Comparing the Efficacy of First and Second Generation Biofuels and Analyzing Future Trends in the Field

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Abstract

Biofuels are widely touted as a strong alternative for alleviating the harmful effects of conventional fossil fuels. Existing data on biofuel CO₂ emissions, net emissions, land area and land type required, fuel yield, and energy efficiency metrics for both existing biofuels and biofuels in the research phase is compiled and a critical analytical review is conducted. Our analysis clearly shows the need to prioritize second generation biofuels and conduct further research into third generation biofuels to maximize the efficacy of this fuel source. Solutions to increase the sustainability and efficiency of biofuels are also proposed in our analysis of the literature explaining applications of biomass residues and emerging biofuel sources such as algae. Residues and algae have significant potential to produce biofuel energy in a more sustainable and flexible way by decreasing the amount of land needed to produce energy. However, significant consideration must be given to the impacts of residue use in the combustion processes and soil, and further research needs to be done with algae to make the harvesting process more cost-effective.

Keywords: First Generation Biofuels; Second Generation Biofuels; Agricultural Residues; Algal Biofuels; Renewable Energy
1. Introduction

A widely known contributor to global climate change is the continued use of fossil fuels and their release of carbon dioxide (CO₂), a prominent greenhouse gas (GHG), into the air. Fossil fuels are a finite fuel resource and stocks are quickly running out. Therefore, it is increasingly vital to develop renewable energy technologies to sustain human energy consumption and alleviate the harmful impacts that fossil fuels have on the environment. Biofuels are a widely applicable technology and their ability to be produced from renewable resources and industry waste make them a waste funnel from which sustainable energy can be obtained. This paper explores the effectiveness, impact, and feasibility of first and second generation biofuels as primary sources of energy from various environmental standpoints. Solutions that increase the sustainability of biofuels have been proposed through literature of studies explaining the applications of biomass residues and emerging biofuel sources. Our research aims to convey a thorough understanding of the benefits and drawbacks to multiple forms of biofuels in addition to analyzing several techniques that increase the flexibility and efficacy of biofuel use.

2. Methodology

Corn and sugarcane, as first generation biofuels, are the most commercially used sources of biofuels in the world (McConnell, 2021). They are not without their drawbacks, however. Our research was designed in order to acknowledge that alternative sources of biofuels, although lesser known, may provide further advances in clean energy compared to first generation biofuels. Review of research from several eminent sources, including Harvard Kennedy School’s Think Tank, the journal database of ScienceDirect, the North Carolina School of Science and
Mathematics Academics Library database, Wiley Online Library, ResearchGate, and JSTOR, was done to find comparable alternatives to fossil fuels that would be feasible to replace 20% of the U.S. petroleum energy usage by 2022 - a goal outlined by the Energy Independence and Security Act of 2007 (U.S. Department of Energy, 2007). We determined that comparison using a single metric would not provide the multifaceted understanding we wished to convey on the benefits and drawbacks of the biofuels compared; therefore, we decided to compare several biofuels to each other, to petroleum, and to other renewable energy sources using multiple metrics.

For the literature review portion of the paper, research published in peer-reviewed scientific journal publications and in government papers were considered. Journals articles were used to find experimental results for metrics regarding the efficacy and impacts of the chosen energy sources. Government publications and international conference proceedings were used to find data and environmental arguments on a larger scale than individual experiments, and to understand the impacts of the real world applications of these energy sources.

3. Examining the Efficacy of Biofuels

Burning of fossil fuels is the primary source of energy production in the United States (U.S. Energy Information Administration, 2021). However, the GHGs that are released as a result of this process contribute heavily to global warming (Shaffer, 2009). Biofuels are defined as any fuel derived from organic matter (Britannica, 2020). In contrast to fossil fuels, the raw materials required for biofuel energy production are renewable. There are two generations of biofuel that can be used to produce large scale energy. First generation biofuels refer to ethanol derived from plant saccharides and biodiesel created from fatty lipids from plants used as food crops. Second generation biofuels are produced from lignocellulosic materials not used as food crops or from
waste materials of food crops. Third generation biofuels, which are not yet economically viable, refer to energy sourced from aquatic microorganisms such as algae (Naik et. al., 2009).

Corn ethanol, a first generation biofuel, is the most commercially available form of biofuel today, with over 50 billion liters produced annually in the U.S. (Biello, 2013). Despite this, ethanol produced from corn may have drawbacks that constitute the study of other crops as potential alternatives. Although growing crops for energy can prove beneficial for carbon sequestration, it can also create new problems such as loss of biodiversity (Elshout et al., 2018), and loss of land used for agricultural production, known as the “food vs. fuel” debate (Mohr & Raman, 2013). It is also pertinent to consider the efficiency of using biomass to generate energy compared to other renewable energies to gain a multifaceted understanding of biomass potential as a prominent fuel source. Multiple scales of measurement will be used to measure the possibility of using first generation and second generation biofuels to replace 20% of the U.S. petroleum energy usage by 2022, which is a goal outlined by the Energy Independence and Security Act of 2007 (U.S. Department of Energy, 2007).

3.1. CO₂ Emissions Comparison

Table 1 compares CO₂ emissions for first generation and second generation biofuel crops to each other and to gasoline.
The total above-ground CO\textsubscript{2} emissions were calculated by compiling emissions produced as a result of feedstock production, the biorefinery process, coproduct credits, and the displacement due to change in land use, assuming non-carbon neutral energy production (Khanna, 2008). Emissions from feedstock production comprise emissions accrued as a result of practices necessary to grow and maintain the raw material that will later be used in manufacturing, including the emissions needed to transport water, fertilize the soil, and harvest the produce. The biorefinery phase includes CO\textsubscript{2} emissions that result from biomass being extracted from the raw material and that biomass being converted into biofuel. Coproduct credits are the emissions reduction potential of any future uses of the material that remains after the raw process.
material initially goes through the biorefinery phase. The displacement due to change in land use includes emissions that occur as a result of direct land use changes from the conversion of cropland to energy crops. The total CO\textsubscript{2} emissions as a net of carbon sequestration were then calculated by factoring in soil carbon sequestration, which is the CO\textsubscript{2} mitigation potential of the crops in question.

Even though biofuels still produce less CO\textsubscript{2} emissions than gasoline, the process of biofuel production is still energy-intensive and is not without GHG emissions. Although first generation biofuel crops offer emissions reductions compared to gasoline, there is still net CO\textsubscript{2} emissions. Corn ethanol, in particular, has fairly high CO\textsubscript{2} emissions (4.75 kg CO\textsubscript{2}/gallon). Corn ethanol production causes more than two times as many CO\textsubscript{2} emissions when compared to the other first generation biofuel - sugarcane ethanol (1.66 kg CO\textsubscript{2}/gallon). As corn ethanol is the most widely used biofuel today, we see that there is significant emissions reduction potential if other crops replace corn ethanol as alternative sources of biofuels. Second generation biofuels have very low total above ground carbon emissions, meaning they are very efficient when it comes to growing, harvesting and converting these crops into bioethanol. The true power of switchgrass and miscanthus (the two second generation biofuel crops), however, is that they are carbon sinks, meaning that they store and accumulate carbon dioxide for long periods of time. This carbon sequestration continues for 100 years in switchgrass (Andress, 2002) and 50 years in miscanthus (Scown et al., 2012).

Switchgrass and miscanthus have net emissions reductions of -5.63 kg CO\textsubscript{2}/gallon and -2.29 kg CO\textsubscript{2}/gallon respectively, which means that more CO\textsubscript{2} is being removed from the environment than is being emitted during the entire production process of these bioethanols. There is currently not adequate infrastructure to grow and refine second generation biofuels, which is one of the main reasons second generation biofuels have not yet been widely adopted. However, if such a framework was put in place, there is tremendous potential for efficient energy production and large-scale CO\textsubscript{2} sequestration. In conclusion, energy derived from both first and
second generation biofuels produces less emissions than gasoline, but it is also clear that second generation biofuels produce considerably less CO$_2$ emissions than first generation biofuels.

### 3.2. Land Area and Yield Comparison

The metrics provided in Table 2 have been used to analyze different first and second generation biofuel crops to see which offers the most biomass and ethanol yield in the least land area.

**Table 2**

*Land Area, Biomass Yield, and Ethanol Yield for First and Second Generation Biofuels*

<table>
<thead>
<tr>
<th>Crop</th>
<th>Generation</th>
<th>Biomass Yield (kg/acre)</th>
<th>Ethanol Yield (gal/acre)</th>
<th>Total Land Area Needed To Produce 36 Billion Gallons of Ethanol (Million Acres)</th>
<th>Percentage of Total Harvested U.S. Cropland (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn ethanol</td>
<td>1st</td>
<td>4,128</td>
<td>456</td>
<td>78.8</td>
<td>25.1</td>
</tr>
<tr>
<td>Sugarcane ethanol</td>
<td>1st</td>
<td>15,783</td>
<td>486</td>
<td>74.1</td>
<td>23.6</td>
</tr>
<tr>
<td>Switchgrass bioethanol</td>
<td>2nd</td>
<td>4,209</td>
<td>421</td>
<td>85.7</td>
<td>27.3</td>
</tr>
<tr>
<td>Giant Miscanthus Biofuel</td>
<td>2nd</td>
<td>11,979</td>
<td>1,198</td>
<td>30.0</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*With the goal of producing 36 billion gallons of biofuels as given by the Energy Independence and Security Act


and


Interestingly, sugarcane has the highest biomass yield, but not the highest ethanol yield.

This shows how the amount of biomass extracted from a crop does not directly translate to a
certain yield of biofuel. Although its yield per acre is the lowest compared to the other biofuel sources, corn ethanol is by far the most widespread biofuel in the US. The primary reason for this is that corn was one of the first crops grown in the US and continues to be farmed extensively. However, it would take an additional 4.7 million acres to produce 36 billion gallons of biofuel with corn than with sugarcane. The land that is saved could then be used for agricultural or commercial purposes. Switching from corn to sugarcane offers just one example of how much space could be saved if the switch from corn to other biofuel crops was made.

The main drawback of using sugarcane bioethanol in the US is that sugarcane does not grow throughout the country. Sugarcane can only be grown in the warmer parts of the US, and today it’s only cultivated commercially in Texas, Florida, Hawaii, and Louisiana (Shahbandeh, 2021). This makes it challenging for the US to rely on sugarcane bioethanol, as there would be extra emissions and costs needed to transport the fuel to the US. In addition, importing sugarcane bioethanol would oppose America’s goal of becoming energy independent. So even though sugarcane has a higher ethanol yield, sugarcane ethanol will likely not address America’s energy needs alone.

Within second generation crops, there is a large variance between the efficacy of the two crops. Miscanthus is by far the most efficient crop, with almost three times the ethanol yield of any of the other crops (1,198 gal/acre) (Table 2) and the lowest land use requirements by far as well (30.0 million acres to produce 36 billion gallons of biofuel) (Table 2).

Alternatively, the other second generation biofuel crop, switchgrass, has the lowest ethanol yield (421 gal/acre) (Table 2) of any of the crops analyzed. Therefore, switchgrass also takes the largest amount of land to produce 36 billion gallons of biofuel (85.7 million acres) (Table 2). Despite this, there are still benefits to using switchgrass. One of the benefits to both miscanthus and switchgrass is that they can be grown in a large portion of the US, as seen below in Figure 1.
As seen in Figure 1, almost half of the mainland United States is suitable for growing miscanthus. The high ethanol yield and the substantial possible growing area makes miscanthus one of the best biofuel crops for the US to grow to achieve the goal given by the Energy Independence and Security Act. Since miscanthus spreads aggressively, growing miscanthus is often seen as a risky proposition. However, miscanthus biofuel is used across mainland Europe, and is starting to gain traction in the US, which shows just how much untapped potential there remains for the biofuels market. According to Figure 1, switchgrass can grow in an even greater area within the US than miscanthus. All but three states in the mainland U.S. have the potential for growing switchgrass. This large expanse of land on which switchgrass can be grown means that switchgrass can be cultivated in areas where other plants cannot be grown. This allows for greater yields of switchgrass than would be possible with other crops. Another benefit to using
switchgrass as biofuel is that there is currently research that is looking into genetically modified switchgrass crops (Zhao et al., 2016). If successful, this would increase the yield for switchgrass substantially, which would make the crop a commercially viable source of biofuel. However, there are concerns that if the genetically modified switchgrass were to crossbreed with other grasses, there could be unintended consequences that could seriously damage the ecosystem (UW-Milwaukee, 2017). Scientists are currently addressing the issue, so there is a lot of potential for switchgrass to one day be an efficient alternative to today’s fuel sources.

One of the main advantages of both of the second generation biofuel crops, however, is that they can be grown on degraded land. Degraded land consists of areas that have low quality soil and are unsuitable for food production, usually as a result of climatic conditions and soil degradation. Since both these crops are very hardy, they are capable of growing in places where almost no other crops would survive. This means that even though switchgrass takes up the most space, it could still be beneficial to make use of land that would otherwise be unusable. Furthermore, planting on degraded lands means that land would not have to be diverted from food crops, which would further ensure the ability to produce the most food possible and not lead to rising food prices. Planting crops on degraded lands also has an added advantage of mitigating any future soil erosion and increasing the fertility of poor soil (Eisentraut, 2010). In conclusion, second generation biofuels, particularly miscanthus, are more efficient than first generation crops at supplying the biomass and ethanol yield needed to produce the 36 billion gallons of biofuel stipulated in the Energy Independence and Security Act.

3.3. Comparing Energy Efficiency

Table 3 compares the energy efficiency of various renewable and non-renewable energy sources to see which one produces the largest energy output to energy input.
According to Table 3, the non-renewable sources of energy have relatively high energy return on investment (EROI) values compared to the renewable sources of energy. Coal has an EROI value of 29, which is greater than EROI for three of the four renewable energy sources. However, many nonrenewable sources of energy like coal and oil have a large drawback: they become less efficient as they become scarcer in nature (Solé et al., 2018). This trend is shown in Figure 2.

**Table 3**

*Energy Efficiency Metrics*

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Energy Type</th>
<th>Energy Invested (MWh)</th>
<th>Energy Gathered (MWh)</th>
<th>EROI $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas $^b$</td>
<td>Renewable</td>
<td>$1.75 \times 10^6$</td>
<td>$6.15 \times 10^6$</td>
<td>4</td>
</tr>
<tr>
<td>Hydroelectric</td>
<td>Renewable</td>
<td>$1.37 \times 10^6$</td>
<td>$6.85 \times 10^7$</td>
<td>50</td>
</tr>
<tr>
<td>Wind</td>
<td>Renewable</td>
<td>$3.75 \times 10^3$</td>
<td>$6.00 \times 10^4$</td>
<td>16</td>
</tr>
<tr>
<td>Solar Thermal</td>
<td>Renewable</td>
<td>$2.08 \times 10^5$</td>
<td>$4.35 \times 10^6$</td>
<td>21</td>
</tr>
<tr>
<td>Nuclear</td>
<td>Non-Renewable</td>
<td>$8.58 \times 10^6$</td>
<td>$6.43 \times 10^8$</td>
<td>75</td>
</tr>
<tr>
<td>Coal $^c$</td>
<td>Non-Renewable</td>
<td>$6.66 \times 10^6$</td>
<td>$1.93 \times 10^8$</td>
<td>29</td>
</tr>
</tbody>
</table>


$b$. Biogas derived from corn

c. Hard Coal (Underground Mining)


Figure 2

Global primary-stage fossil fuel EROI ratios from 1995–2011

*EROIPRIM represents the aggregate fossil fuel primary-stage EROI, with associated primary-stage EROI ratios for coal, oil and gas denoted by EROIPRIM_COAL, EROIPRIM_OIL and EROIPRIM_GAS, respectively.

EROSFIN denotes aggregate final-stage fossil fuel EROI.

As shown in Fig. 2, the EROI for coal, oil, and gas have gone down over time. Fig. 2 also shows how aggregate final-stage fossil fuel EROI has decreased over the period shown. Since nonrenewable sources of energy are limited, they are becoming more and more sparse from perpetual consumption. As nonrenewable fuels become harder to locate and extract, there is a greater energy input needed to produce the same amount of energy. As the energy output-input ratio decreases, these sources of energy will become less efficient over time. As these irreplaceable resources are continuously utilized, it follows that the trends shown in Fig. 3 will continue and the EROI for nonrenewable sources of energy will continue to decrease in the future. The exception to this trend is nuclear energy. Even though nuclear power is a non-renewable source of energy, the energy used to extract and enrich uranium is dwarfed by the energy outputs of the uranium because the fuel used to produce nuclear power is so energy dense (Hanania et al., 2018). This will cause the decrease in EROI for nuclear energy to be almost negligible over time.

For the renewable sources of energy, hydroelectric power has the highest EROI value, followed by solar thermal power and then wind energy. Even though biogas has the lowest EROI of any of the energy sources shown in Table 3, it is important to note that the biogas is derived from corn - a first generation biofuel. Second generation biofuels, on average, have higher EROI values than first generation biofuels (Wang et al., 2021). For instance, two second generation biofuels, switchgrass and miscanthus, have EROI values of 18 (Hall et al., 2011) and 39 (Morandi et al., 2016), respectively. These EROI values parallel almost all other sources of energy, renewable and non-renewable. In addition, algae-based biofuels, a third generation biofuel source, is approaching an EROI similar to conventional petroleum (Liu et al., 2013). Second and third generation biofuels have not been used extensively to date, as people have opted for first generation biofuels because raw materials and infrastructure were readily available and because further research is needed in advanced biofuels. However, if second or third generation biofuels were adopted, there is potential for the EROI values for biofuels and biogas
to increase tremendously. Therefore, the future of biofuels and the key to making them more energy efficient is transitioning to second and third generation biofuel sources.

4. A Literature Review on Alternative Biofuel Sources and Applications

Although the biofuel sources illustrated by the data in Table 2 are quite prevalent in global production, they do not fully address the most prevalent issue pertaining to biofuels: how to get enough land to grow biofuel crops. As a result of increasing rates of urbanization, unused land is quickly running out. When considering implementing more land for biofuel growth, complications often arise in determining whether to displace native ecosystems or agricultural land for food crops (Eisentraut, 2010). In this section of the paper, two alternative biofuel sources that have potential to alleviate the impacts of biofuels on land usage are introduced, and their impacts on land use and other aspects of fuel production are discussed.

4.1. Agricultural Residues: An Overview of Usage and Usage Effects

In harvesting crops for biofuels, the use of crop residues provides a way to extract more fuel from the same tract of land. After the main crop is harvested there are still a variety of plant materials left on the field. These make up residues and are classified as a second-generation biofuel (Dahman et al., 2019) that encompasses different subcategories. Primary residues are produced during the harvesting process, and include materials such as stover and branches. Secondary residues are left from the processing of crops into new products, including various shells, husks, and pulps (Eisentraut, 2010). There are many advantages in utilizing both of these residue categories in biofuel production. Residues can increase the economic value and fuel production of farmland without requiring increases in land productivity, area, or growth resources (Eisentraut, 2010; Dahman et al., 2019). The utilization of residues also contributes to
a lesser effect from land use change. Negative environmental effects from land use change are often created when forest or grassland is replaced with agricultural crops. This typically results in a loss of carbon sequestration ability for that area (Eisentraut, 2010).

However, primary residues have the disadvantage in their low GHG emissions avoidance, (Sims et al., 2010). Primary residue collection processes also pose disadvantages as the residues are typically distributed across a wide expanse of agricultural fields, complicating collection efforts. In comparison, secondary residues are collected primarily at crop processing sites. Reduced transportation needed to collect the secondary residues translates into increased economic efficiency towards the utilization of these materials. This also alleviates the need for farms to invest in additional labor or technological resources to harvest secondary residues (Eisentraut, 2010).

The traditional use of residues must be taken into account when considering allocating residues for energy. Some forms of agriculture often see residue as waste and burn it, releasing the stored carbon directly into the atmosphere. In this case, using the residues as a source of energy is a much more productive use. However, it is also quite common for residues to be either removed and used as animal feed, or kept on the ground as a natural fertilizer and a carbon fixation mechanism (Eisentraut, 2010). Therefore, many see the removal of residues as harmful to the health of the soil and to soil carbon storage. There are several ways this problem can be mitigated. To address carbon storage concerns, much of the residue on the surface decays there and not deeper down in the soil. Therefore, the carbon in the residue doesn’t significantly enter the soil carbon storage (Cowie et al., 2006). In addition, a large amount of carbon is also kept in the soil by roots, which are not used as residues (Eisentraut, 2010; Cowie et al., 2006). Root carbon input as well as other biomass inputs like leaf litter are also continuously returned to the soil over the growing period of the plant, so the carbon content of the soil is not solely dependent on keeping residues on the soil (Cowie et al., 2006). Aside from the carbon storage science of the soil and plants, the entirety of residues do not have to be removed from a field in order to utilize
residues for energy. Increases in agricultural production have made it possible for more residues to be produced than are needed to maintain soil nutrition (Tanigawa, 2017). Careful measures are always taken by researchers to determine the safe amount of residue to take from the soil, considering factors such as crop rotations and harvesting/tilling technologies (Perlack & Stokes, 2011). To determine the energy generation impacts of partial removal of residues, the International Energy Agency (IEA) completed studies that showed vast potentials in residue energy yield from only utilizing 10% or 25% of global agriculture and forestry residues (Eisentraut, 2010). The IEA study predicted that in 2030, just 10% of global residues would fulfill 45%-63% of the total projected biofuel need of 349 billion l	extsubscript{ge} (liters per gasoline equivalent) for the WEO 2009 450 scenario (Eisentraut, 2010). This policy calls for strategies implemented that would lead to a 50% chance of keeping global temperature increases under 2°C in the long term and atmospheric concentrations of CO	extsubscript{2}-equivalent under 450 ppm (International Energy Agency, 2009, International Energy Agency 2020). The IEA study also found that 10% of 2030 projected residue use would lead to 155 billion l	extsubscript{ge} of biomass-to-liquid diesel (BTL-diesel) or 222 billion l	extsubscript{ge} of Bio-synthetic natural gas (Bio-SNG). This would equate to 4.1% and 5.8% of the projected transport fuel demand respectively (Eisentraut, 2010). Just 10% of agricultural residues alone is already a substantial portion of what is needed to meet the requirements of a prominent GHG mitigation plan (Figure 3)
The data in Figure 3 demonstrates that total removal of residues from field areas is not needed for agricultural residues to have a significant impact on the renewable fuel sector. The data also exhibits the potential for residues to make a substantial contribution to future energy needs when renewable energy sources will likely be needed the most.

**4.1.1. Use in Fluidized Bed Combustion Systems**

For the combustion of agricultural residues, a fluidized bed combustion system (FBC) is often preferred. FBC utilizes an area of solid particles that are fluidized with a high-velocity stream of gas (Nuamah et al., 2012; Hower et al., 2017). The fuel is added into the fluidized bed, mixing with the bed material as it is combusted to create heat for power generation. There are several advantages for the use of FBC for agricultural residue combustion. Primarily, the bed
mixture has a high heat capacity, allowing for combustion to take place at lower temperatures (800-900 °C). The fluidized bed also allows the temperatures to be uniform through the combustion area due to the constant mixing (Werther et al., 2000; Yin, 2013, Nuamah et al., 2012). The lower temperature flexibility, as well as compatibility with larger fuel particle sizes, allows more flexibility for fuel utilized in FBC systems. Since milling to reduce particle size of residues isn’t always utilized, this is ideal for residues. This also creates opportunities for co-combustion, the benefits of such with residues will be discussed later in this section. (Yin, 2013).

When agricultural residues are combusted alone in FBC systems, some problems are caused by the intrinsic nature of the biomass. One such problem is the moisture within the residues. Moist fuels can impede the quality and heat of the combustion process. However, many secondary residues such as husks and shells naturally dry out during the process of removal from the crop so this is not a problem for all residues (Werther et al., 2000). A more substantial problem is the low bulk densities of agricultural residues. Higher fuel bulk densities lead to easier transport, processing, and feeding into combustion systems, as well as greater concentrations of energy potential. The chemical composition of residue ashes also presents difficulties for the mechanics of FBC systems. Because of the prevalence of artificial fertilizers, high concentrations of potassium oxide (K₂O) are found in the ashes of combusted agricultural residues. Experiments on residues have found that higher weight percent (wt %) of K₂O in various residues’ ash led to lower melting points for the ash (Trebbi et al., 1995, Wilen et al., 1987). Table 4 also supports the link between higher K₂O wt% in ash with lower deformation temperatures in the ash of residues. Ash deformation is one of the first signs that the ash is beginning to melt and starting the agglomeration process (Celignis Analytical, 2021). Agglomeration poses severe problems for FBC systems, as it causes the particles of the bed in FBC to clump together instead of staying fluidized. This decreases the uniformity of the temperature and severely reduces the ability for combustion to happen properly. As temperatures
start to destabilize, areas of the bed heat up, increasing the rate of the ash melting and creating a positive feedback loop.

Table 4

<table>
<thead>
<tr>
<th>Material</th>
<th>Straws</th>
<th>Coals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wheat</td>
<td>Rye</td>
</tr>
<tr>
<td>K₂O (wt% in ash)</td>
<td>6.6</td>
<td>19.2</td>
</tr>
<tr>
<td>Initial deformation</td>
<td>900–</td>
<td>800–</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>1050</td>
<td>850</td>
</tr>
</tbody>
</table>


Table 4 also brings to light the lower K₂O wt% in ash of coals, leading to less agglomeration for those fuels at the typical temperatures at which FBC systems combust. In order for residues to be
competitive with coal in this form of combustion, solutions are needed to reduce the agglomeration caused by residues.

There is a diverse range of approaches to the agglomeration problem. One such solution is additives. Additives are not a new technology for FBC, as they are commonly used in FBC systems with the usage of limestone in the bed material to reduce SO\textsubscript{x} emissions (Nuamah et al., 2012). Additives can also be used to reduce agglomeration of residue ashes. One additive that has been proven quite effective is kaolin clay. In experiments, kaolin at amounts of 3 wt% was used in chopped oat straws. When combusted, the deformation temperature of the resulting ash rose from around 770 °C to a range of 1200–1280 °C (Wilen et al., 1987). Seeing as how most FBC systems are run at temperatures below 1000 °C, additives that are as effective as kaolin are very beneficial towards maintaining fluidization of the bed and increasing the ability for residues to be successfully used in FBC combustion. Kaolin is also readily available in parts of the southern US, increasing the validity of this solution in this country (Voiland, 2020).

Aside from the combustion of residues alone, they can also be combusted with other fuels such as coal. Co-combustion reduces the need for agricultural residues alone to fuel a power plant, alleviating the concern of fluctuating residue supplies due to changing seasons or other domestic demands (Eisentraut, 2010). From a technological standpoint, the combustion technology that is used to combust coal alone is also used with the co-combustion of coal and residues. Therefore, no additional time or money resources would have to be allotted towards new infrastructure (Werther et al., 2000). Many lab experiments of FBC with co-combustion of coal and residues have seen no negative effects on combustion from the addition of residues, although slight increases in corrosion were seen. Some experiments even saw an improvement in combustion under the right circumstances, namely increased milling of the residues and a staggered release of the combustion air (Kicherer et al., 1995; Gulyurtlu et al., 1995).
4.1.2. Use as Reburning Fuel

In addition to being used as a combustion fuel, residues can also be used to mitigate the nitrogen oxide (NO$_x$) emissions of combustion by serving as a reburning fuel. Combustion systems can emit various nitrogen oxides which contribute towards the atmospheric formation of harmful GHGs. Therefore, a mechanism to remove NO$_x$ will contribute a great deal toward mitigating the environmental impacts of combustion. In a reburning process, natural gas is traditionally used as the reburning fuel. Reburning ultimately triggers several chemical reactions in a fuel-rich zone to reduce nitrogen oxides from the first stage of combustion into molecular nitrogen. New techniques in reburning called Advanced Reburning (AR) have also been developed with even greater NO$_x$ reduction. It differs in the addition of a nitrogen agent such as urea or ammonia to the reburning zone, as well as completing reburning in more balanced conditions rather than fuel-rich conditions (Maly et al., 1999). They conducted extensive experiments to determine if alternative fuels could be included in reburning, including a finely-milled lumber biomass. In reburning at higher initial NO$_x$ concentrations and where the fuel was given more time in the reburn zone, the biomass out-performed all reburn fuels tested, including natural gas. Reburning fuels with high amounts of alkali compounds have been found to accelerate the reactions that reduce NO$_x$ concentrations (Maly et al., 1999). Werther et al. (1999) found that many residues had a large amount of these alkali compounds. Even though these compounds hindered the efficacy of residues combusted as the main fuel in FBC systems, they benefit the efficacy of residues as a reburning fuel, including in AR systems, as shown in Table 5.
Table 5

Summary of Fuel Performances in Reburning and AR

<table>
<thead>
<tr>
<th>Reburn fuel</th>
<th>NO&lt;sub&gt;x&lt;/sub&gt; Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reburning alone</td>
</tr>
<tr>
<td>Natural gas</td>
<td>47%</td>
</tr>
<tr>
<td>Biomass</td>
<td>50%</td>
</tr>
<tr>
<td>CRDF</td>
<td>50%</td>
</tr>
<tr>
<td>Coal fines</td>
<td>44%</td>
</tr>
</tbody>
</table>


4.2. Conclusion of Usages

There is great potential for the usage of residues to be a feasible solution for increasing the sustainability for biomass usage. Taken in quantities that avoid depleting residue nutrients returning to the soil, residues can be used in the combustion of energy alone or with other fuels. Residues even have the ability to make significant reductions in NO<sub>x</sub> emissions when used as a reburning fuel in combustion. The unique flexibility of residues provides a multitude of opportunities to supplement other sources of biofuels in the goal to reduce non-renewable fuel usage. With urbanization and land degradation greatly reducing available land for farming, using residues that increase the energy output in the land remaining will be of great importance in the future of biofuels.
5. Third Generation Algae-Based Biodiesel

Algae is an experimental but promising source of biofuel. It does not require a specific soil type or location; indeed, all that is required for algae to grow is water and sunlight. This implies that many different climates and areas in the US, such as abandoned land, degraded land, or land not suitable for agriculture or development can be used to cultivate and harvest algae on an industrial level (McDonald, 2009). The ecological diversity of algae allows selection of species with advantageous characteristics; output can be easily observed and controlled through biochemical and nutrient deprivation and manipulation (Xu et al., 2019; Hu et al., 2008; Dismukes et al., 2008); and it can supply various forms of energy, including (but not limited to) ethanol, diesel, and hydrogen (Figure 4).

The majority of microalgae produce a class of lipid known as tricylglycerols which are easily converted into biodiesel (Wen, 2009). Therefore, several strains of microalgae have been studied to catalogue their lipid, protein, and carbohydrate compositions (Shuba & Kifle, 2017). The two most studied are *Microcystis aeruginosa* and *Scenedesmus obliquus*. These strains have
been recorded as having dry mass lipid concentrations of up to 21.3% (Ashokkumar et al., 2014,) and 61.3% (Mandal & Mallick, 2009), respectively. When allowed to reproduce, this could mean that even algae with moderate lipid content could produce thousands of liters per hectare per year. A comparison of possible biodiesel productivity between second generation sources and microalgae with different lipid contents is shown in Table 6.

Table 6

*Comparison of oil content, oil yield, and biodiesel productivity of microalgae with the first and the second generation biodiesel feedstock source*

<table>
<thead>
<tr>
<th>Feedstock source</th>
<th>Oil content (% oil by wt. in biomass)</th>
<th>Oil yield (oil in litres/ha/year)</th>
<th>Biodiesel productivity (kg biodiesel/ha/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil palm</td>
<td>36</td>
<td>5366</td>
<td>4747</td>
</tr>
<tr>
<td>Maize</td>
<td>44</td>
<td>172</td>
<td>152</td>
</tr>
<tr>
<td>Physic nut</td>
<td>41–59</td>
<td>741</td>
<td>656</td>
</tr>
<tr>
<td>Caster</td>
<td>48</td>
<td>1307</td>
<td>1156</td>
</tr>
<tr>
<td>Microalgae with low oil content</td>
<td>30</td>
<td>58,700</td>
<td>51,927</td>
</tr>
<tr>
<td>Microalgae with medium oil content</td>
<td>50</td>
<td>97,800</td>
<td>86,515</td>
</tr>
<tr>
<td>Microalgae with high oil content</td>
<td>70</td>
<td>136,900</td>
<td>121,104</td>
</tr>
</tbody>
</table>


Another benefit of algal biofuels is that they provide a possible source of carbon sequestration. Microalgae’s efficiency at fixing carbon dioxide is 10-50 times higher than that of other terrestrial plants (Bohutskyi & Bouwer, 2013), its growth rate is much higher than terrestrial plants - the fastest recorded doubling time of a species of algae is 2.2 hours (National
Renewable Energy Laboratory, 2019), and algae are extremely tolerant of a variety of extreme climates (Xu et al., 2019). Furthermore, microalgae can turn industrial and municipal waste into carbon sources for growth (Xu et al., 2019).

One disadvantage of the use of algae-based biofuels is that they may not be economically viable. The cheapest form of algal cultivation is in open ponds; in this scenario, the algae would have to reproduce quickly and be able to withstand any predatory protozoa or contaminating bacteria, while simultaneously attaining a high enough lipid content for it to be worth harvesting and refining into biodiesel. No such taxa of alga has been discovered as of yet, but existing species can be genetically modified to fit the requirements stated previously in Section 4 (Ratledge & Cohen, 2008).

5.1. Photobioreactors

An alternative to open-pond algae cultivation is photobioreactors (PBRs). There are many PBR designs, but the most common include tubular, annular, and flat-panel PBRs. Tubular PBRs operate through pumping of algae through long tubes, and airlifts allow for O₂-CO₂ exchange. Annular PBRs are a form of stirred-tank reactors in which large tanks of algae are agitated. These tanks are aerated from below and provide access to light from transparent walls. Flat-panel PBRs are constructed from layers of thin, flat, clear panels upon which a layer of more dense cultures are smeared and allowed to absorb light within the first few millimeters of the culture (Medipally et al., 2015). An example of a tubular PBR is shown below in Figure 5.
Figure 5

A tubular photobioreactor inclined at 45 degrees to the horizontal plane, consisting of riser and downcomer tubes.


Compared to open-pond systems, PBRs offer advantages such as higher sterility, preventable water loss, better light utilization, better temperature control, and higher harvesting efficiency (Medipally et al., 2015). However, the costs associated with building these reactors, operating them, and maintaining them limit the cost-effectiveness of PBRs; the average cost of production of algal crude bio-oils in PBRs is USD $76.98 gal\(^{-1}\) compared to USD $5.15 gal\(^{-1}\) for US oil (Richardson et al., 2014; WSJ News Graphics, 2016).

Another shortcoming of the use of algae is that it is difficult to harvest and separate the lipids from other raw products. Some species of algae are as small as 1 to 30 μm, and having to harvest the lipids from the already miniscule algae accounts for 20-30% of the total cost of algal biofuel production (Barros et al., 2014). One method to separate the solids from the liquids is coagulation, and in recent years, sedimentation with coagulation has been employed to harvest
microalgae in laboratory studies (Zhang et al., 2018). As of now, there is no commercially available microalgal harvesting method that is both economically viable and efficient (Barros et al., 2014).

5.2. Summary of Algal Biofuels

To conclude, although third generation algal-based biofuels have a myriad of benefits from a multitude of fuel outputs to carbon sequestration to oil production increases, technological advancements need to be made in the production and harvesting of algal oils before they can be made commercially available.

6. Results

Our analysis of the benefits and drawbacks of biofuels can be summarized by 5 findings: a) that although all known sources of biofuel will emit some CO$_2$ as a product of the refining, processing, and eventual use of said biofuel, second generation biofuels emit much less CO$_2$ than both conventional fossil fuels and first generation biofuels, b) that the species Miscanthus X giganteus in particular can provide a variety of benefits in its decreased land use requirements, ethanol production, and capacity to be grown in a variety of areas in the continental United States, c) that although the efficiency of biogas is quite low compared to other renewable energy novel technologies are being developed in order to further the use of second generation biofuels, d) that other biofuel materials such as agricultural residues can be further utilized to increase the economic and energy efficiency of agricultural land, and that e) novel sources of biofuels, like microalgae, are in the process of being studied and applied to industrial-scale processes to further advance the independence from the pollution-prone energy sources. Future research could focus on techniques of processing raw materials for the creation of biofuels on the industrial scale.
7. **Acknowledgments**

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