, DDGS is a lot cheaper and offers net energy savings. One proposed method is to burn DDGS in a biomass burner and obtain the thermal energy. This energy is utilized in making the process steam and running dryers. In a case study [64], the DDGS was evaluated, as fuel to meet the energy needs to run an ethanol plant. It is estimated that with the present technology, 78% of energy is

obtained through coal and natural gas while the remainder requirement is met with diesel, gasoline and LP gas. The energy return ratio from ethanol when fossil fuel is used is as low as about 1.6-1.7. However, the requirement of process heat alone is achieved by utilizing 69% of DDGS. In this case, the energy returns realized are 2.9:1. Again by consuming 76% of DDGS, process heat as well as electricity demands are met with this the energy returns shift up to 4.7:1. In case all the DDGS is utilized for energy needs, not only process heat and electricity needs are met but also surplus electricity can be returned to the grid and that energy return from corn ethanol becomes similar to that of lignocellulose ethanol i.e. 5:1 [64]. Selling this electricity generates additional revenues. However, the flip side of the story is that burning efficiency in a biomass burner is not high, and DDGS is rich in proteins and lipids. Therefore, burning leads to the emission of particulate matter and green house gases such as SO_x , NO_x and other volatile organic compounds. Such compounds accrue to air pollution.

1.9.4 Mycotoxins

One of the important issues associated with the feed value of DDGS is mycotoxin contamination. Mycotoxins are toxins produced by an organism from fungus kingdom, which includes mushrooms, molds and yeasts [65]. They feed on organic matter, and proliferate when humidity and temperature is sufficient. Mycotoxins are of various kinds some are lethal, some cause diseases, some weaken the immune system, some act as allergens or irritants, while some have no known effect on humans. Such toxins enter the food chain due to fungal infection of crops. These toxins greatly resist decomposition in digestion. They remain in the food chain in meat and dairy products. Even temperature treatments such as cooking and freezing, are not enough to destroy many mycotoxins .

Some of the important mycotoxins are Aflatoxins; they are produced by Aspergillus species, mostly found in groundnuts, other edible nuts, figs, spices and maize. Aflatoxin B1 is the most toxic one, it is a potent carcinogen and associated with liver cancer. Mycotoxin such as Ochratoxin A, produced by Penicillium verrucosum, generally grows in temperate climates. Aspergillus ochraceus, found as a contaminant in cereals and related products, fruit, beverages and spices. It causes kidney damage in humans and is a potential carcinogen. Patulin is a mycotoxin found in moldy fruits, vegetables, cereals and other foods. It is destroyed by alcoholic fermentation. It may be carcinogenic and is reported to damage the immune system and nervous systems in animals. Other mycotoxins such as Fusarium, Trichothecenes. Deoxynivalenol, and zearalenone are very stable and can survive cooking. The trichothecenes are acutely toxic to humans, causing sickness and diarrhea or even death [65].

Mycotoxins are a fungal infection that enters the corn kernels when the corn plant is infected. Since these mycotoxins can survive fermentation process therefore they are accumulated in every stage of processing. Mycotoxins concentration in DDGS are three fold the initial concentration present in corn. In order to avoid the mycotoxins in DDGS is to reject infected corn kernels. Swines and poultry are very sensitive to mycotoxin contaminations. The issue of mycotoxin contamination is an important factor that limits the scope of DDGS as feed to swine and poultry [66].

1.9.5 Carbon dioxide: a green alternative

Carbon dioxide is a colorless, odorless, non-flammable and slightly acidic gas in nature. Carbon dioxide is produced by different processes in combustion or fermentation

of organic matter. Our source of consideration is corn starch fermentation. Today about 18 lb of carbon dioxide is produced by fermentation of a bushel of corn. In the year 2006, 1.8 billion bushels of corn were dedicated for ethanol production [25]. Such amount of corn when fermented produced about 32.4 billion lbs CO_2. This amount of carbon dioxide is cumulative of dry milling and wet milling of corn. Carbon dioxide finds numerous applications in food industry that include its use as a green chemical used for solvent extraction techniques, carbonating agent in beverage industry, water treatment. Carbon dioxide gets dissolved in water to form carbonic acid. This finds water treatment application in reducing and controlling the pH of water. Conventionally sulfuric acid is used for water neutralization purposes. However sulfuric acid has lots of environmental considerations and operational hazards associated with it. There are many advantages of carbon dioxide over mineral acids. Carbon dioxide has no carcinogenic effects on humans, while the sulfuric acid mist has carcinogenic effects and that stringent control are required to maintain permissible exposure limits below $1mg/m^3$ [67]. Unlike mineral acids, CO_2 is safer and cheaper. Typically sulfuric acid has a trade value of $ 55 to $ 65 per ton and in contrast CO_2 is sold approximately $ 4 per ton [68]. Regarding water treatment, CO_2 has improved controllability over mineral acids. The mineral acids, in particular sulfuric acid initially shows a little change in pH till a certain point followed by a steep decline in the pH values which makes it difficult to control the neutralization end point [69]. Performance suggests that depending upon the nature of impurity, a lesser amount of carbon dioxide is required for neutralization. Also the unit price differences justifies the overall cost effectiveness for the use of CO_2 in water treatment. Another aspect is the raw material handling and storage. As regards to the piping system, to

handle the chemicals, there is lots of maintenance associated with the pipes carrying sulfuric acids. Mineral acid tends to corrode the internal surface of pipelines [70]. In case of carbon dioxide, the carbonic acid is in situ produced when it comes in the contact of water. The dry carbon dioxide gas itself is harmless in nature thus the pipelines that carry CO_2 have little associated maintenance. The continuous water treatment demands to have a bulk onsite storage of mineral acids and the equipment costs and maintenance of the storage system is very high. In contrast, there is no need for bulk storage of carbon dioxide as there is a convenient option of pipeline transportation for continuous supply. An important application of carbon dioxide is to prepare precipitated calcium carbonate (PCC). Rectangular flakes of PCC having average diameter and thickness of about 1.75 micrometer and 0.2 micrometer respectively. CO_2 gas fed at a rate of 200 ml/ min into the suspension containing 0.10% (m/v) of $Ca(OH)_2$ at 25 ^{o}C [71, 72]. Industrial use of this compound is as filler in the process of paper making. PCC is known to enhance the optical properties and print characteristics of paper and related products. It makes paper more machine able. PCC is added as a filler in the paper this helps reducing more expensive pulp fiber while papermaking. This filler is low cost filler thus contributes to the capital savings and helps conserving precious wood. For the premium brand of paper it serves as an optical brightening agent. PCC is used in plastic industry as filler. Nano PCC acts as a viscosity modifier and sag reducer in automotive parts and construction sealants. PCC as a filler in the polymer matrix improves the elastic modulus and at the same time synergistically improves the low temperature impact strength. Therefore PCC is an alternative to expensive organic impact modifiers. In the paint formulations, due to its optical properties, it replaces costly titanium dioxide and improves opacity. For health

care applications, PCC is used as an acid neutralizer, typically as a calcium-based antacid tablets and liquids. PCC is rich in calcium content that allow a drug formulation having high dosage of calcium supplements in mineral tablets. Controlled small particle sizes and unique particle shapes of PCC finds application in good tasting calcium fortified foods and beverages. Carbon dioxide finds applications such as in making dry ice, refrigerant, textile dying, fire extinguisher [73-75].

1.10 Resource utilization of corn plant

A sustainable approach demand maximum resource utilization. A laboratory scale experiment was conducted in order to assess what fraction of the corn plant by weight (dry basis) gets converted into ethanol. Experiment deals with selection of a genetically modified variety of corn *Bacillus Thuringiensis* (BT). Corn plants were procured from 3660 meridian farm (courtesy Bruce Noel). Gathered plants were fully matured and ready to harvest. Procured plants were then oven dried at 110 °C for 8 hours until the dry weight was constant. Dry weight measurement was done for 26 corn plants. Weight of various parts were measured separately and correlated for weight fraction of carbohydrate source that is utilized for ethanol conversion. Weight distribution of various parts of corn plant are shown in Table 3 and Table 4 [76]. On dry weight basis, assume the total corn plant to weight 100 lbs. Based on the experimental findings, the weight of the ear would be 63 lbs of which 52 lbs (0.928 bu) accounts for the weight of kernels. Present rate of fermentation of corn sugars into ethanol accounts for a conversion of 2.8gal/bu [34]. Therefore, the amount of ethanol produced per 100 lbs (dry basis) of corn plant equals 2.6 gal (0.928Bu* 2.8gal/bu) which is equivalent to 17 lb of ethanol. Material balance suggests that, a 100 lb corn plant has a productive output of 17 lb of ethanol this

corresponds to $1/6^{th}$ of total corn plant by weight. Amount of DDGS that is formed is 16lbs and about 16lbs of carbon dioxide is produced. Remaining 48 lbs which corresponding to stalk, roots and leaves is referred to as corn fodder.

Table 3: Corn plant weight distribution on dry basis (*after ref. 76*)

Corn plant components	Average Value	SD
Stalk weight (g)	50	16
Leaves weight (g)	33	10
Ear weight (g)	183	40
Roots (g)	24	12
Total Dry Weight (g)	290	71
Total height (inch)	85	10

Table 4: Ear weight distribution on dry basis (*after ref. 76*)

Ear Weight Distribution	Average Weight (g)	SD
Kernels	152	34
Cob	23	6
Ear leaves	11	4

1.11 Economic impact

Economy is an integral aspect of sustainability. Stringent environmental conditions, choice of raw materials, advanced technologies and infrastructure leave little room for the situation to be cost effective. Now on the other side, consider the pathways

that rely on petroleum based raw materials and fossil fuels, although convenient but they leave no room for things to be lasting for the generations to come. Sustainable growth and development is definitely expensive, but this is not an economic stalemate. A sustainable system in the initial phase is expensive however, in the long term it pays back with better future in terms of material security, quality environment and health. Economy is the most important driving force that defines the scope of industrialization, exploitation of resources, demography and their related issues. Any geographical terrain has its limited resources and ecological tolerance. Now consider a situation that in a given city/region there is a industrial setup due to such an infrastructure there is forced human population density and resource utilization. Economical growth leads to expansion in infrastructure, transportation and production therefore more people will be drawn to reside in that region. Now with increasing non sustainable economic activity the ecosystem gets more and more stressed. Resource per capita depletes, and environmental conditions deteriorate and so do the human health and environment in spite of their tolerance limits. Environmental conditions worsen once there is accumulation of pollution in the ecosystem. Consider the concept of micro ecosystem where economy is local and so will be the associated environmental burdens. Burning example is the corn ethanol industry with an ever-increasing demand of sustainable green fuel; it has led to the exponential growth of ethanol distilleries. This is a situation of an economic boom where the industrial growth is concentrated around the corn-belt regions due to factors like ease of transportation and low prices of corn. Corn dry milling generates enough DDGS as coproducts whose production will exceed consumption in the immediate future. Absence of sustainable pathways to handle the surplus of DDGS makes it a potential

environmental hazard. Therefore, the growth of any industry should be done a sustainable manner. Another important aspect is energy efficiency and material reutilization. A sustainable system has well defined boundaries beyond which the criterion is not met with. The concept of sustainability that holds true for micro ecology holds true for global ecosystem at large. Analogy is extended when we consider earth as ecosystem and analyze effects of growing economy on the global population growth and global atmosphere.

Nevertheless in contrast to fossil fuels, corn based ethanol is green and it is has contributed substantially to the US economy. In the year 2006, the ethanol industry including operations, fuel transportation and infrastructure development, has lead to an increased gross output of $41.1 billion. The ethanol industry generated 160,231 job opportunities in almost all economic sectors of which ~ 20,000 jobs in the manufacturing sector alone [25]. These job opportunities contributed to a house income of $6.7 billion. The ethanol industry contributed to tax revenues worth $2.7 billion to the federal government and $2.3 billion for the state respectively [25]. The consequence of such an economic impact is socio-economic growth and the tax revenues can be utilized for the benefit of society. Thus corn ethanol is utilizing renewable resources to make green fuel, and in turn provides opportunity for employment and prospering society. Corn ethanol is a good example of a potentially sustainable economy. Table 5 suggests the prospects of the growth of corn ethanol industry [77]. As per the projections, it looks that the expansion of ethanol plants is exponential till 2007 after that there is drastic decline in the growth rate of ethanol infrastructure [77]. By 2015 the contribution of corn to make bio

ethanol is likely to decrease a little bit due to the use of other grain feed stocks and lingo-cellulose ethanol inputs.

Table 5: Prospects of the growth of corn ethanol industry *(after ref. 77)*

Year	Ethanol Production (MGY[a])	Net New Capacity (MGY)	Corn Share (%)	Ethanol Yield (gal/Bu)
2005	4003	686	90	2.75
2006	5615	1625	90	2.765
2007	7230	1700	90	2.78
2008	7943	750	90	2.795
2009	8323	400	90	2.81
2010	8703	400	89	2.825
2011	8988	300	88.5	2.84
2012	9225	250	88	2.855
72013	9463	250	87.5	2.87
2014	9653	200	87	2.885
2015	9843	200	86.5	2.9

a: MGY= Million gallons per year

Table 6 compares the benefits realized by a corn ethanol plant of 50 million gallons and 100 million gallons capacity [77].

Table 6: Economic implications of ethanol facilities (*after ref. 77*)

Parameters	50 MGY	100 MGY
Annual Expenditures (Million 2005$ [a])	$46.7	$88.2
Gross Output (Million 2005$)	$209.2	$406.2
Household income(Million 2005$)	$29.7	$51.2
Employment (jobs)	836	1573

[a] 2005$ = Value of the US dollar in the year 2005

Ever growing bioethanol production has influenced the price of corn. Evaluating the implications of corn ethanol on the food prices, some consider that the bioethanol is responsible for the food prices hike [78]. While others believe that, the rising crude oil price is responsible for food price hike. These viewpoints are compared using Consumer Price Index (CPI), which is an important tool to study inflation. CPI is the ratio of the cost of specific consumer items in any one year to the cost of those items in the base period. In the US, CPI for food had accelerated in the recent past. Apparently, it seems that the increase in the CPI for food is solely due to the high prices for corn influenced by increasing ethanol production. However, hike of the corn price is only one of many other contributing factors that control the CPI. In fact, there is little direct influence of corn price on retail food prices. In contrast, the rise in the prices of fuel and energy has a lot greater impact on not only to the food prices but also on any other material in market; as every thing requires energy for manufacturing. In order to estimate economic influence, it is important to compare the effect of the fuel price hike to that of the corn price hike. Consider a $1.00 per gallon increase in the price of gasoline, doing so increases the CPI

for food by 0.6 percent to 0.9 percent. While an equivalent increase in corn prices ($1.00 per bushel) would cause the CPI for food to increase only 0.3 percent [78]. Corn prices have half the influence on CPI than does the fuel price hike. Table 7 shows the price of a variety of food stuff. Prices of commodity are compared for year 2006 and 2007 [79, 80]. On the basis of selected food stuff, which is the leading components of US grocery, the average increase in the price for these food items is about 3% and that average annual food inflation over 25-year is 2.9%. Thus, there is not a significant impact on the inflation of food prices due to corn price hike. In the US, corn is the most valuable agriculture produce. Crop value of corn in the year 2006 was 33.71 billion dollars followed by soybean, which ranks second most valuable crop having half the worth of corn [52]. Figure 11 shows the relative worth of major crops produces in the US [52]. Continuation to the discussion of corn prices, Fig 12 shows the price trend for past 50 years [52]. In 2006, there is a jump in the price of corn of about $1/Bu. This is indicative of rising local economy. Prior to this, the corn prices fluctuated around $2/ bu when averaged for almost a decade. The US is a leader in the corn exports. In the Figure13, US alone contribute to the worlds 69% of the corn exports followed by Argentina (5%of worlds export) and China (55 of world exports). The US exported about 2250 million Bu in the year 2006 [52]. Historic trend of the US corn exports is shown in the Figure 14 [52]. The impact of corn ethanol has not affected the international trade of corn. In the year 2006 the US became the largest producer of bioethanol and this year it had an all time high in corn export yet the sensitive balance of international trade maintained. Bioethanol and DDGS are generated in proportional quantum ratio; the growth trend of DDGS follows a similar

exponential trend. Figure 15 shows the production in millions of ton of DDGS for last 8 years [25].

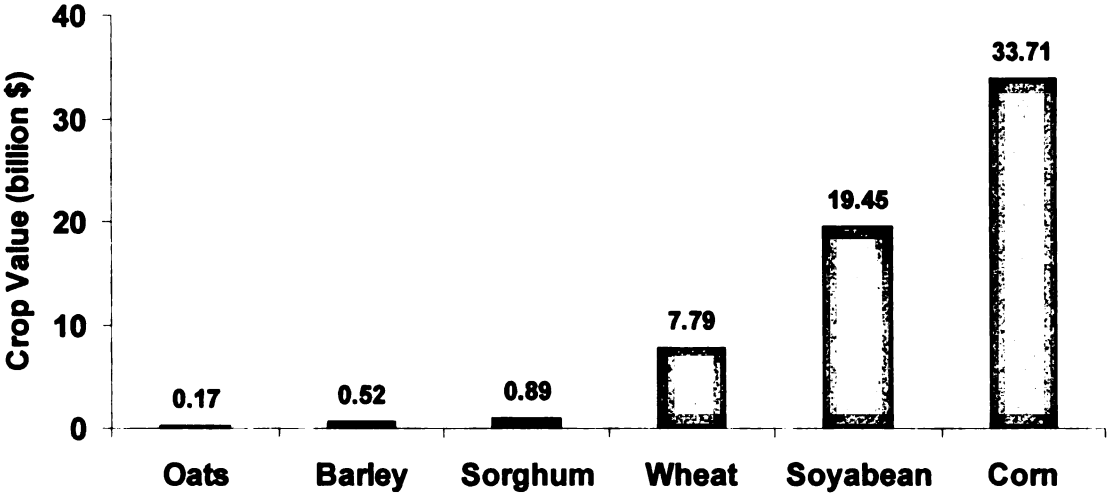

Figure 11: US Crop value for different crops (*after ref. 52)*

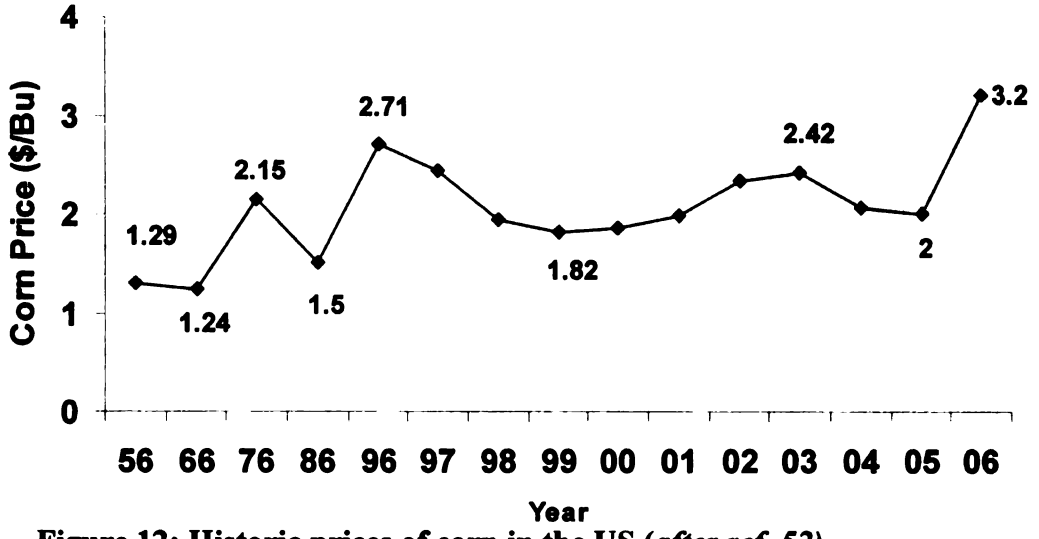

Figure 12: Historic prices of corn in the US (*after ref. 52)*

Table 7: Comparative prices of food for year 2006 and 2007, *(after ref. 79,80)*

Commodity	Qty	Price (April 06)	Price (April 07)
Milk	1 gal.	$3.12	$3.14
American Cheese	1 lb.	$3.81	$3.73
Butter	½ lb.	$1.40	$1.43
Ice cream	½ gal.	$3.62	$3.79
Turkey	2 lbs.	$2.22	$2.16
Chicken breast	2 lbs.	$6.62	$6.74
Eggs	1 dz.	$1.28	$1.62
Pork Chops	2 lbs.	$6.34	$6.30
Bacon	2 lbs.	$6.68	$7.00
Ground beef	1 lbs.	$2.74	$2.82
Beef steak	2 lbs.	$10.18	$10.82
Cola, non-diet	2 ltrs.	$1.10	$1.20
Malt Beverage	72 ozs.	$5.00	$5.00
TOTAL		**$54.11**	**$55.75**

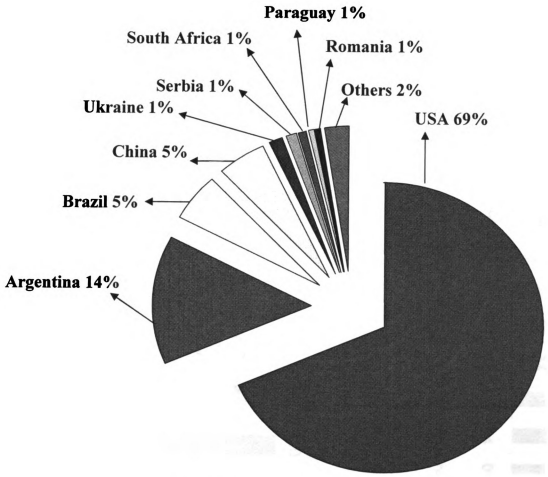

Figure 13: The US leadership in world corn export (*after ref. 52*)

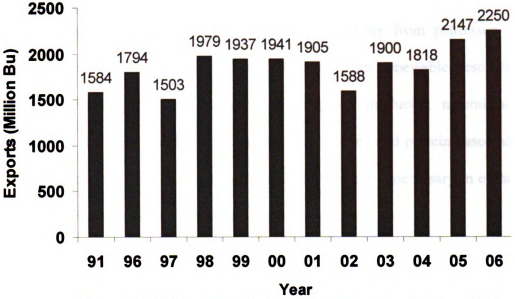

Figure 14: Historic trend of the US corn export (*after ref. 52*)

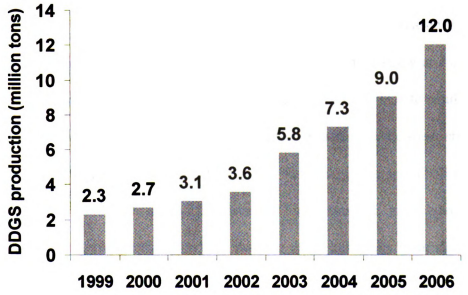

Figure 15: Recent trend of DDGS production (*after ref. 25*)

Chapter – Bioadhesives

1.12 Introduction

Most of the adhesives those are currently used are from petroleum sources. Therefore, there is an urge to produce adhesives from renewable resources [81]. Nowadays there are a lot of research is going on producing natural adhesives (bioadhesives) for the environmental concern. Starch based and protein based adhesives are the major bioadhesives. A variety of chemical treatment is necessary in extracting or formulating bioadhesives from the starch or protein source.

For wood products, the commercially used adhesives are synthetic one and due to environmental reasons, the non-toxic adhesives are required. Non-toxic starch based adhesives have been reported for application in wood products [82]. High strength straw particleboards can be produced when bonded with soy proteins modified with urea, citric acid, boric acid and sodium hydroxide [83]. NaOH-modified SPI increased the tensile strength and compression strength of the particleboard from wheat straw and corn stalk pith [84]. Guanidine hydrochloride (GuHCl) denatured soy protein isolate resulted in an unfolded and loose protein conformation, which helped in improved the shear strength of SPI adhesive to fiberboard [85]. Modification of rice barn using heat and alkali improved its adhesive strength over the unmodified bran to bind plywood, particleboards, and fiberboards [86]. Many treatments have been done to make adhesives from starch based material. Another approach is to make starch based adhesives that go for corrugated cardboard applications. Here the corn starch has been treated with sodium hydroxide (NaOH) along with other salts. This adhesive provides good bond strength for application in corrugated cardboard manufacture [87]. Another use is in paper packaging where starch based adhesives can be used. Here the flour have been treated with different

compounds resulting in adhesive which has high adhesion, fast drying time and stable storage [88]. Adhesives for corrugated board were prepared by alkali treatment of corn starch [89]. Carbohydrate adhesives derived from yam corn, potato and cassava starch when modified by acid moisturing and roasting resulted in high tack having adequate bonding strength for paper–paper and paper–glass substrates [90]. Environment friendly adhesive was prepared by crosslinking starch and PVOH for wood binding applications, adding latex in the formulation showed further increase in the adhesion [91] .

Soy protein based adhesives has shown great adhesion properties to cellulosics and other materials for the production of particleboard, plywood, and various composites [92]. The main weakness of a protein-based adhesive lies in its relatively poor water resistance for outdoor uses. Various chemical and enzymatic methods have been tried to improve the adhesion of soy protein. Research has been done to study the effects of esterification of soy protein on adhesive strength. Free-carboxyl groups of soy protein are esterified with ethanol along with different concentrations of hydrochloric acid as catalysts. Moderate esterification resulted in better adhesion strength and better water resistance. With the optimum esterification the wet strength increased around 62 % [93]. Another approach also has been taken in improving wet strength of the soy adhesives. Different chemical modifications have been done to increase the wet strength of the soy bean based adhesive [94]. Increasing mercapto functionality significantly improves the wood adhesion for soy proteins. The adhesion strength and water-resistance of the wood adhesive increases as –SH groups increase in the soy protein [95]. Polyurethane (PU) adhesives that were synthesized from potato starch and natural oils by a transesterification reaction resulted in adhesive which was superior than commercial

counterparts [96]. Soy protein when blended with polycaprolactone using coconut oil as compatibilizer improves strength and cost effectiveness [97]. Most of the adhesives that are used mostly comprised of formaldehyde resin like urea-formaldehyde or phenol-formaldehyde. Formaldehyde is carcinogenic [98]. Therefore it is much important to prepare formaldehyde-free adhesives from soy protein [99, 100]. In this process formaldehyde – free curing agent like amine, amide, etc. have been tried to make bioadhesive more eco-friendly. These adhesives can be used for application on lignocellulosic materials as well as in composite manufacture. For the fiberboard production, that is widely used for packaging materials, containers, tubes, and cartons, these soy protein based adhesives resulted in better dry, wet strengths [81]. Therefore, from the sustainability and environmental point of view there is the need for producing bioadhesives from DDGS, which will help in supporting the economy of the corn-ethanol industry.

1.13 Materials and methods

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) were obtained from Columbus Chemical Industries, Inc. (Columbus, WI). Urea was obtained from Spectrum Quality Products, Inc. (Gardena, CA). Distillers' dried grains with solubles (received DDGS contains 9% moisture) were obtained from Michigan Ethanol (Caro, MI). The bioadhesive compositions were prepared from as received DDGS. The protein content of the DDGS was measured to be 27% using a Perkin-Elmer elemental analysis instrument (CHN 2400, Series II CHNS/O). Protein Glue (Ground Hide Glue, Item #TAD032001) and precooked wheat starch (Wheat Paste No. 301, Item #TAD002001) were obtained from Talas, New York. Paperboard: Custum Kote® from Mead Westvaco, the thickness

of paperboard was 18 mils, having white coating on one side for printing purposes while the other side was brown were used in our experiments to study the adhesive strength. Pressure cooker used for the cooking was MAXI-MATIC® EC-8, Maxi-matic Appliances Industry, CA.

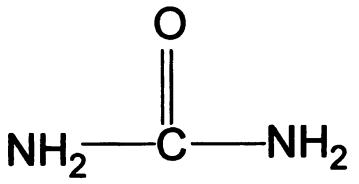

Figure 16: Chemical Structure of Urea

1.14 Preparation of bioadhesive from DDGS

1.14.1 Variation in reagent concentration NaOH and Urea

For the synthesis of bioadhesives, key destructurizing reagents i.e NaOH and urea shown in Figure 16, were dissolved in distilled water to prepare a NaOH-urea solution. 140 mL of the NaOH-urea solution containing NaOH (1.4g to 5.6 g), Urea (0 to 4.2 g) and water (131.6 g), were mixed with 30 g of DDGS. The resulting slurry was cooked in a pressure cooker for 15 minutes. The cooking pressure as calculated was 1.6 atmospheres (refer section 3.4.3). The cooked slurry was then diluted with 50 g of water followed by filtration under vacuum using Buckner funnel that is mounted over an Erlenmeyer flask. In this filtration process, a polyester-cotton cloth was used as the filtering medium. After filtration, the solids were retained over the cloth while suspension was collected in an Erlenmeyer flask. The solids collected over the filter cloth were

washed again with distilled water (about 200 g) for 10 min and filtered again. The washed solids were collected and dried at 110 °C. The suspension was concentrated into a three-necked flask and concentrated at 100 °C for about 4 hours to evaporate most part of water. The concentrated suspension resulted in a brown and viscous fluid; considered as the bioadhesive from DDGS [101].

1.14.2 Effect of pressure

In order to determine the effect of pressure as a processing variable, 140 mL of the NaOH-urea solution containing NaOH (4.2 g), Urea (4.2 g) and water (131.6 g), were mixed with 30 g of DDGS. The slurry was cooked at ambient atmosphere (1.0 atm) for 15 minutes. The cooked slurry was diluted using about 50 g of water followed by filtration under vacuum using Buckner funnel that is mounted over an Erlenmeyer flask. In this filtration process, a polyester-cotton cloth was used as the filtering medium. After filtration, the solids retained over the cloth while suspension was collected in the Erlenmeyer flask. The solids were washed with distilled water (about 200 g) for 10 min and filtered again. The washed solids were collected and dried at 110 °C. The suspension was charged into a three-necked flask and concentrated at 100 °C for about 4 hours to evaporate most part of water. The concentrated suspension was a brown and viscous fluid is referred to as the bioadhesive from DDGS.

1.14.3 Effect of cooking time

In order to study the cooking time as processing variable, 140 mL of the NaOH-urea solution containing NaOH (4.2 g), Urea (4.2 g) and water (131.6 g), were mixed with 30 g of DDGS. The slurry was cooked in a pressure cooker for 25 minutes and 35

min. The cooking pressure was 1.6 atmospheres. The cooked slurry was diluted using about 50 g of water followed by filtration under vacuum using Buckner funnel that is mounted over an Erlenmeyer flask. In this filtration process, a polyester-cotton cloth was used as the filtering medium. After filtration, the solid residues were retained over the cloth while suspension was collected in the Erlenmeyer flask. The residues were washed with distilled water (about 200 g) for 10 min and filtered again. The washed residues were collected and dried at 110 °C. The suspension was charged into a three-necked flask and concentrated at 100 °C for about 4 hours to evaporate most part of the water. The concentrated suspension was a brown and viscous fluid; considered to as the bioadhesive from DDGS.

1.14.4 Effect of filtration

Two sets of adhesive batches were prepared. In one of the formulations, NaOH was dissolved in distilled water to prepare a NaOH solution. 140 mL of the NaOH solution containing NaOH (4.2 g) and water (135.8 g) were mixed with 30 g of DDGS to form slurry. In another formulation, 140 mL of the NaOH-urea solution containing NaOH (4.2 g) and urea (4.2 g) and water (131.6 g), were mixed with 30 g of DDGS to form slurry. In both the formulations, the slurry was cooked at ambient atmosphere (1.0 atm) for 15 minutes. The cooked slurry was collected in a polyester-cotton cloth and squeezed by hands thereby separating solid residues (retained in the filter cloth) from aqueous suspension. The residues were washed by use of distilled water (about 200 g) for 10 min. and squeezed again. The residue was finally collected and dried at 110 °C to obtain dried residues. The suspension was concentrated in a three-necked flask and concentrated at

100 °C for about 4 h to evaporate most part of the water. The concentrated suspension was a brown and viscous fluid, which was considered as the bioadhesive from DDGS.

1.15 Characterizations

1.15.1 Yield of DDGS bioadhesive

The yield of the bioadhesive composition was based on the amount of DDGS that was converted into bioadhesive systems. The yield is calculated by using the following equation:

Yield of bioadhesive (%) = 100 – (Weight of dried residues/initial weight of the as received DDGS taken) x 100.

1.15.2 Moisture content measurement

Weighed sample (W1) was dried in an oven at 110°C. Eight hours later, the dried sample was taken out and weighed (W2). Water content of the sample is calculated using the following equation

Moisture (%) = [(W1 - W2)/W1] x 100

1.15.3 Cooking pressure measurement

Pressure cooker operates at a constant pressure which is maintained by periodic discharge of steam through a nozzle over which a weight rests. The cooking pressure is calculated by using the following equation

Cooking pressure (atm) = weight over the nozzle/the area of the nozzle cross section.

1.15.4 Lapshear strength

Lapshear samples were prepared from paperboard that was cut into rectangular; two such strips were bonded with bioadhesive having 50% of solid content. Bioadhesive was applied to only one of the paperboard strips having a spread area of 1 square inch containing 0.053 g of adhesive on wet basis. The adhesive was applied to bind the non-coated sides of the paper board. Bonded paperboard samples as shown in Figure 17 , were pressed and cured for around 9 hours time at ambient conditions. The bonded paperboards were subjected for lapshear strength testing. Failure of lap joint during testing of lap shear specimens is shown in Figure 18. The testing details were provided in standard of TAPPI T813 for paper samples. Samples were tested at a cross head speed of 0.5 inch per min. In regard to the curing of paperboard specimens for lapshear testing, the prepared samples were placed between two thin metal sheets with dimensions 10" x 10". Pressure was applied to the specimens by placing a rectangular iron slab weighing 22 lbs over the lap joints which were sandwiched between metal sheets. Set up for curing is shown in Figure 19. Under these conditions, samples were allowed to dry for about 9 hrs. Curing conditions for the samples prepared using commercial starch and protein adhesives were kept the same as that of other bioadhesives made from DDGS. Then the lap shear strength was measured. Solid content in the bioadhesive compositions were maintained as 50% and the method is explained as follows: The bioadhesive formulation was concentrated until the solids content of the adhesive was greater than 50%. The water content of the bioadhesive was measured. Then the adhesive was weighed and added with distilled water to adjust the total water content to be 50%. The 50% starch slurry has no spread ability thus for convenience a 25 wt% starch slurry was prepared. In order to keep

amount of solid content consistent with bioadhesive, the wet amount of starch adhesive was doubled over the lap area.

Figure 17: Test specimen for lap shear strength

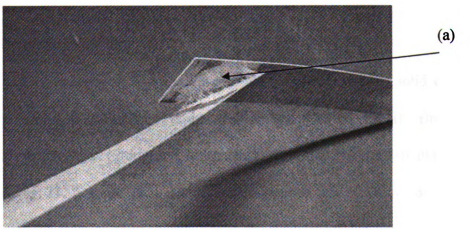

Figure 18: Post lap shear testing mode of failure.
(a): Lap joint

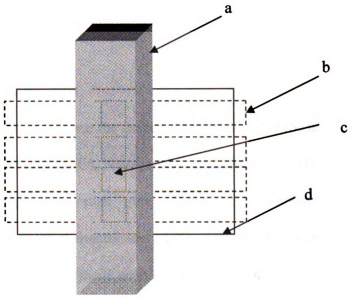

Figure 19: The setup for curing; (a): Iron bar weighing 22 lbs placed over iron sheet for uniform distribution of load, (b): Paperboard samples, (c): Lap joint, (d): Iron sheet placed at top and bottom of samples

1.15.5 Viscosity measurements

Brookfield viscosities of bioadhesive compositions with various solid contents were measured using a Brookfield digital viscometer (Model DV-II, Brookfield Engineering Laboratories Inc. (Stoughton, Massachusetts) with a thermal cell attachment. Spindle number is 21. Sample (8 - 13 mL) was poured into a vessel at a given temperature. After the samples were equilibrated in the thermal cell for 10 min, the motor of the viscometer was turned on to record Brookfield viscosity at a given speed.

1.15.6 Infrared spectroscopy

The infrared spectrum was obtained using a FTIR spectrophotometer (Spectrum 2000, Perkin Elmer, MA). The spectrophotometer had an attached ATR facility.

Spectrum of DDGS, residual fibers and dried bioadhesives were taken in order to observe the chemical structural modifications. The samples were analysed in the wavenumber range of 4000- 650 cm^{-1}.

1.15.7 Elemental analysis

In order to determine the protein content of DDGS, an elemental analysis was carried out where carbon (C), Nitrogen (N) and Hydrogen (H) contents were estimated. For each samples three runs were carried out to obtain the average elemental composition. For CHN elemental analysis the samples were oven dried over night at 100 °C. The samples were then made powder using a mortar and pestle prior to testing.

1.15.8 Thermal gravimetric analyzer

The thermal behavior characteristics were evaluated using thermal gravimetric analyzer 2950 series from TA Instruments(TA Wilmington, DE). The mass loss measurements were conducted in a nitrogen atmosphere. Using an auto sampler, the samples were mounted on the TGA balance. Temperature was equilibrated before each sample run. The nitrogen gas flow rates were maintained at 70 cc/min. The samples were exposed to a temperature ramp of 20 °C/ min.

Chapter - Results and Discussions

1.16 Synthesis of bioadhesive

Bioadhesive was prepared from DDGS in the presence of aqueous alkaline media and boiling temperature. The variables used in the making bioadhesives are alkali concentrations, residence time and cooking pressure.

1.17 Variation in reagent concentration NaOH

Various bioadhesive formulation were prepared in which the alkali (NaOH) concentration was varied from 0 to 5.6 g/30g DDGS. Samples in which the alkali concentration was varied had urea content constant i.e. 4.2 g/ 30g DDGS and keeping the cooking time 15 min and cooking pressure of 1.6 atmospheres. Sample in which urea alone was present, after cooking, showed no tack initially inspected by hand feel and preliminary test on paperboard adhesion. In the samples where the alkali concentration was increased in the multiples of 1.4g , it was observed that with increase in alkali concentration there was increase in the bioadhesive yield while the lapshear strength had fluctuating yet increasing trend. For the highest alkali concentration the bioadhesive conversion yield was maximum however, the lapshear strength decreased in the case of paperboard samples. Lapshear strength dependence on the alkali concentration is shown in the Figure 20. In case of wooden samples the trend of lapshear strength was monotonously increasing as shown in the Figure 21. The effect of alkali reagent concentration on bioadhesive yield is shown in the Figure 22. The plotted data is shown in the Table 8 and Table 9.

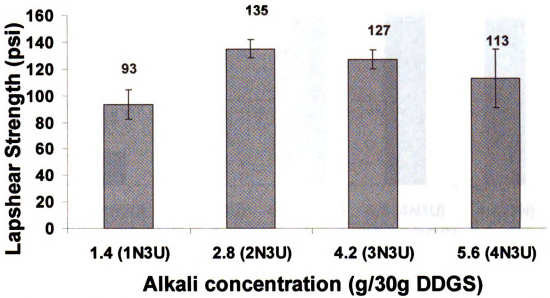

Figure 20: Lapshear strength dependence on the alkali concentration for paperboard samples

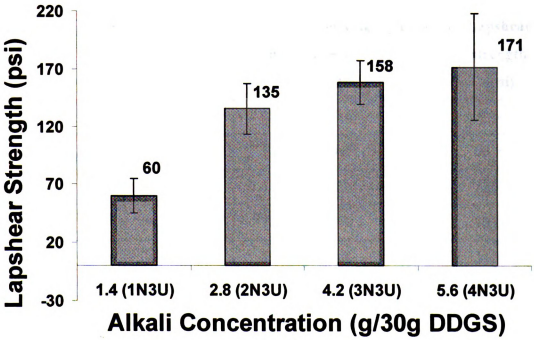

Figure 21: Lapshear strength dependence on the alkali concentration for hard maple wood samples

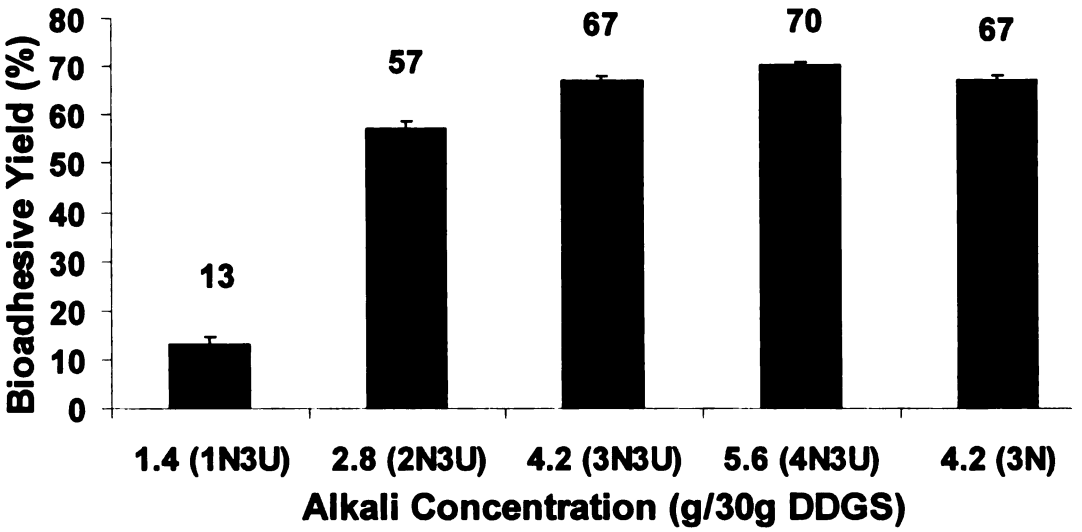

Figure 22: Effect of alkali concentration on the yield of bioadhesive

Table 8: Lapshear strength of different bioadhesive for paperboard samples

Sample code	DDGS (g)	NaOH (g)	Urea (g)	Cooking time (min)	Cooking pressure (atm)	yield (%)	Lapshear strength (psi)
3U	30.0	0	4.2	15	1.6	-	-
1N3U	30.0	1.4	4.2	15	1.6	13 ± 1.55	93 ± 11
2N3U	30.0	2.8	4.2	15	1.6	57 ± 1.52	135 ± 7
3N3U	30.0	4.2	4.2	15	1.6	67 ± 0.77	127 ± 7
4N3U	30.0	5.6	4.2	15	1.6	70^{c} ± 0.78	113 ± 2

Table 9: Lapshear strength of different bioadhesive for hard maple wood samples

Sample code	DDGS (g)	NaOH (g)	Urea (g)	Cooking time (min)	Cooking pressure (atm)	yield (%)	Lapshear strength (psi)
3U	30.0	0	4.2	15	1.6	-	-
1N3U	30.0	1.4	4.2	15	1.6	13 ±1.55	60 ± 15
2N3U	30.0	2.8	4.2	15	1.6	57 ±1.52	135 ± 22
3N3U	30.0	4.2	4.2	15	1.6	67 ±0.77	158 ± 19
4N3U	30.0	5.6	4.2	15	1.6	70^{c}± .78	171 ± 46

From the above results it can be inferred that the principal de-structurizing agent is alkali and that urea has negligible role. Urea upon cooking, was degraded as indicated through a pungent ammonia smell. Attempts were made to increase the yield of bioadhesive by using alternate bases. Alternatives such as calcium carbonate, guanidine hydrochloride, sodium sulfite were used in place of sodium hydroxide. Most promising results came from potassium hydroxide however the bioadhesive yield and lapshear strength were both compromised. The effects of sodium hydroxide and potassium hydroxide in bioadhesive formulation vs performance are shown in Table 10.

Table 10: Effect of alone sodium hydroxide and potassium hydroxide on bioadhesive yield and lapshear strength for paperboard samples

Received DDGS (g)	NaOH (g)	KOH (g)	Urea (g)	Cooking time (min)	Cooking pressure (atm)	Bioadhesive yield (%)	Lapshear strength (psi)
30	0	4.2	0.0	15	1.6	53	109 ± 6
30	4.2	0	0.0	15	1.6	67	123 ± 7

1.17.1 Curing time characteristics of adhesive

The lapshear samples were optimized for the curing time and temperature. The optimization is based on the lapshear strength form the samples of paperboard. It was observed that for paper board the optimal curing time at room temperature was 9 hours. However at elevated temperature of 80 °C the optimal time was 4 hours. The rational behind the high temperature curing is lesser adhesive curing times. The curing temperature of 80 °C was chosen because at still higher temperatures there were bubble formations due to high evaporation rates of water vapor originating from wet adhesives. The data for curing time optimization is shown in Table 11

Table 11: Curing time optimization

Temperature(°C)	Time (hours)				
	2	4	6	9	12
23 °C	-	-	119 ± 13	127 ± 7	130 ± 4
80 °C	104 ± 9	116 ± 5	115 ± 4	-	-

1.17.2 Effect of pressure

The bioadhesives were prepared by varying cooking pressure keeping residence time , reagent concentration and other processing variables constant . In a pressure cooker the amount of pressure developed was 1.6 atmospheres. Two reagent systems were compared one having the urea and the other one without urea. The atmospheric cooking, in both cases, showed a slight increase in the lapshear strength values than compared with those adhesive formulations prepared at 1.6 atmosphere cooking pressure. The increase in the lapshear strength is not significant therefore it can be concluded that there was practically no significant effect of pressure on the yield and lapshear strength of DDGS based bioadhesives. Lapshear strength and conversion yield data are shown in the Table12.

Table 12: Effect of pressure on the bioadhesive yield and lapshear strength for paperboard samples

Sample code	Received DDGS (g)	NaOH (g)	Urea (g)	Cooking time (min)	Cooking pressure (atm)	yield (%)	Lapshear strength (psi)
$3N3U_{atm}$	30.0	4.2	4.2	15	1	67 ± 1.6	129 ± 3
3N3U	30.0	4.2	4.2	15	1.6	67 ± 0.77	127 ± 7
$3N_{atm}$	30.0	4.2	-	15	1	67 ± 0.8	129 ± 7
3N	30.0	4.2	-	15	1.6	67 ± 0.28	123 ± 7

1.17.3 Effect of residence time

Another process variable is the residence time while cooking. The cooking time was varied from 15 min to 35 min in the interval of 10°C. The objectivity was to find effect of residence time on the yield of bioadhesive. It was observed that there was no significant increase in the yield. The data for the yield against the residence time is shown in the Table 13.

Table 13: Effect of residence time on the bioadhesive yield and lapshear strength for paperboard samples

Sample Code	Received DDGS (g)	NaOH (g)	Urea (g)	Cooking time (min)	Cooking pressure (atm)	Bioadhesive yield (%)	Std Dev
3N3U	30.0	4.2	4.2	15	1.6	67	0.77
3N3U`	30.0	4.2	4.2	25	1.6	68	0.35
3N3U``	30.0	4.2	4.2	35	1.6	69	0.87

1.17.4 Effect of filtration

All the bioadhesive samples prepared from DDGS unless specified were filtered under vacuum using Buckner funnel mounted over an Erlenmeyer flask. In this filtration process, a polyester-cotton cloth was used as the filtering medium. The yield of bio adhesive is drastically affected by the method of filtration. Two filtration methodologies were compared in term of the yield of bioadhesive. The polyester-cotton filter cloth in both the cases was kept constant. Other filtration method adopted for comparison is squeeze filtration. In this method, the cooked slurry was collected in a polyester-cotton

cloth and squeezed by hands thereby separating solid residues (retained in the filter cloth) from aqueous suspension. The residues were washed by use of distilled water for 10 minutes and squeezed again. In vacuum filtration it was observed that solids near filter cloth formed cake and hampered the flow of bioadhesive. The time required in this method was about 2 hrs. In contrast the squeeze filtration is very fast process however the yield of bioadhesive is a function of applied force. This method by hand has variable results. Moreover when the slurry is squeezed the pore size of the filter gets expanded. This allows ultra fine fibers to pass through. The effect of filtration on the lapshear strength is shown in the table 14. As a control experiment a bioadhesive sample was prepared which was not filtered but instead after cooking the slurry was blended in a mixer for 5-10 minutes. It was observed that the ultrafine cellulose fibers present in DDGS even after alkaline treatment really does not impart to the tack. In the Table 14 it is evident that as the fiber content increases in the adhesive the lapshear strength decreases monotonously.

Table 14: Effect of filtration on the bioadhesive yield and lapshear strength for paperboard samples

DDGS (g)	NaOH (g)	Urea (g)	Time (min)	Pressure (atm)	Filtration Mode	Yield (%)	Lapshear strength (psi)
30.0	4.2	4.2	15	1.6	Vacuum	67	127 ± 7
30.0	4.2	4.2	15	1.6	Squeeze	85	111 ± 7
30.0	4.2	4.2	15	1.6	nil	100	80 ± 12

1.18 Thermal gravimetric analysis

Thermo gravimetric analysis estimates the weight loss with increasing temperature. It measures the thermal stability of a material. It helps estimating the temperature up to which the material can be safely used. Weight loss data at different temperature of DDGS along with other natural fibers are shown in the Table 15. From the percent weight loss data it is evident that DDGS when dried becomes thermally very stable up to 200 °C. The residual fibers obtained after extracting bioadhesive had similar thermal stability as kenaf or maple fibers. The thermal plot of their weight loss versus temperature are shown in the Figure 23. Another significant observation as evident from the thermal stability data is that dried DDGS has highest char yield in present case the char yield of dried DDGS is twice more than that of the kenaf fibers. From the derivative weight loss plot, shown in Figure 24, the onset of degradation point of dried DDGS fibers is around 250°C which is slightly less than the other natural fibers. As regards bioadhesive, its thermal stability in contrast to DDGS and residual fibers are shown in the Figure 25. The data in the Table 15 suggests that bioadhesive is suitable for applications up to 200°C.

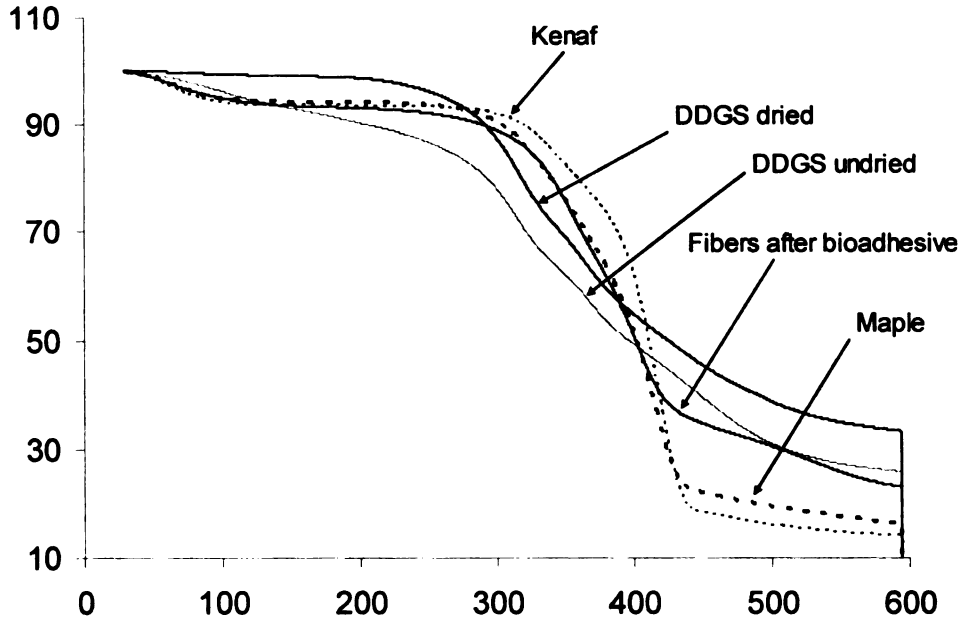

Figure 23: TGA plot of weight loss versus temperature for natural fibers, DDGS, and residual fibers

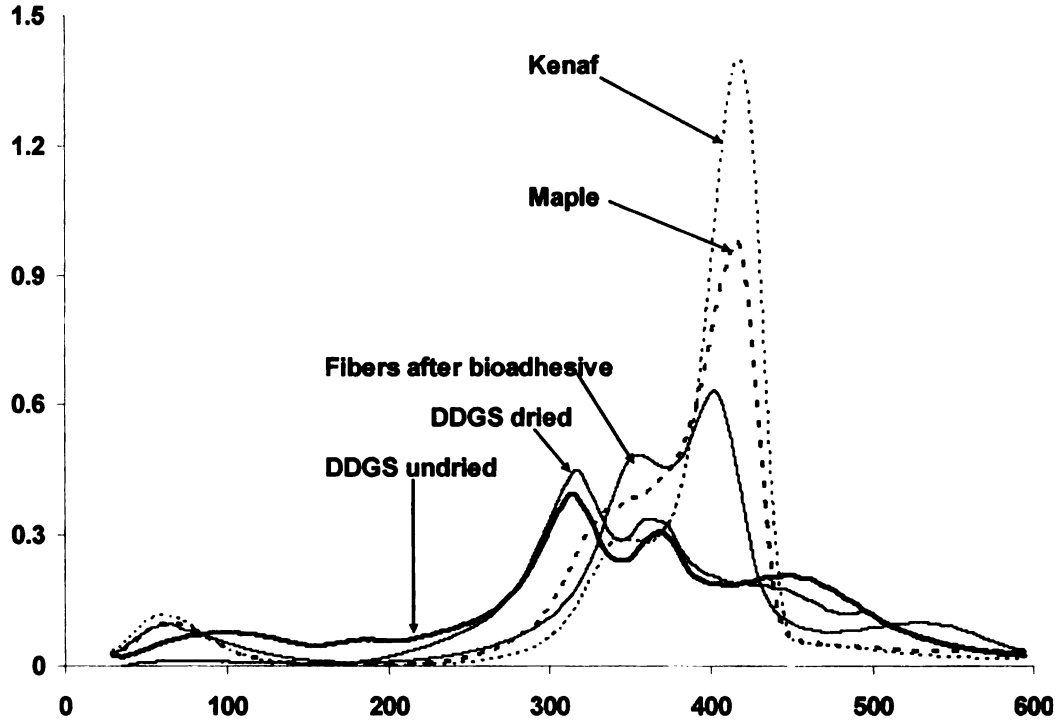

Figure 24: TGA plot of derivative weight loss versus temperature for natural fibers, DDGS, and residual fibers.

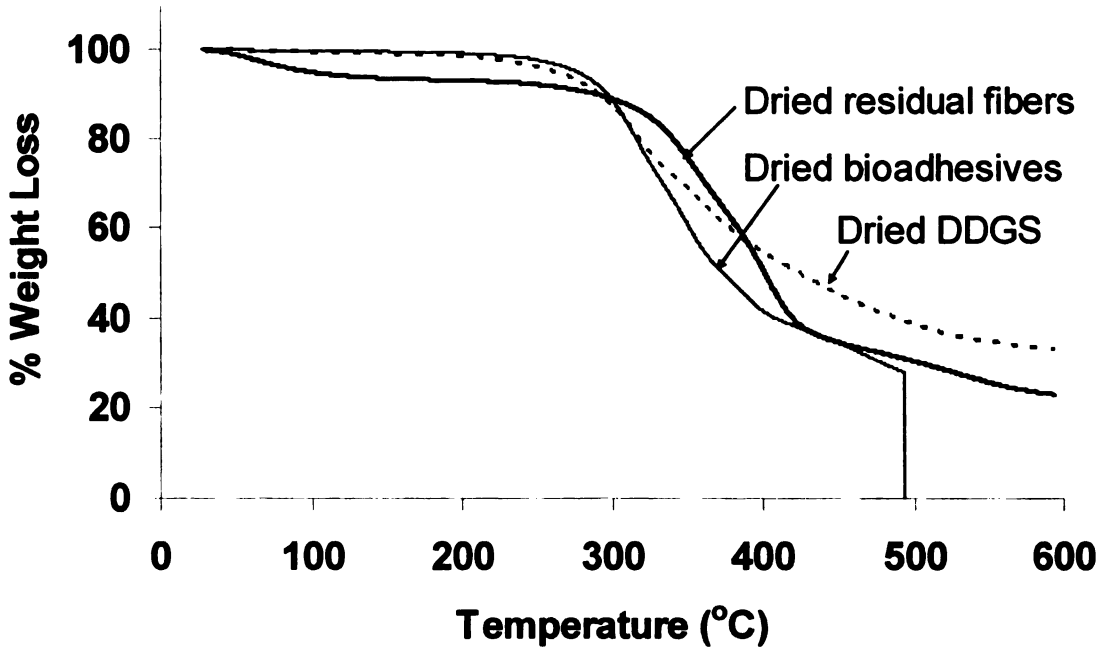

Figure 25: TGA plot of weight loss versus temperature for bioadhesive, DDGS, and residual fibers

Table 15: Percent weight loss at different temperatures for natural fibers, DDGS, and residual fibers

Fibers	% Weight Loss at:			
	100 °C	200 °C	300 °C	400 °C
Kenaf	6	6	10	40
Maple	5	6	10	50
DDGS dried	1	2	14	46
DDGS	4	10	23	50
Residual Fibers	5	6	12	51

1.19 Elemental analysis

Elemental analysis was conducted in order to estimate the amount of proteins present in the DDGS. In the elemental analysis, the sample was evaluated for its carbon (C), hydrogen (H) and nitrogen (N) contents. Percentage of protein can be estimated form the CHN elemental analysis by multiplying %N by a factor. For corn proteins the multiplying factor is 6.25 [102]. DDGS is a rich source of corn proteins, however there is a substantial difference in the composition of DDGS. It is therefore important to have an estimate the amount of corn protein in the given DDGS sample. Table 16 shows CHN elemental analysis of the DDGS and bioadhesive. In the case of bioadhesive, the percent nitrogen cannot be correlated with amount of proteins, as it is difficult to quantify the nitrogen from the protein and that from urea.

Table 16: CHN elemental analysis of the DDGS and bioadhesive

Sample	%C	%H	%N	% Proteins (%N*6.25)
DDGS	46.09	7.44	4.13	26
Bioadhesive (4.2 g NaOH+ 4.2 g Urea)	39.055	5.795	8.245 (including N from urea)	-

1.20 Brookfield viscosity

It is important to understand the rheological characteristics of these bioadhesives. Brookfield viscosity data of the bioadhesives were analyzed. Apart from the denatured

proteins there is substantial amount of carbohydrates in the bioadhesive as well. Brook field viscosity was measured as a function of shear rate, temperature and solid content. Data suggests that bioadhesives exhibit a shear thinning behavior for almost all the temperature ranges and solid content. The solid content of the bioadhesive was varied from 30 wt% to 50 wt% and the temperature ranged from 25 to 60 °C. Shear rates were varied from 50 to 1000 sec^{-1}. Based on the yield and lapshear strength, four adhesive formulations were studied for their viscosity. Below is the Brookfield viscosity data for various bioadhesive as a function of shear rate, solid content and temperature.

1.20.1 Brookfield viscosity profile for bioadhesive sample 3N3U

Viscosity profile in Figure 26 represents the data for bioadhesive at 50% solid content at room temperature to 60°C. 3N3U at this solid content shows a very mild shear thinning behavior. At higher shear rates, more Newtonian behavior is observed. At lower shear rates for 25°C and 40 °C the data almost overlapped.

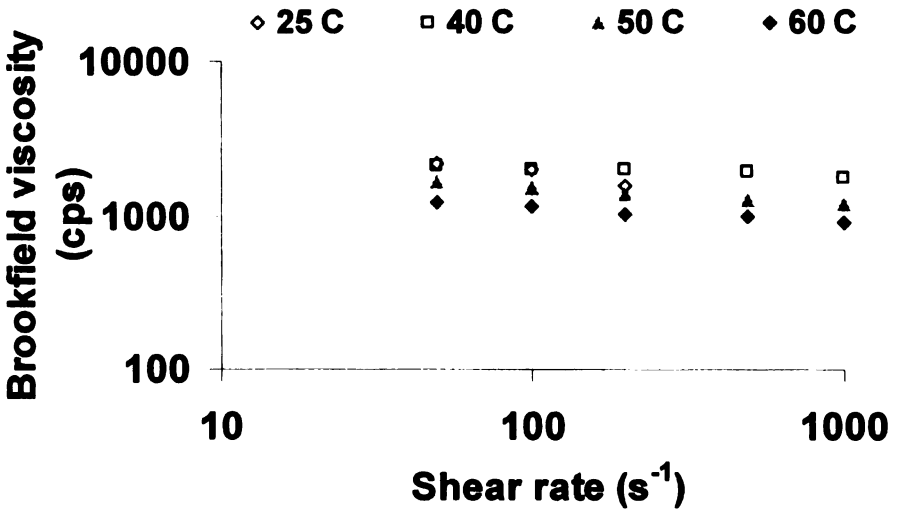

Figure 26: Brookfield viscosity profile for sample 3N3U at 50% solid content at room temperature to 60°C

Viscosity profile in Figure 27 represents the data for bioadhesive at 40% solid content at room temperature to 60 °C. As the dilution is increased, the shear thinning behavior is more pronounced. The viscous response of the bioadhesive looks overlapping for temperature responses at 25 and 40° C for all shear rates.

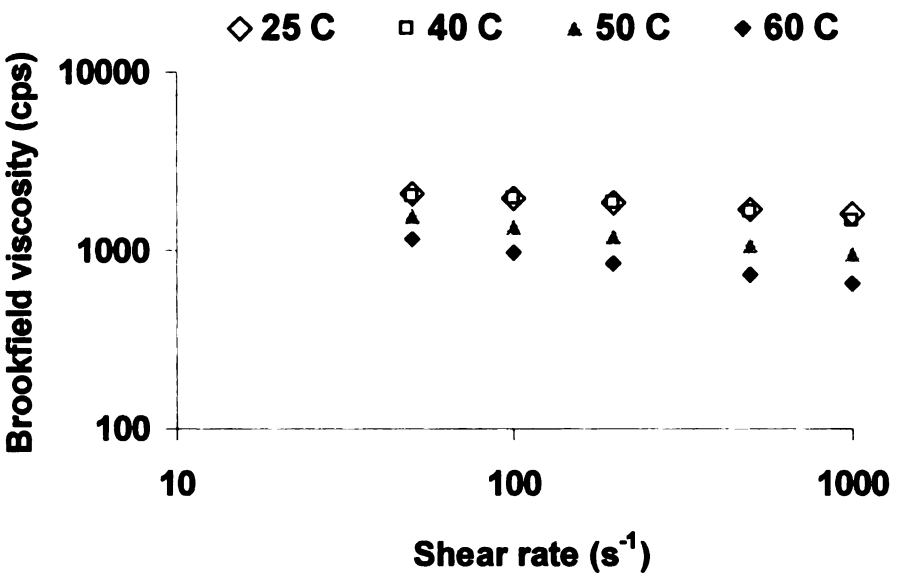

Figure 27: Brookfield viscosity profile for sample 3N3U at 40% solid content at room temperature to 60°C

Viscosity profile in Figure 28 represents the data for bioadhesive at 30% solid content ranging from room temperature (25 °C) to 60 °C. Lower shear rates show shear thinning behavior. However, at higher shear rates, more Newtonian behavior was observed. The shear thinning was pronounced at lower temperatures and is diluted at elevated temperatures.

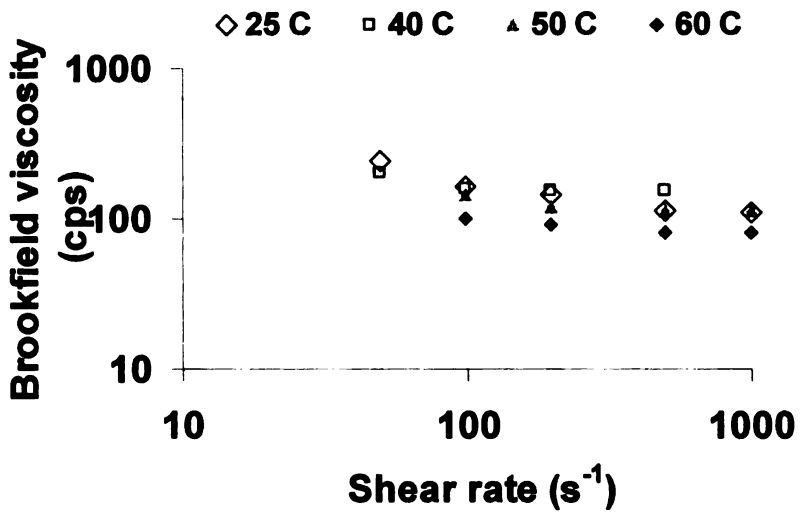

Figure 28: Brookfield viscosity profile for sample 3N3U at 30% solid content at room temperature to 60 °C

1.20.2 Brookfield viscosity profile for sample 3N3Uatm

Viscosity profile in Figure 29 represents the data for bioadhesive at 50% solid content at room temperature to 60 °C. Strong trends of shear thinning over all temperature ranges and shear rate ranges.

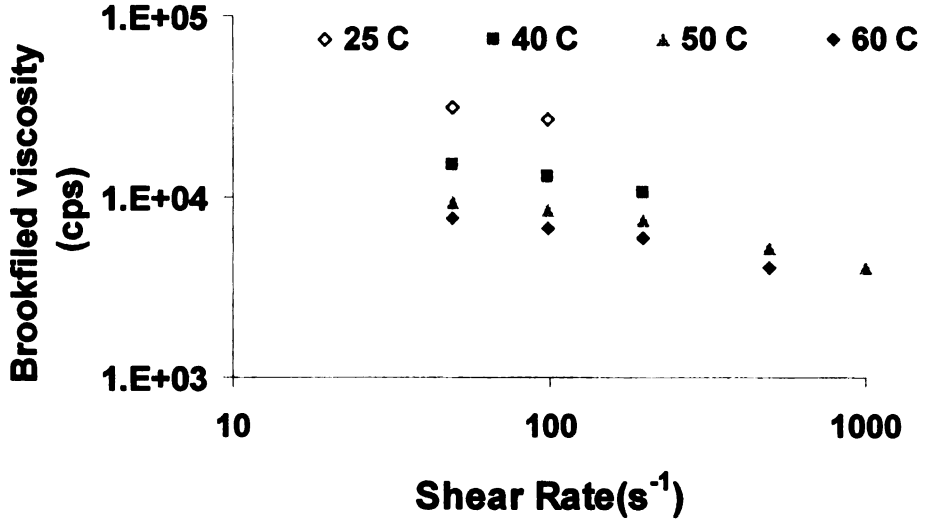

Figure 29: Brookfield viscosity profile for sample $3N3U_{atm}$ at 50% solid content (SC) at room temperature to 60°C

Viscosity profile in Figure 30 represents the data for bioadhesive at 40% solid content from room temperature to 60 °C. Gradual shear thinning behavior is observed at lower shear rates however; at higher temperatures and shear rates, more Newtonian characteristic is observed.

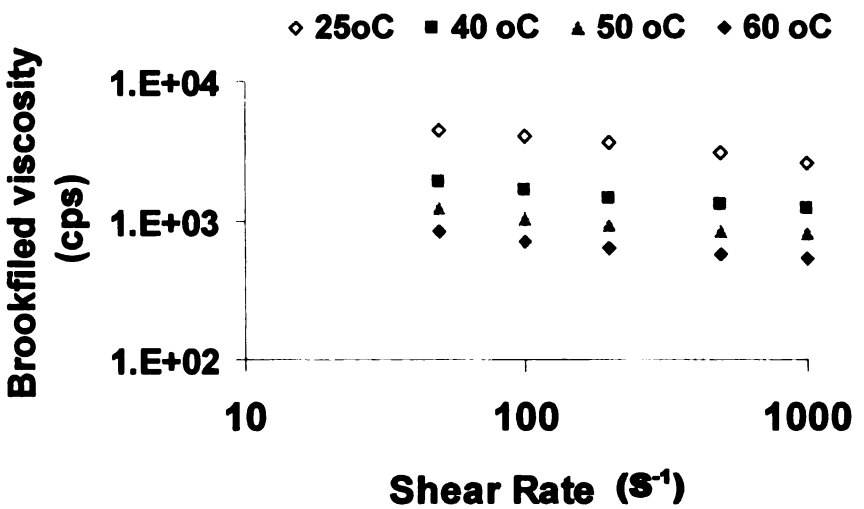

Figure 30: Brookfield viscosity profile for sample 3N3Uatm at 40% solid content (SC) at room temperature to 60°C

Viscosity profile in Figure 31 represents the data for bioadhesive at 30% solid content at room temperature to 60°C. Little shear thinning and more Newtonian nature is observed at all shear rates and lower temperatures. At higher temperatures and lower shear rates shear thinning behavior are more pronounced that fades out at higher shear rates

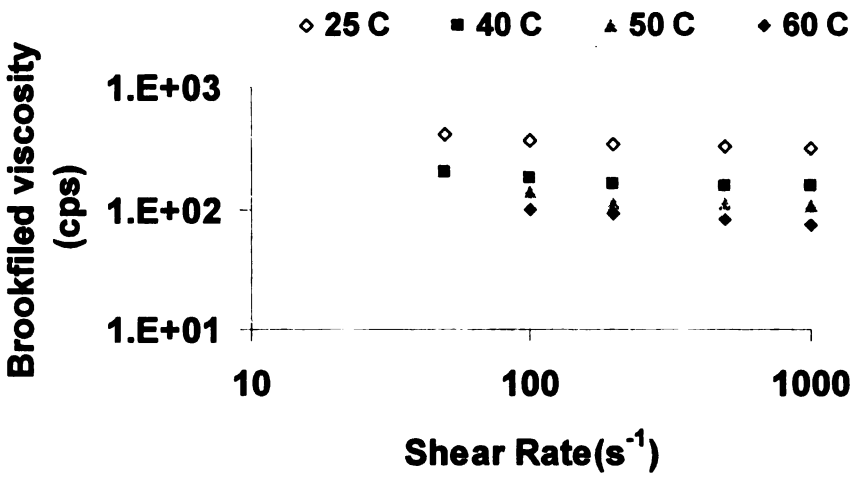

Figure 31: Brookfield viscosity profile for sample 3N3Uatm at 30% solid content (SC) at room temperature to 60°C

1.20.3 Brookfield viscosity profile for sample 3N

Viscosity profile in Figure 32 represents the data for bioadhesive at 50% solid content at room temperature to 60°C. At lower temperatures, shear thinning is observed for all shear rates, however at 60°C, at lower shear rates Newtonian behavior is observed followed by shear thinning at higher shear rates.

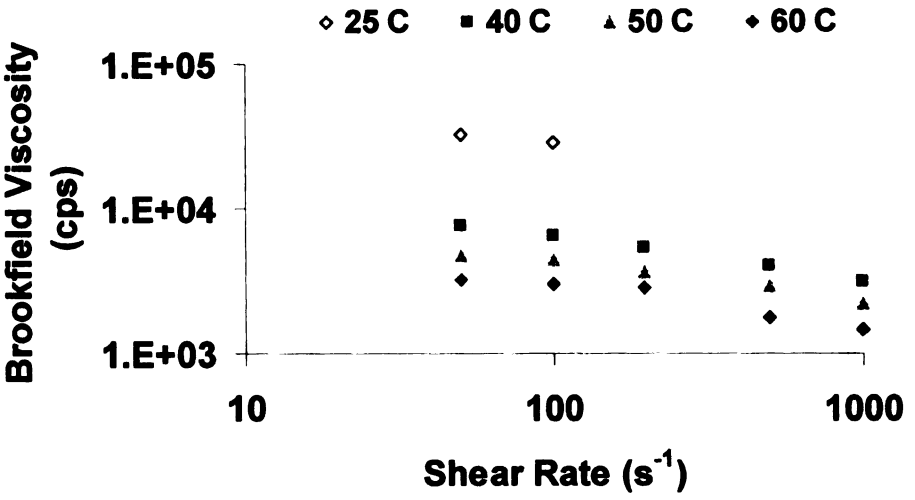

Figure 32: Brookfield viscosity profile for sample 3N at 50% solid content (SC) at room temperature to 60°C

Viscosity profile in Figure 33 represents the data for bioadhesive at 40% solid content at room temperature to 60 °C. Clear trend of shear thinning was observed over all temperature ranges and shear rate ranges.

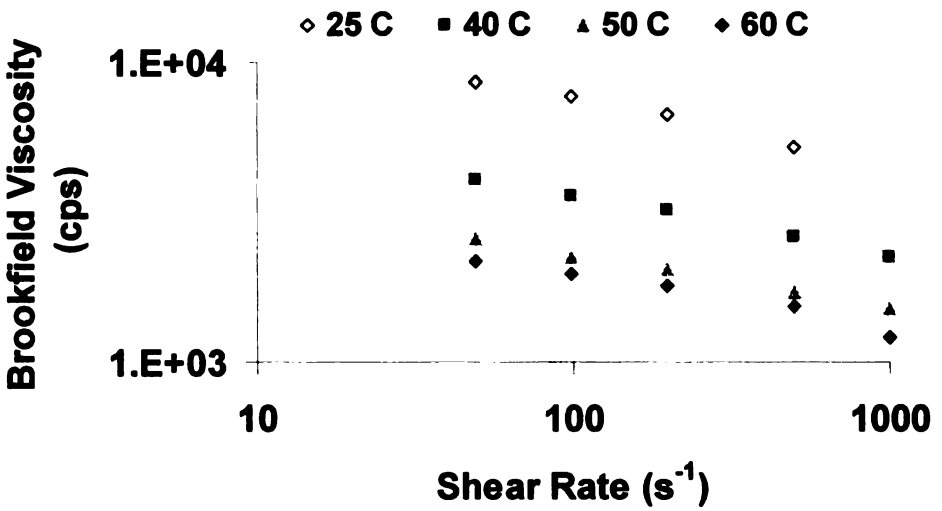

Figure 33: Brookfield viscosity profile for sample 3N at 40% solid content (SC) at room temperature to 60°C

Viscosity profile in Figure 34 represents the data for bioadhesive at 30% solid content evaluated from room temperature (25 °C) to 60 °C. Strong trend of shear thinning was observed over all temperature ranges and shear rate ranges. At higher shear rates, the Newtonian like behavior was observed.

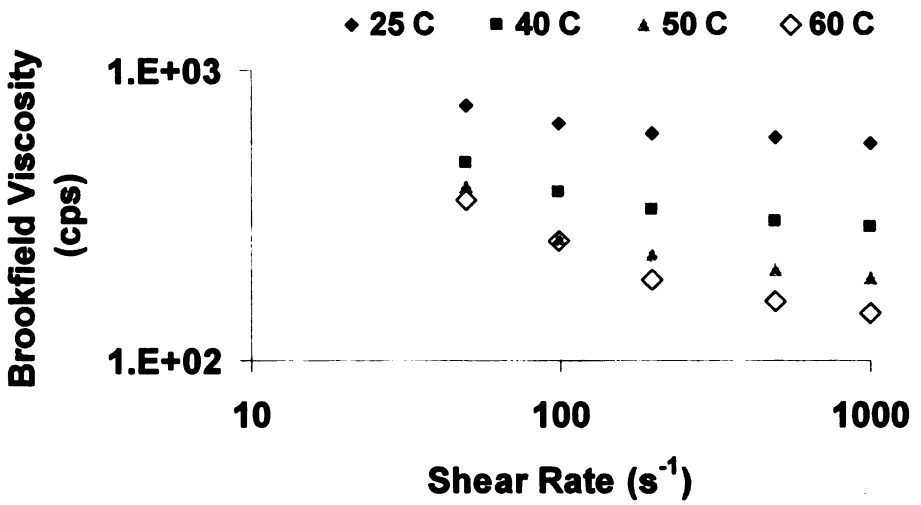

Figure 34: Brookfield viscosity profile for sample 3N at 30% solid content at room temperature to 60 °C

1.20.4 Brookfield viscosity profile for sample 3Natm

Viscosity profile in Figure 35 represents the data for bioadhesive at 50% solid content from room temperature to 60 °C. It is difficult to predict the trend however; at 40 °C a mild shear thinning behavior is observed.

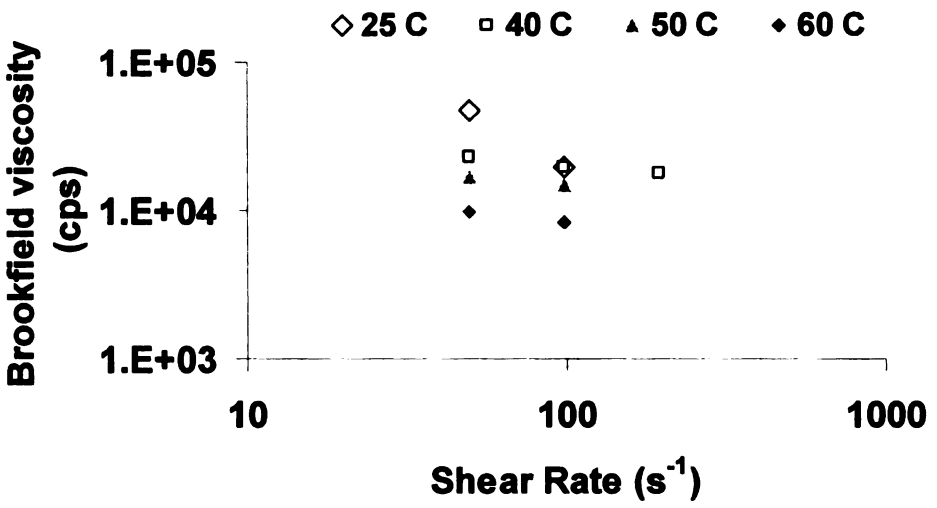

Figure 35: Brookfield viscosity profile for sample $3N_{atm}$ at 50% solid content at room temperature to 60 °C

Viscosity profile in Figure 36 represents the data for bioadhesive at 40% solid content from room temperature to 60 °C. At low shear rates, a shear thinning behavior was observed.

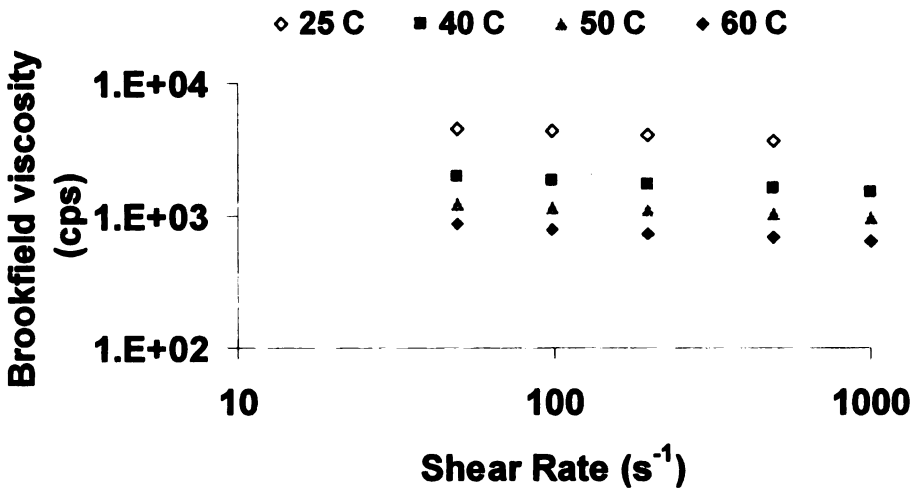

Figure 36: Brookfield viscosity profile for sample $3N_{atm}$ at 40% solid content at room temperature to 60 °C

Viscosity profile in Figure 37 represents the data for bioadhesive at 30% solid content at room temperature to 60°C. At room temperature, Newtonian behavior was observed at lower shear rates. At higher temperatures and lower shear rates strong shear thinning trends are observed; however, at higher shear rates shear thinning is mild.

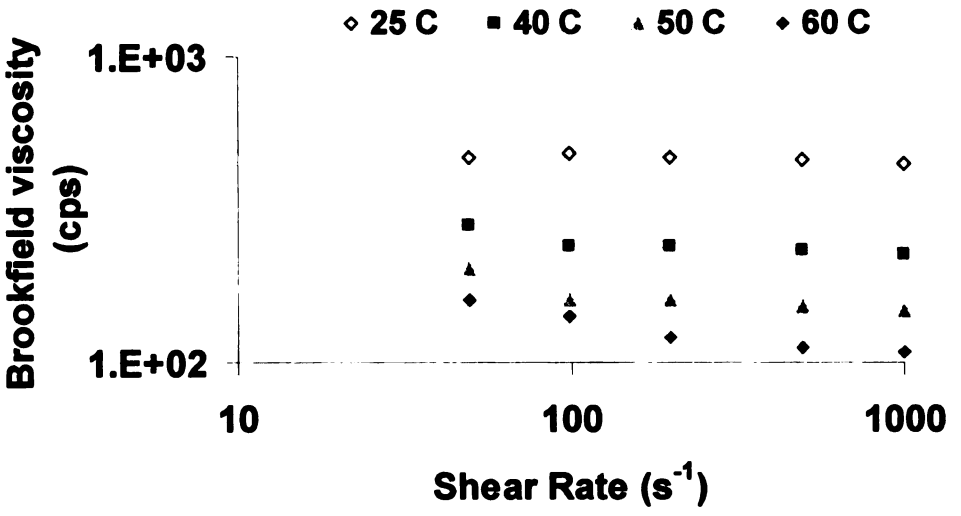

Figure 37: Brookfield viscosity profile for sample 3Natm at 30% solid content (SC) at room temperature to 60°C

1.21 Fourier transform infrared spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was conducted to analyze the effect of chemical modifications on DDGS and resulting bioadhesive. Figure 38 shows the transmission spectra for DDGS and bioadhesive 3N3U and $3N3U_{atm.}$ All the samples were dry when evaluated for FTIR spectra. In the Figure 38 there is a broad peak at 3288-3343 cm^{-1} this is characteristic of polymeric OH. As we know that in DDGS and bioadhesive there is presence of polypeptide and polysaccharides. Thus, this peak is a combination of both. The peaks at 2921 cm-1 and 2854 cm-1 are due to the methyl and methylene. In the spectra of DDGS, at 1743 cm^{-1}, there is a characteristic peak of carbonyl. This peak is shifted towards 1634 cm^{-1} this is due to the hydrolysis of carbonyl groups to COO^- . In the fingerprint region the peak ranging from 1150 to 1000 there is

characteristic of C-O-C stretching. This is indicative of the presence of polysaccharides. This peak disappears in the case of adhesive prepared under atmospheric conditions which suggests that glycoside linkages present in the polysaccharides are affected. Therefore there should be reduction in the molecular weight of carbohydrates present.

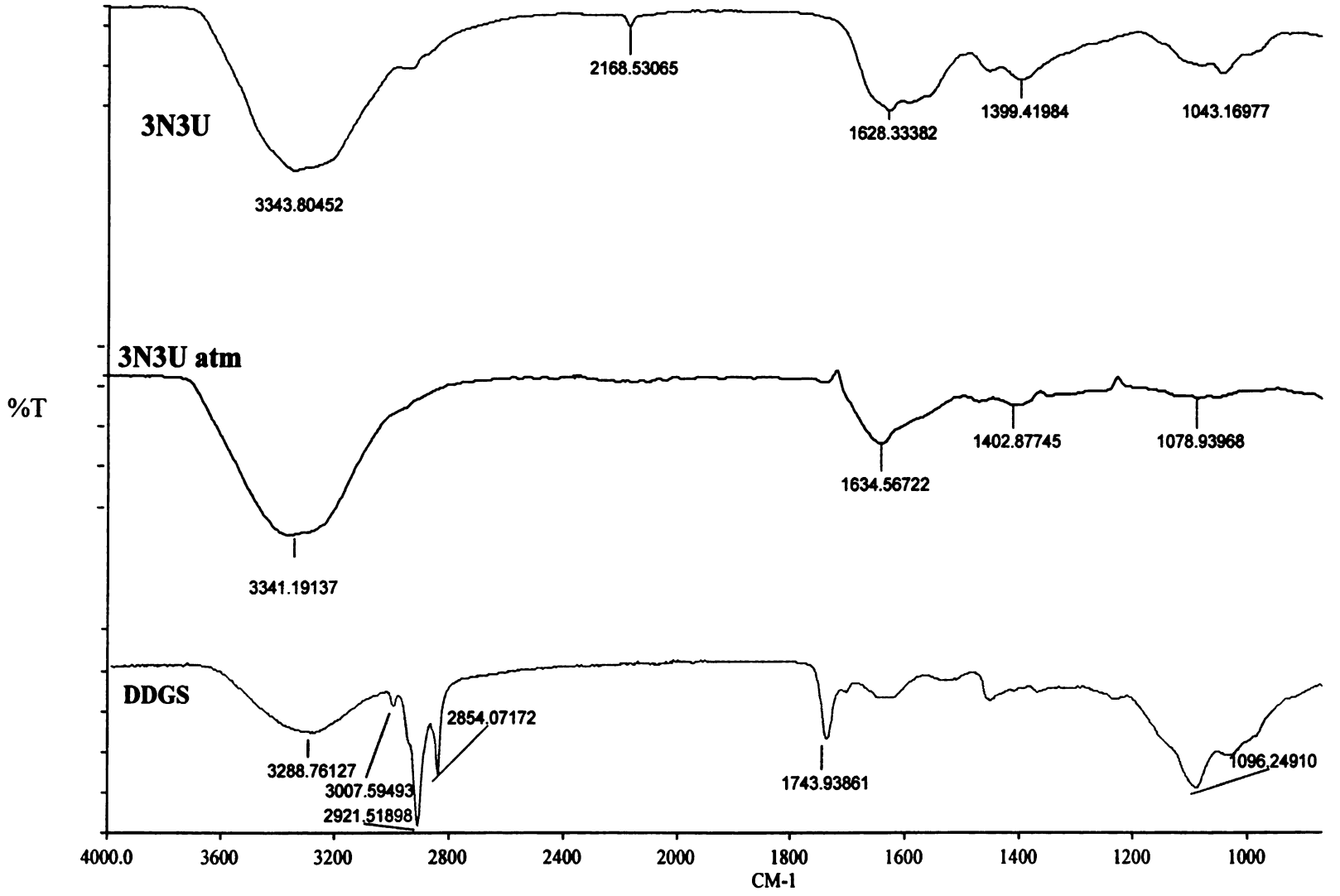

Figure 38: FTIR spectra of DDGS, 3N3U and $3N3U_{atm}$

Chapter - Conclusions

- Bioadhesive derived from DDGS is an attempt for making the corn ethanol sustainable. Bioadhesive is a combination of corn polysaccharides and proteins that makes it an inherently biodegradable.
- Presently for paper and paperboard packaging more than half of the demand is met by starch based adhesives mostly derived from corn. The DDGS based adhesive is intended to find an alternative to the conventional starch adhesive.
- Bioadhesive has been tested on the paperboard the results prove that the adhesive is strong enough to meet the purpose. The mode of failure in paperboard samples shows fibers cohesive failure.
- Unlike starch based adhesive, the DDGS based bioadhesive is not susceptible to microbial attack. This was based on the observation of stored samples in a glass bottles. The starch sample after 4 days gets degraded characterized by the high flowability mixture starting from initial thick paste. In contrast, bioadhesive did not show the drop in viscosity (based on visual observation) even after six months.
- The lapshear strength on paperboard suggests a comparable strength of commercial wheat starch based adhesive and DDGS based bioadhesive, however in case of wood the starch adhesive was superior.
- Based on the TGA results the thermal stability of bioadhesive was above 200 ^{o}C this suggests DDGS based bioadhesive application over a broad temperature range.

- Protein content in the bioadhesive was about 40 % by weight, this makes it a hybrid bioadhesive that has good spreadability even at 50% solid content. While in the case of starch, even a 10% solution was too viscous.
- Rheological properties of bioadhesive when evaluated as a function of shear rate, solid content and temperature suggests that they exhibit shear thinning behavior almost over all temperature , shear rates and solid content.
- There are growing environmental concerns due to very high macro-nutrients in DDGS that limits its use as animal feed. Various factors such as high phosphorus content, mycotoxin contamination, lack of flowability and energy returns, just to name a few, were studied to understand the scope of utilization and market of DDGS. Many environmental issues associated with DDGS can be tackled through value added applications like biobased material pathways.
- Shelf life of DDGS is small thus unmanaged DDGS can lead to environmental hazard that can raise question marks on the sustainability of bioethanol derived from corn.
- Utilization of DDGS as value added materials helps to maintain the balance between food, fuel and biobased materials.
- Changing gears from hydrocarbon economy to carbohydrate economy shall ensure nation's energy security.

Future Recommendations

- To derive lingo-cellulose ethanol from the residual fibers and DDGS
- Estimation of molecular weight and its distribution is critical to predict rheological characteristics.
- Chemical separation of complex DDGS to obtain various value added chemicals
- Chemical modification of adhesive to make it less alkaline and improve color
- Infestation study of the bioadhesives
- Microbial degradation of adhesives upon storage.
- Effect of humidity on the lapshear strength.
- In order to quantify the sustainability parameters it is important to conduct life cycle analysis of DDGS.

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Appendix 1

The US total energy demand and their fuel wise consumption pattern (*after ref. 11*)

Year	Total energy	Fossil fuels (petroleum + coal + natural gas)	Coal	Natural Gas	Petroleum	Renewable	Nuclear
2001	97	83	22	23	38	5	8
2002	98	84	22	24	38	6	8
2003	98	84	22	23	39	6	8
2004	101	86	22	23	41	6	8
2005	101	86	23	23	41	7	8