Biofuel Technology: Current Design Principles, Feedstocks Analysis, Environment Impact and Future Growth

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Abstract: This work aims to analysis the advance and disseminate knowledge in all the biofuel-related areas. The biofuel has been researched and developed in the last two decades. Newly emerged theories and techniques has prompted the progress of the biofuel commercial application. In this work, the histories of the development of the biofuels were researched. The physical principle of biofuel reaction was discussed. The two major feedstocks of producing biofuel and their cultivation technologies were discussed. The major methods of producing the biofuels including hydrolysis, fermentation, and transesterification were introduced. This work also analyses the economic and environmental impact of biofuel application.

1 INTRODUCTION

Biofuels, as the name implies, are fuels derived from biomass, including crops, herbs, and other materials. The two most common types of biofuels in use today are ethanol and biodiesel, both of which represent the first generation of biofuel technology. Today, fossil fuels are still the main fuel used in most countries, but it is recognized that fossil energy sources are limited, and the diminishing availability of fossil fuel resources is causing prices to skyrocket, and sooner or later fossil fuels will be depleted, leading to the creation of renewable energy sources, of which biofuels are one. While fossil fuels usually take millions of years to form, biofuels are any hydrocarbon fuel produced from organic matter in a short time.

2 PHYSICAL PRINCIPLES

In order to efficiently and economically produce and apply biofuel, the physical principles of the biofuel must be understood, which are also true for other types of fuel.

2.1 Chemical Reactions

Generally, the released energy of the biofuel comes from the chemical reaction. Chemical reaction, by definition, is a process that involves rearrangement of the molecular or ionic structure of a substance.

The rearrangement of the molecule is exhibited by the breaking of original bonds and formation of the new bonds. The net energy difference of the rearrangement is required to be absorbed from or released to the environment in a form such as internal energy. Chemical reactions can be investigated and represented by two different components: reaction thermodynamics and reaction kinetics.

2.2 Reaction Thermodynamics

Reaction thermodynamics is defined as the system needing either to absorb or to release energy to the surrounding environment to proceed the reaction. Endothermic reactions require absorbing energy (net input) while the exothermic reactions result in releasing energy (net output) (Ott, Bevan J.; Boerio-Goates, Juliana 2000). To examine the thermodynamic properties of a biofuel, most biofuel will be observed under steady-state conditions during the chemical equilibrium. To characterize the thermodynamic entity, Gibbs free energy was

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introduced, which was named after the nineteenth-century scientist Willard Gibbs. The Gibbs free energy was commonly presented by the following form:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where the G represents Gibbs free energy, H represents enthalpy, T represents temperature, and S represents entropy. A negative Gibbs free energy indicates that the reaction is spontaneous process and proceeds in the forward direction of the reaction, while a positive Gibbs free energy indicates that the reaction is a non-spontaneous process (Li, Khanal 2017). In the equation, enthalpy and entropy can usually be calculated by the thermodynamics properties of the reactant and product by the following equations.

$$\Delta H_{rxn} = \Delta H_{f,products} - \Delta H_{f,reactants} \quad (2)$$

$$\Delta S = \Delta S_{products} - \Delta S_{reactants} \quad (3)$$

2.3 Reaction Kinetics

Reaction kinetics is another important field to study for determining the physical properties of biofuels and their related reaction. Instead of determining the spontaneity of the reaction by thermodynamic study, kinetics study determines the rate of process of the reaction (Hoff, J. H. van't (Jacobus Henricus van't); Cohen, Ernst; Ewan, Thomas 1896). To simplify the kinetics study of the reaction, most biochemical reactions were assumed to occur in an isothermal environment to preserve the biological activity of the microbial community. To determine the rate of the reaction, rate constant k was introduced and can be represented by the following expression:

$$k = Ae^{E/RT} \quad (4)$$

where the k is the first-order rate constant of the reaction, A is the Arrhenius constant, E is the activation energy of the reaction, R is the gas constant, and T is the temperature. The rate constant, or the specific rate constant, is the proportionality constant in the equation that expresses the relationship between the rate of a chemical reaction and the concentrations of the reacting substances. By specifying the rate constant, the reaction rate can be deducted and represent by the following expression:

$$r_A = -kC_A^x C_B^y C_C^z \quad (5)$$

where the C is the concentration of each component and. The exponents x, y, and z correlate with the stoichiometric number of each component according to the chemical equilibrium in most cases.

3 TECHNOLOGY IMPLEMENTATION

In order to effectively produce biofuel, raw materials or so-called feedstocks are also an important field to study. Based on different bio-properties, the major categories of feedstocks are starch-based, oilseed-based, lignocellulose-based, and algae-based feedstocks. This article will focus on the major and massive production feedstocks: starch based.

3.1 Starch-based Feedstock

Starch-based feedstocks are grown and cultivated for food and feed supply. The major crops of Starch-based feedstocks are cereals (such as wheat, rice, maize, oat, barley, rye, millet, and sorghum) and starchy roots (such as potatoes and yams). Based on the data collecting by FAOSTAT (Etipbioenergy EU, 2012), the total global starch product is around 3.07 billion metric tons at current. Approximately 6% of the starch production is used for biofuel production, and the major biofuel product from the starch feedstock is bioethanol (40%). Corn is the major cereal crop that produces about 98% bioethanol.

3.2 Corn

This article will use corn as an example of starch-based feedstock to specify the technical implements during biofuel production.

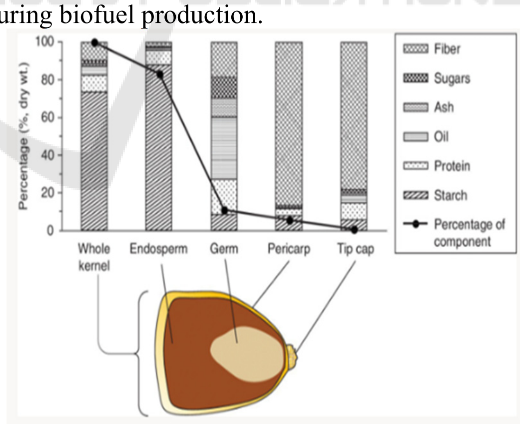

Figure 1: Percentage Components of Corn.

Cron was an original tropical plane only after centuries of modification, cron was well adapted to and effectively grown at temperature climates. Globally, the U.S. is the largest corn producer providing 35% production, followed by China (21%) and Brazil (8%). For bioethanol production, Yellow dent corn (Zeamays var. indentata) is the commonly used corn at present. Figure 1. illustrates the profile of the corn and its composition.

3.3 Growth Cycle of Corn

After selecting cultivars, the corn will be planted to absorb water and nutrients in the endosperm. The growth cycle of corn was typically divided into three stages: emergence, vegetative and reproductive. The VEG stage is further designated numerically to represent the highest leaf and visible collar. Such numerical designation is also applied to the REP stage representing kernel development. Figure 2. illustrates the corresponding observation of each stage.

3.4 Growing Degree Day

Environmental temperature is an important factor influencing Plant growth. Most plants including corn can only grow at a temperature above their base temperature, while the growth rate of the plant generally increases with the increasing temperature with sufficient light, water, and nutrients. However, a ceiling temperature exists for most plants, and the growth rate will decrease as the temperature reaches the ceiling temperature. The growing degree day (GDD) was introduced to reflect the accumulated heat of a given period of time and predict the plant growth rate (Prentice, I. Colin et al 1992). Following expression is the calculation of ht GDD and the prediction of the GDD for corn growth:

Vegetative Stages	Reproductive Stages
VE = emergence	R1 = silking
V1= first leaf collar	R2 = blister
V2 = second leaf collar	R3 = milk
V3 = third leaf collar	R4 = dough
V(n) = nth leaf collar	R5 = dent
VT = tasseling	R6 = maturity

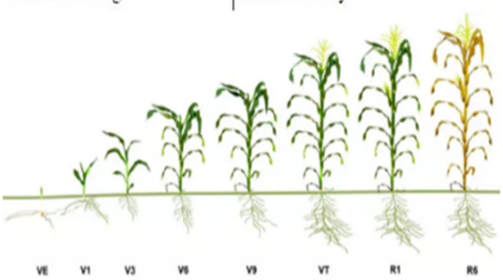

Figure 2: Growth Stage of Corn.

3.5 Bioethanol from Starch-based Feedstock

To produce bioethanol, two types of processes, wet milling and dry milling, have been designed and developed. Both of the processes were able to utilize the starch-based feedstock to produce while simultaneously produce co-products.

3.5.1 Fermentation Process

In the fermentation process, the essential step is hydrolysis since starch-based feedstock cannot be directly fermented by yeast directly. The upstream feedstock of starch will be cooked at a high temperature (90-100°C) with the enzyme alpha-amylase for gelatinization and liquefaction, which is able to dissociate the intermolecular bond of starch feedstock and breaks down to the long-chain molecule. Then, the liquified feedstock will be cooked at a low temperature (55°C) to proceed the saccharification. In most cases, the saccharification process can be proceeded prior to the fermentation or simultaneously with the fermentation (Li, Khanal 2017). Recently, a newly designed and developed enzymes, STARGEN, commence its industry operation, allowing the starch hydrolysis process to occur at a low temperature and targeting to reduce the energy consumption of the fermentation.

3.5.2 Wet Milling and Dry Milling

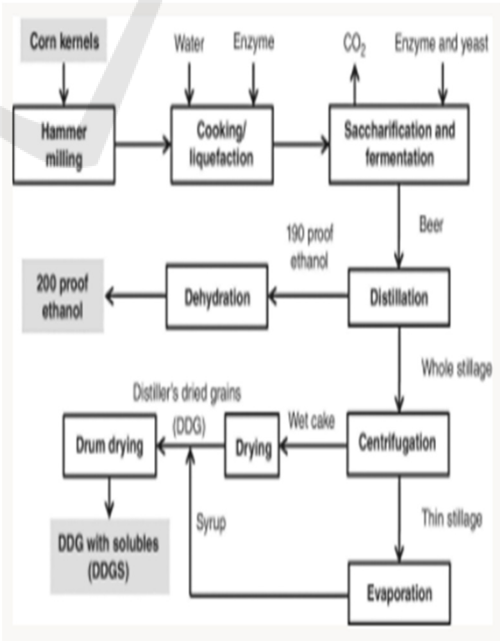

Figure 3: Flow Diagram of Dry Milling.

As aforementioned, two different types of technical (wet milling and dry milling) were applied. The following process flow diagrams indicate two typical fermentation processes of using corn as the starch-based feedstock.

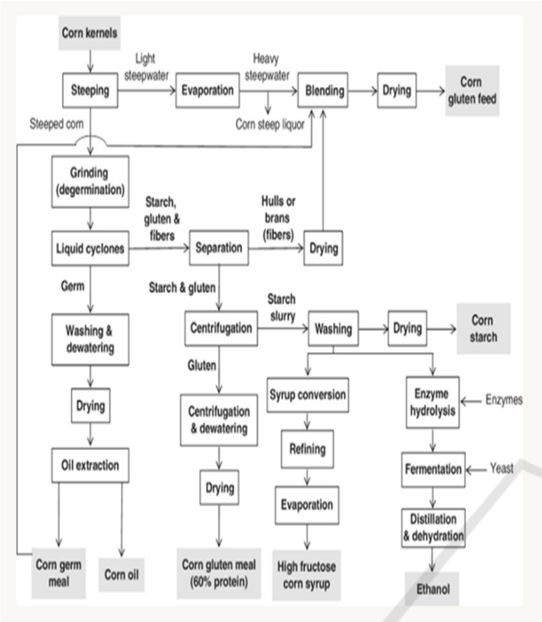

Figure 4: Flow Diagram of Wet Milling.

The dry milling or dry grind technique is the major method of producing bioethanol production. During the dry milling, the whole corn kernel was ground and mixed with water and enzymes forming a mash. After gelatinization and liquefaction, the mash was cooled and mix with more enzymes to proceed with saccharification and fermentation (Stock 2000). Figure 3 shows the process of the dry milling.

Instead of grinding corn kernel directly, the wet milling process allows the corn to steep for 48 hours and separate into different parts. The germ of the kernel can be further separated into fiber, starch, and gluten by processing slurry separation. The wet milling process produces multiple high value-added co-products, while also enables “food and fuel” production. Figure 4 shows the process of the wet milling.

4 TYPICAL SYSTEM DESCRIPTION

4.1 Bioethanol

Bioethanol is mainly derived from star-based and sugar-based and lignocellulose-based natural materials, such as wheat starch and crops. The ethanol is produced through several processes, firstly, those carbohydrates will convert into sugars by hydrolysis process, those feedstocks would be cooked under high temperature of 90-100℃. And then, under the action of microorganism and carbon dioxide, usually yeast, the feedstock is being fermented at a low temperature of 55 ℃ which turn into a liquid that contains ethanol. Finally, the liquid is going to be refining into high purity bioethanol through distillation and dehydration.

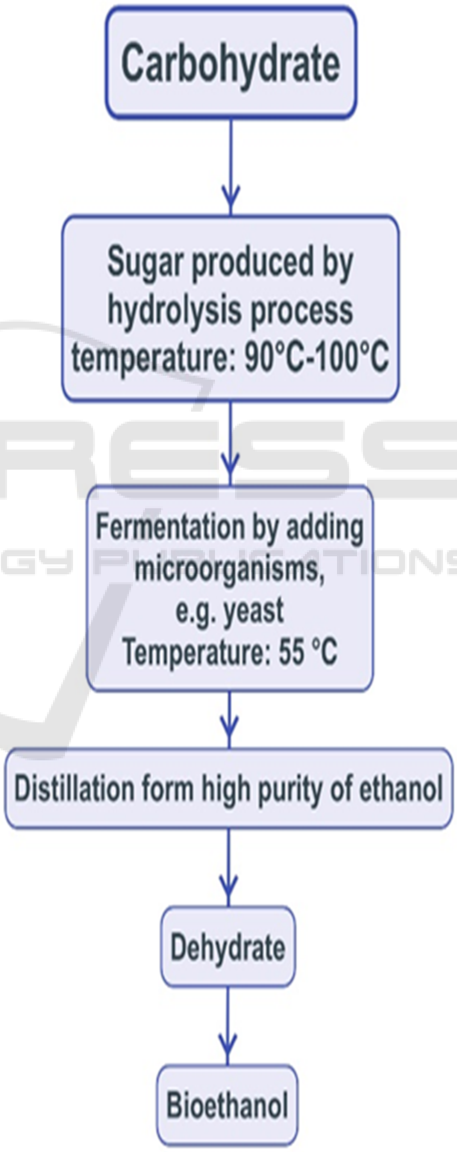

Figure 5: Production of ethanol with starch-based materials.

However, for lignocellulose-based feedstock, the production process and condition required is different compare to starch-based and sugar-based materials. Pretreatment is used to prepare the lignocellulosic material for enzymatic hydrolyses of cellulose and hemicelluloses to generate fermentable sugars, including physical, chemical, and biological pretreatments. Firstly, chemical pretreatment is used through alkaline hydrolysis at high temperature of 100-170℃.Or physical pretreatment is used, including process of mechanical communication, steam explosion (160-260℃), ammonia fiber explosion (around 100℃) and pyrolysis (over 220℃), or biological pretreatment. After this, enzymatic hydrolysis converts cellulose and hemicellulose into glucose and pentose respectively under the condition of pH 4.8 and temperature 45-50℃.finally, ferment and distillation the feedstock to get bioethanol. Figure 5 and 6 indicates the process of the production of the ethanol via starch-based materials and lignocellulos-based materials.

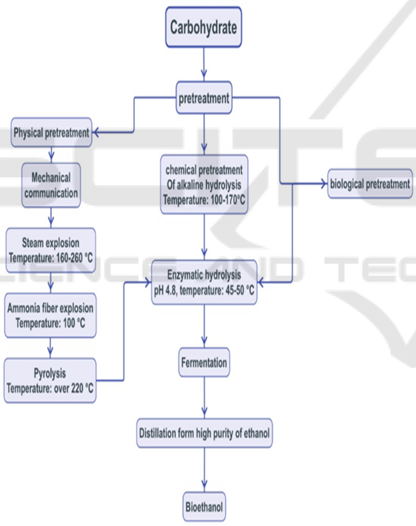

Figure 6: Production of ethanol with lignocellulos-based materials.

4.2 Biodiesel

The feedstock used to produce biodiesel has two generations, the first generation uses animal fat and oils from vegetables. Those oils need pretreatments like degumming, deacidification, bleaching, and dehydration, the use of pretreatment depends on the compositions of the materials. Degumming is used to remove phosphatides from most feedstock; deacidification is used to remove free fatty acids; bleaching is used to remove pigments and trace metals and reduce oxidation; and finally, dehydration is to remove water from oil or fats, as it is toxic to transesterification and can affect the efficiency of biodiesel conversion.

After pretreatment, is the process called transesterification which can produce glycerin and biodiesel by using alcohol as reactants, methanol is commonly used in this process as it is cheaper and easier to find compared to ethanol. And to separate glycerin and biodiesel, settling, filtration and decantation are used to find crude glycerin and crude biodiesel. To increase the quality of biodiesel, it can be done through refining.

5 ENVIRONMENTAL IMPACT

The production and use of biofuels can also release air pollutants other than greenhouse gases that can affect people and their surroundings. Air pollutants from biofuels include carbon monoxide, sulfur dioxide, nitrogen oxides, and ozone; these pollutants have a variety of effects, including damage to human health (e.g., cardiovascular disease, and respiratory irritation) and to the environment (e.g., reduced visibility, water, and soil acidification, and crop damage).

Increased biofuel production will dramatically increase water use, measured at some locations where corn irrigation or production facilities draw water from depleted groundwater sources. In some large corn grain ethanol-producing countries, agricultural irrigation has been increasing, resulting in competition for freshwater with other uses (USDA Foreign Agricultural Service 2018).

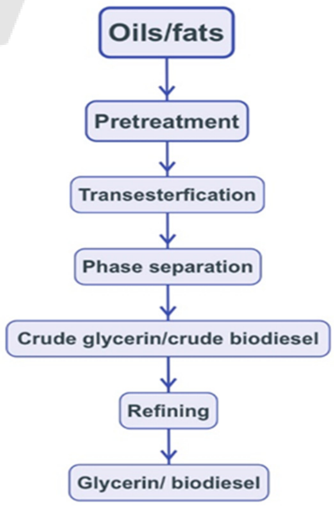

Figure 7: Production of biodiesel with first generation feedstock.

6 ECONOMICS OF BIOFUEL

6.1 Introduction

Biofuel production is constantly developed worldwide. In the U.S., ethanol production has three times more than 5 years ago, from 2.8 billion gallons in 2003 to over 9 billion gallons in 2008. Moreover, Brazil produces secondly around the world with approximately 5 billion gallons in 2007.

Biodiesel production is also growing rapidly from 25 million gallons in 2004 to 700 million gallons in 2008 in the U.S, which lays a solid foundation of maintain the increased demand of renewable energy in the market. However, recently, markets for fuels and feedstocks fluctuate dramatically. The prices of Petroleum have increased from $20 per barrel in 2002 to $140 per barrel in 2008.

6.2 Corn Ethanol

As forementioned, Drys-grind and wet-milling are two methods of producing ethanol. In the U.S., dry-grind methods are applied to more than 80% of ethanol production. The advantage of applying the dry-grind method is the relatively low capital cost, which more eco-friendly for most plants. Dry-grind plants produce ethanol and animal feed. Wet millings, by contrast, are able to further produce value-added co-products. Thus, ethanol yields from dry-grind processes are higher. Table 1 lists the cost of each typical item of the ethanol production.

Table 1: Ethanol production cost in USDA 2002.

US average	2002	1998
Feedstock costs ($/gal)	0.8030	0.8151
By-porduct credit ($/gal)	-0.2580	-0.2806
Net feedstock cost ($/gal)	0.5450	0.5345
Operating cost ($/gal)	0.4124	0.4171
Total cost ($/gal)	0.9574	0.9516

7 CONCLUSIONS

In conclusion, this work discussed the thermodynamic principles of biofuels and identified four major feedstocks of biofuel production. Focusing on the starch-based feedstocks, the work introduced the cultivation of corn, which is the major source of the starched-based feedstock. The process of the fermentation of the corn was researched. The typical processes of the biofuel via different feedstock were introduced and illustrated by a flow diagram. The economy and commercial application of the biofuels were also analyzed and concluded as a sustainable and growing market. In the foreseeable future, the biofeul will continuely and increasely replace the current fossil fuels and serves as an important role in reducing global carbon emmsion and enviromental impacts.

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