A Review of the Advances in Biofuels Production

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Abstract: The finitude of fossil fuels, concerns for energy security and the need to respond to climate change have led to growing worldwide interests in biofuels. Biofuels are often viewed as a key to reducing reliance on foreign oil, lowering emissions of greenhouse gases and meeting rural development goals. Biofuel is defined as solid, liquid or gaseous fuel derived from relatively recently dead biological material and is distinguished from fossil fuels, which are derived from long dead biological material. Biofuels are alternative renewable fuels that have received considerable attention in the recent past namely: bioethanol, which is made from crop grains or sugarcane and biodiesel, which is made from vegetable oils and animal fats, and both are used as a source of power for cars, trucks, and aircrafts. Theoretically, biofuels can be produced from any biological carbon source, although the most common sources are photosynthetic plants. This paper highlights the on-going developments in biofuel feedstock selection and production technologies, evaluating the environmental and economic effect of biofuels use.

Keywords: Biofuels, biodiesel, biomethanol, bioethanol, biogas.

1. Introduction

Fossil fuels (oil, natural gas and coal) contribute to most of the world energy supply. Regarding production and consumption rates, the presently known reserves of fossil fuels are estimated to last anywhere from 41 to \( \approx 700 \) years [1], [2]. The finitude of fossil fuels, concerns for energy security and the need to respond to climate change have led to growing worldwide interest in renewable energy sources such as biofuels.

Biofuels are alternative renewable fuels that have received considerable attention in the recent past, among the most popular being biomethanol and bioethanol, which are made from crop grains or sugarcane and biodiesel, which is made from vegetable oils and animal fats and both are used as sources of power for cars, trucks, trains and aircrafts. German engineer Rudolf Diesel’s prototype engine in 1897 was ran using peanut oil at a Paris exhibition. Henry Ford, one of the pioneers of automobile manufacture designed his equipment to run on ethanol. These visionary inventors expected that their new machines would run on fuels derived from plants, but cheap petroleum proved to be more popular at that time. The oil crises of the 1970’s sparked new interest in the use of renewable fuels and the following main factors sustained this interest to date:

- The rising prices of petroleum based products;
- Political instability and conflicts in some oil producing countries which leads to uncertainties in oil supplies;
- The limitation of petroleum supply stock.

An increasing number of developed (the United States) and rapidly developing nations (China) see biofuels as a key to reducing reliance on foreign oil, lowering emissions of greenhouse gases, mainly carbon dioxide and methane, and meeting rural development goals [3], [4].

Although worldwide production of biofuels increased dramatically, political and public support for biofuels has been undetermined due to environmental and food security concerns as well as the radical benefit that biofuels substantially reduce carbon emissions.

The diversion of food crops or croplands to produce biofuels has been blamed for global food shortages and associated increasing price of food crops [5], [10], [9]. Also recent research suggests that certain biofuel production pathways may lead to positive greenhouse gases emissions. Nevertheless, there are those that remain optimistic that with the development of next generation biofuels such as cellulosic ethanol, there are real opportunities for using biomass to meet some of our energy needs.

The overall objectives of this review are to highlight on-going developments in biofuel feed-
stock (raw material) selection and production technologies and critically evaluate the environmental and social costs of biofuel use.

2. Biofuels for transportation

Biofuel as fuel has several virtues, which include the following:
- Biofuels have calorific value of up to 90% that of petroleum diesel and offer comparable engine power;
- They have higher viscosity, and offer better lubricity than petroleum diesel, hence reduced wear of engine and injector pump;
- They have no aromatics and almost no sulphur;
- They are biodegradable and increase the degradability of biofuel when blended with it, thus any spillage of the fuel does not contaminate the environment;
- It reduces greenhouse emissions since the CO₂ emitted when it is combusted is equal to the amount consumed by the plant during its growth period;
- They dissipate engine heat better than problem fuel;
- Its feedstock is renewable.

Research work has generally shown that using biodiesel could dispense with the negative engine conditions encountered by the use of SVOs. Endurance tests performed by Kaufman and Ziejetauski (1984) using sunflower methyl ester (ME) in a diesel engine revealed that a 200-hour durability test was successfully completed. Kaufmann et al. (1986) [6] run four tractors on two blends of sunflower ME and petroleum diesel for a period of 7,616 hours (spanning more than three years) and found that bearing wear was normal and there were no power loses or injector and ring coking problems. In another work, two trucks fuelled with biodiesel and operated for a combined distance of 80,467 km showed normal rate of engine wear [7], [8], reported better results with peanut ME compared to the qualitative low-sulphur petroleum diesel.

While the suitability of biodiesel as a fuel is being researched, concurrent studies are also being conducted to determine the quality of the renewable fuel with respect to its emission products.

3. Types of biofuels

3.1 First generation biofuels

“First-generation biofuels” are biofuels made from sugar, starch, vegetable oil, or animal fats using conventional technology, Figure 1. The basic feedstocks for the production of first generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel. These feedstocks could instead enter the animal or human food chain, and as the global population has increased their use in the production of biofuels has been criticized for diverting food away from the human food chain, leading to food shortages and price rises. The most common first generation biofuels are described below.

3.1.1 Vegetable Oil

Edible vegetable oil is generally not used as fuel, but lower quality oil can be used for this purpose. Used vegetable oil is increasingly being processed into biodiesel, or (more rarely) cleaned of water and particulates and used as a fuel. To ensure that the fuel injectors atomize the fuel in the correct pattern for efficient combustion, vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers. This is easier in warm or temperate climates.

3.1.2 Biodiesel

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by Transesterification of vegetable oil or animal fat (tallow), which can be used alone, or blended with conventional petro diesel in unmodified diesel-engine vehicles.

Feedstocks for biodiesel include animal fats, vegetable oils, soy, rapeseed, jatropha, mahua, mustard, flax, sunflower, palm oil, hemp, field pennycress, and algae. Pure biodiesel (B100) is by far the lowest emission diesel fuel. Although liquefied petroleum gas and hydrogen have cleaner combustion, they are used to fuel much less efficient petrol engines and are not as widely available.
3.1.3. Bioalcohols

Biologically produced alcohols, most commonly ethanol, and less commonly methanol, propanol and butanol, are by microorganisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (which is more difficult). Biobutanol (also called biogasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engine (in a similar way to biodiesel in diesel engines).

Alcohol fuels are produced by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane, molasses and any sugar or starch that alcoholic beverages can be made from (like potato and fruit waste, etc.). The ethanol production methods used are enzyme digestion to release sugars from stored starches, fermentation of the sugars, distillation and drying. The distillation process requires significant energy input for heat, often unsustainable natural gas fossil fuel, but cellulosic biomass such as bagasse, the waste left after sugar cane is pressed to extract its juice, can also be used.

3.1.4. Bioethers

Bioethers (also referred to as fuel ethers or fuel oxygenates) are cost-effective compounds that act as octane enhancers. They also enhance engine performance, whilst significantly reducing engine wear and toxic exhaust emissions. Greatly reducing the amount of ground-level ozone, they contribute to the quality of the air we breathe.

3.1.5. Biogas

Biogas is produced by the process of anaerobic digestion of organic material by anaerobes. It can be produced either from biodegradable waste materials or by the use of energy crops fed into anaerobic digesters to supplement gas yields. The solid byproduct, digestate, can be used as a biofuel or a fertilizer. In the UK, the National Coal Board experimented with microorganisms that digested coal in situ converting it directly to gases such as methane.

Biogas contains methane and can be recovered from industrial anaerobic digesters and mechanical biological treatment systems. Landfill gas is a less clean form of biogas, which is produced in landfills through naturally occurring anaerobic digestion. If it escapes into the atmosphere it is a potent greenhouse gas.

3.1.6. Syngas

Syngas is produced by the combined processes of pyrolysis, combustion, and gasification. Biofuel is converted into carbon monoxide and energy by pyrolysis. A limited supply of oxygen is introduced to support combustion. Gasification converts further organic material to hydrogen and additional carbon monoxide.

The resulting gas mixture, syngas, is itself a fuel. Using the syngas is more efficient than direct combustion of the original biofuel because more of the energy contained in the fuel is extracted.

Syngas may be burned directly in internal combustion engines. The wood gas generator is a wood-fueled gasification reactor mounted on an internal combustion engine. Syngas can be used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process to produce a synthetic petroleum substitute. Gasification normally relies on temperatures >700°C. Lower temperature gasification is desirable when co-producing biochar.

3.1.7. Solid biofuels

Examples include wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops (see picture), and dried manure.

When raw biomass is already in a suitable form (such as firewood), it can burn directly in a stove or furnace to provide heat or raise steam. When raw
biomass is in an inconvenient form (such as sawdust, wood chips, grass, agricultural wastes), another option is to pelletize the biomass with a pellet mill. The resulting fuel pellets are easier to burn in a pellet stove.

A problem with the combustion of raw biomass is that it emits considerable amounts of pollutants such as particulates and polycyclic aromatic hydrocarbons. Even modern pellet boilers produce much more pollutant agents than oil or natural gas boilers. Pellets made from agricultural residues are usually worse than wood pellets, producing much larger emissions of dioxins and chlorophenols.

Another solid biofuel is biochar, which is produced by biomass pyrolysis. Biochar pellets made from agricultural waste can substitute for wood charcoal. In countries where charcoal stoves are popular, this can reduce deforestation.

### 3.2. Second generation biofuels

Supporters of biofuels claim that a more viable solution is to increase political and industrial support for, and rapidity of, second-generation biofuel implementation from non food crops, including cellulosic biofuels.

Second-generation biofuel production processes can use a variety of non food crops. These include waste biomass, the stalks of wheat, corn, wood, and special-energy-or-biomass crops (e.g. Miscanthus). Second generation (2G) biofuels use biomass to liquid technology, including cellulosic biofuels from non food crops. Many second generation biofuels are under development such as biohydrogen, biomethanol, Fischer-Tropsch diesel, biohydrogen diesel, mixed alcohols and wood diesel.

Cellulosic ethanol production uses non food crops or inedible waste products and does not divert food away from the animal or human food chain. Lignocellulose is the "woody" structural material of plants. This feedstock is abundant and diverse, and in some cases (like citrus peels or sawdust) it is a significant disposal problem.

Producing ethanol from cellulose is a difficult technical problem to solve. In nature, ruminant livestock (like cattle) eats grass and then use slow enzymatic digestive processes to break it into glucose (sugar). In cellulosic ethanol laboratories, various experimental processes are being developed to do the same thing, and then the sugars released can be fermented to make ethanol fuel.

The recent discovery of the fungus Gloiocladium roseum points toward the production of so-called myco-diesel from cellulose. This organism was recently discovered in the rainforests of northern Patagonia and has the unique capability of converting cellulose into medium length hydrocarbons typically found in diesel fuel.

Scientists also work on experimental recombinant DNA genetic engineering organisms that could increase biofuel potential.

### 3.3. Third generation biofuels

Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. Algae are low-input, high-yield feedstocks to produce biofuels. It produces 30 times more energy per acre than land crops such as soybeans. With the higher prices of fossil fuels (petroleum), there is much interest in algalculture (farming algae). One advantage of many biofuels over most other fuel types is that they are biodegradable, and so relatively harmless to the environment if spilled.

The United States Department of Energy estimates that if algae fuel replaced all the petroleum fuel in the United States, it would require 15,000 square miles (38,849 square kilometers), which is roughly the size of Maryland.

Second and third generation biofuels are also called advanced biofuels.

Algae, such as *Botryococcus braunii* and *Chlorella vulgaris*, are relatively easy to grow, but the algal oil is hard to extract. There are several approaches, some of which work better than others.

### 3.4. Fourth generation biofuels

An appealing fourth generation biofuel is based on the conversion of vegetable oil and biodiesel into gasoline.

Craig Venter's company "Synthetic Genomics" is genetically engineering microorganisms to produce fuel directly from carbon dioxide on an industrial scale.

Another fourth generation biofuel involves genetically engineering crops to consume more carbon from the atmosphere than they release during combustion resulting in a carbon negative fuel.

### 4. Impacts on food prices and the poor

For decades before 2000, declining food prices have allowed millions of people worldwide to escape from poverty [5], [9]. However, since the turn of this millennium, prices of basic food commodities, such as wheat and rice, have
climbed steadily [10]. In 2007 and 2008, price increases of food products reached alarming proportions triggering concerns of a global food crisis that has been widely reported in the media [11]. During this period, export prices of wheat, rice, and corn increased [9].

Among the most gravely affected are the poor who spend 50–60% of their income on food [12]. As many as 1.2 million Asians are at greater risks of malnutrition and food deprivation because of the inflation in food prices [9]. The underlying causes of rising food prices are many and complex. They include factors such as adverse weather conditions that affect crop productivity, speculative or precautionary demand for food commodities, and inappropriate policy responses such as export bans of foods [5], [10], [9]. More important are structural factors that include rising energy costs, stagnation in crop productivity, policy inadequacies or failures that constrain agricultural development, climate change, and diversion of crops or croplands to biofuel production. Among these factors, biofuels have borne most of the blame due largely to the media’s presentation of the ‘food vs. fuel’ debate. A popular allegory to illustrate the impacts of biofuels on food equates the grain required to fill the tank of a sports utility vehicle to grain that could otherwise feed a person for an entire year [13].

Although biofuels may have received a disproportionate amount of the blame for increased food prices, it clearly does deserve some of the blame: the use of corn to produce bioethanol in the US has increased from 6% of total corn production to 23% over the last three years [9] and this has undoubtedly contributed to tightening food supplies and rising food prices.

5. Competition for water resources

Set against the backdrop of the energy and food crises is yet another unfolding and arguably more important threat to human survival and well-being – that of a water crisis. Pressures on water supply are increasing worldwide due to population growth, rural-to-urban and trans-boundary migrations, global climate change, natural disasters, poverty, and warfare [14]. Additionally, agricultural expansion in response to higher prices for food commodities will likely further add to the demand for irrigation. In many developing countries, the lack of clean water and sanitation often results in malnutrition, diseases, and deaths. Agricultural expansion for biofuels may compete with other uses for water and thus contribute to rising water demands [15]. The extent to which biofuel use will enhance the water crisis depends on how much irrigation is required to grow biofuel crops, which will vary with the type and location of the crop being cultivated. In other regions of the world, such as Malaysia or Indonesia, abundant rainfall supplies much of the water needed for agriculture. In these regions, drainage is a greater concern for farmers than irrigation, and the production of biofuel crops (e.g., oil palms for Biodiesel) is not expected to have a dramatic impact on water availability [16].

5.1. The future of biofuels

Over the last few years, biofuels have garnered worldwide interests for their potential to reduce GHG emissions, improve energy security, and enhance rural development. At the same time, reports on the environmental and societal costs associated with biofuel production have generated controversy. Nevertheless, there remain several advantages in terms of developments in feedstock selection and production technologies that may yet allow biofuels to fulfill their promise as a viable source of renewable energy.

6. Next generation biofuel feedstocks

Almost all of the commercially available biofuels today are produced from crops that have considerable starch or sugar content (for bioethanol), or oilseeds (for biodiesel). Producing biofuels from these sources is less than ideal because they compete with food or feed production. Recent research attention has turned to the use of dedicated feedstocks for biofuel production, including perennial grasses, wood, algae, and agricultural, forestry, or municipal wastes. The candidate grass species for cellulosic ethanol production include switchgrass, miscanthus (Miscanthus spp.), reed canary (Phalaris arundinacea), and giant reed (Arundo donax) [17]. Most of these crops can be cultivated on marginal or agriculturally degraded lands, and thus may not compete with food production.

Forest plantations can also serve as potential sources of cellulosic feedstocks for bioethanol production.

Macroalgae is another potential source of biofuel feedstock. Aquatic unicellular green algae, such as Chlorella spp., are typically
considered for biodiesel production owing to their high growth rate, population density, and oil content. In addition to their high yields, macroalgae cultures are not land-intensive and may provide further benefits of wastewater remediation or nutrient reduction [18].

Waste biomass forms a diverse group of potential feedstocks that include agricultural (e.g., wheat straw), forestry (e.g., wood pieces leftover after timber extraction), and municipal wastes (e.g., waste paper, waste food scraps, used cooking oils). A recent study estimated that a city of one million people could provide enough organic waste (1300 tons per day) to produce 430,000 l of bioethanol a day, which could meet the needs of about 58,000 Americans, 360,000 French, or 2.6 million Chinese at current rates of per capita fuel use [19]. Horticultural waste biomass (e.g., tree trunks, twigs, and leaves) could also be a potential source of cellulosic feedstock [20].

7. Next generation technologies

In addition to diversifying the biofuel feedstock resource base, there is also a need to develop process technologies that convert these next generation feedstocks to liquid fuels.

The two primary pathways for converting biomass to biofuel are biochemical and thermochemical conversion.

Biochemical conversion pathways are used to convert cellulosic biomass to biofuel by breaking down the recalcitrant components of plant material (cellulose 40–60% and hemicellulose 20–40%) into sugars, which are then fermented to produce ethanol [3], [21], [19]. The limiting factor in terms of yield is the rate of cellulose breakdown, which can be accomplished by either acid or enzymatic hydrolysis. Acid hydrolysis involves the use of either dilute acid at high temperatures, which is cheap but low yielding, or concentrated acid at low temperatures, which is high yielding but expensive.

Biochemical research has also focused on the use of enzymes (cellulases) produced by bacteria or fungi (e.g., Trichoderma reesei) to hydrolyze cellulose [21]. Many experts believe that enzymatic hydrolysis is the key to cost-effective bioethanol production in the long term. A second limiting factor in biochemical conversion pathways is the inability of yeasts used in conventional industrial applications (e.g., beer fermentation) to digest five-carbon sugars (e.g., xylose) produced from the breakdown of hemicellulose. Xylose-digesting yeasts are a major focus of current research is to search for new strains of microorganisms, including bacteria, yeasts, and fungi that can perform this function efficiently.

 thermo-chemical pathways for converting biomass to biofuel include gasification and pyrolysis [22], [3], [19]. Cellulosic biomass can be gasified in a high-temperature (600 – 1100°C) vessel at low oxygen levels to produce “syngas.” Syngas can then be converted to a variety of fuels, including hydrogen, methanol, or dimethyl ether. Synthetic diesel and gasoline can also be produced from syngas by Fischer–Tropsch (FT) synthesis. A major advantage of the gasification/FT pathway is that all organic matter in biomass (including lignin) can be converted to liquid fuel, which makes it a more efficient conversion process than biochemical methods. Because the gasification of fossil fuel feedstocks (e.g., coal) is a well established technology, there is potential for adapting existing infrastructure for gasification (i.e., 117 plants worldwide) to produce bioethanol from biomass feedstocks [19]. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen to produce liquid “bio-oil”, solid “biochar” (charcoal), and light gases [22], [19]. Fast-flash pyrolysis, in which biomass is heated to 500 °C for less than ten seconds, is used to maximize bio-oil production.

Biototechnology may also determine the future role of biofuels [3], [23]. Advances in plant genomics could lead to the production of higher yielding biofuel crops, reducing both land requirement and energy input, which may reduce land-use conflicts and GHG emissions [3], although lower production costs may also enable greater penetration of the transportation fuel market, which may in turn increase biofuel demand and the amount of agricultural land required to grow biofuel crops [24]. Biofuel crops may also be genetically engineered to be more resistant to pests, diseases, or abiotic stresses (e.g., drought), which would ensure a stable supply of feedstock [25]. Furthermore, dedicated biofuel crops may be genetically modified to grow faster, have lower lignin content, or even contain cellulates within the crop biomass itself in order to enhance the efficiency of cellulosic ethanol production.

8. Conclusions

Rising fuel prices coupled with concerns about carbon emissions are making biofuel production more cost competitive and attractive. There are
global implications for the shift towards biofuels, and this review paper highlights food price increases, and competition for water resources as the key negative impacts of biofuel use. On the other hand, it is just to conclude that the development and use of next generation biofuel feedstocks and production technologies may reduce some of the environmental and societal costs associated with biofuels.

In conclusion, certain types of biofuels do represent potential sources of alternative energy, but their use needs to be tempered with a comprehensive assessment of their environmental impacts. Together with increased energy conservation, efficiencies and technologies such as solar, wind, geothermal, and hydroelectric power, biofuels should be included in a diverse portfolio of renewable energy sources in order to reduce our dependence on the planet’s finite supply of fossil fuels.

References

[27] Lian Pin Koh, J. Ghazoul, Biofuels, biodiversity, and people: Understanding the conflicts and finding opportunities, Biological Conservation 141, 2450-2460.