




## Review Article

# Advancing Sustainable Biofuel Production from Agricultural Residues: A Comprehensive Mini-Review

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**Abstract:** Fossil fuels widely satisfy the world's energy demands; however, they are unsustainable. Rational energy management is therefore one of humanity's greatest challenges in the 21st century. The sustainable resources of energy are speculated to minimize the global environmental challenges and consequences concerning the air and water quality, greenhouse effect, acid rain, etc. Biofuels -widely regarded as the "fuel of the future"-are a type of sustainable fuel, extracted immediately from living matter that is most likely produced over and over again. Biofuels are majorly categorized into four groups based on the types of biomasses utilized as their raw material including food crops, agricultural and industrial wastes, and algae. A significant portion of lignocellulosic biomass consists of agricultural residues, presenting an opportunity to use them as feedstock for generating biofuels. Agricultural wastes encompass more than just residues from cultivation; they also comprise wastes generated during the processing of agricultural products, livestock management, and distribution of fruits and vegetables. This review highlights the use of agricultural residues for the production of various types of Biofuels. Agricultural residues can be pretreated and treated through a myriad number of methods, for instance, acid catalysis, anaerobic digestion, hydrothermal carbonization, simultaneous saccharification, transesterification, and pyrolysis; for the production of biodiesel, biogas, hydro-char, syngas and bioethanol. Each of these methods has several benefits and drawbacks since they are all conditional on some factors. Furthermore, the following study also mentions the advantages and disadvantages of biofuel production and usage.

**Keywords:** bio-wastes, bio-oils, carbonization, biogas, anaerobic digestion

## 1. Introduction

Fossil fuels are still regarded as the primary source of energy in the world, yet they are unsustainable, directly contribute to air and water pollution, and are projected to deplete eventually.<sup>1</sup> The combustion of fossil fuels, leading to the release of carbon dioxide (CO<sub>2</sub>) emissions, is widely recognized as a major driver of climate change, particularly global warming. Consequently, it is imperative to implement proactive measures and explore more sustainable energy alternatives to reduce dependence on fossil fuels and mitigate CO<sub>2</sub> emissions.<sup>2</sup> Combustible fuels known as "biofuels" are made from biomass, which is an organic material created by living things (often plants), and is likely produced

repeatedly.<sup>3</sup> Additionally, biofuels contain less proportion of nitrogen and sulphur in comparison with fossil fuels,<sup>4</sup> are therefore more ecologically sound. The sustainable resources of energy are assumed to attain an enhanced role in trivialization of the future environmental challenges and consequences concerning the air and water quality, greenhouse effect, acid rain, etc.<sup>5</sup> Therefore, many people consider biofuels to be the “fuel of the future”. In this essay, we strive to present a thorough analysis of the efficient use of renewable agricultural biomass for the generation of renewable energy. The report also discusses recent developments that have closed the earlier knowledge gap in biofuel manufacturing.

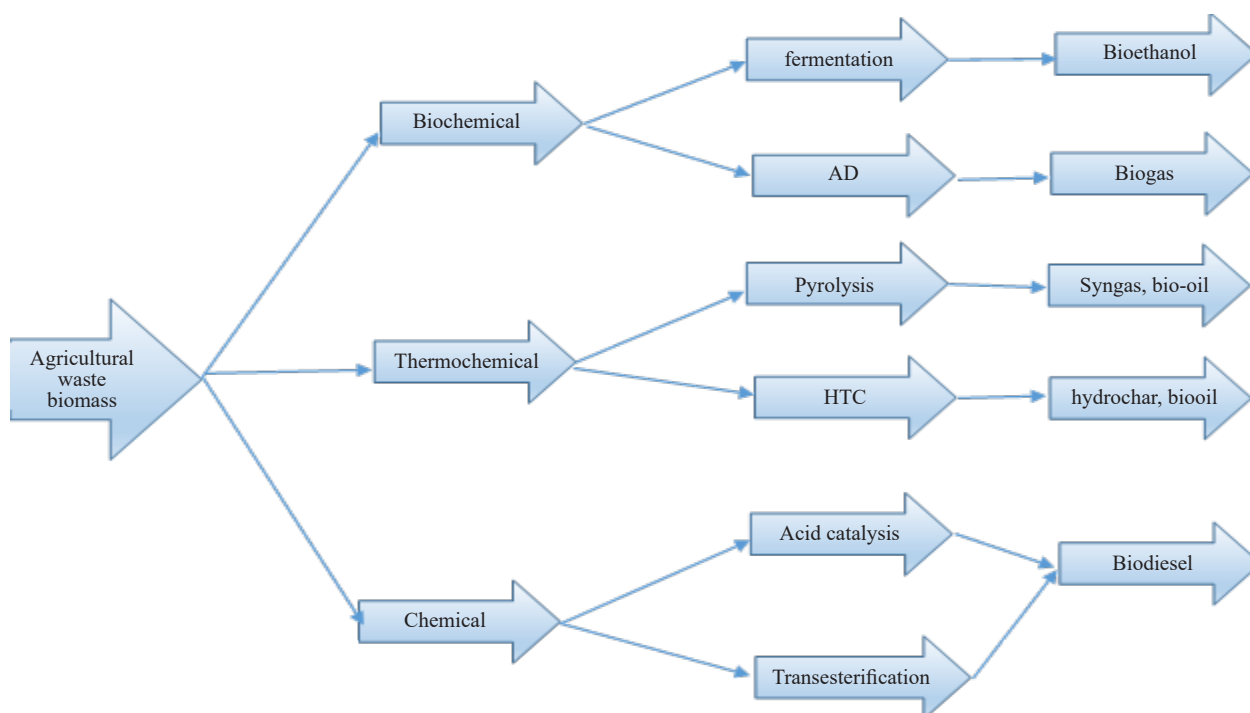
The main categories of biofuels include Solid biofuels, Liquid biofuels (such as biogasoline, biodiesel, jet kerosene, etc.), and Biogases. Additionally, there are four generations of biofuels depending on the type of biomass used.<sup>6</sup> First generation biofuels are synthesized via microbial digestion of food wastes or food crops (e.g. corn, sugar cane, wheat etc), for instance, bioethanol and biodiesel are first generation biofuels. With a rapidly growing population the need of edible crops also increased and additionally, the increase in demand for biofuel led to the diversion of food crops from global food markets to biorefineries.<sup>7</sup> This later (in 2015) turned into the main factor influencing the development of the second generation biofuels. Lignocellulosic biomasses, which comprise 33%-51% cellulose, 19%-34% hemicellulose, and 20%-30% lignin, are used to make second-generation biofuels.<sup>8,9</sup> In order to facilitate bioconversion, separate cellulose and hemicellulose from lignin, and increase the surface area of carbohydrates for subsequent treatment, second generation biomasses need pretreatment.<sup>10</sup> Pretreatment methods are typically broken down into three groups: physical (ultrasonication, size reduction, irradiation, and boiling), chemical (using acid, bases, or salts), and biological (fungal or bacterial treatment).<sup>11</sup> Typically two or more pretreatment techniques are utilized together,<sup>8</sup> however, fungal pretreatment is suggested to be the option for pretreatment of agricultural residues (for example corn stover); since it is a speedy technique that requires negligible amount of acid and low temperature and improves cellulose digestibility.<sup>12</sup> Nonetheless, biomasses consisting of high amounts of lignin and hemicellulose are merely preferred to be hydrolyzed in strong acids such as HCl and H<sub>2</sub>SO<sub>4</sub> for 1 to 24 h.<sup>13,14</sup> Furthermore, second generation bio-refineries use modern-green chemical production processes, such as pyrolysis, enzymatic action, Fisher Tropsch, scarification and acid catalysis.<sup>10,15</sup> Second generation biomasses are widely preferable for they are usually the lignocellulose-rich, postharvest agricultural residues, namely rice crop residues,<sup>9</sup> wheat straw and corn stover,<sup>16</sup> wood chips and non-food crops and vegetable oil.<sup>17</sup> Agricultural residue yields substantial amounts of lignocellulosic biomass, serving as a sustainable source material for the generation of a diverse range of bio-products.<sup>18</sup> Contrarily, the synthesis of second-generation biofuels is complex due to the second-generation biomasses' need for numerous chemical transformations, which result in high energy expenditures.<sup>19</sup> The third generation biofuels i.e. a more sustainable fuel choice, are produced from algal biomass and are thereupon termed as “algae fuel”.<sup>20</sup> Algae produce all sorts of biofuels, including biodiesel, gasoline, butanol, propanol, and ethanol, with an output that is roughly ten times greater than that of second-generation biofuels.<sup>21</sup> Although third generation biomasses are the most eco-friendly but processing of third generation biofuels requires high amount of energy that is typically produced from fossil fuels, thus their mass production is considered to be unsustainable.<sup>22</sup> Lately, genetically modified (GM) algae- known as fourth generation biomasses- are used to enhance biofuel production.<sup>23</sup> For addressing the economic challenges hindering the feasibility of third-generation biofuels microalgae genetic modification has been extensively researched in the past few years.<sup>23-24</sup> The natural capacity and heightened efficiency of microalgae in converting sunlight into solar bioenergy are augmented by the greater quantity of oils accumulated in microalgae in comparison to other terrestrial plant species.<sup>25</sup> Microalga does not compete with food, exhibiting minimal water and land utilization when compared to other generations of biofuels.<sup>26</sup> The wide-spreading manufacturing of fourth-generation biomasses is currently unfeasible due to environmental challenges such as eutrophication, legitimacy concerns, inadequate production of biomass and high production expenses.<sup>23,27,28</sup> Despite the substantial amount of literature on biofuel production limited focus has been directed towards addressing challenges associated with the mass production of fourth-generation biofuels.

As per literature the development of biofuels using agricultural residues as raw material helps to mitigate environmental and nutritional crises. Wastes produced from different crop differ widely Table 1 shows a few crops residues and the composition of biomass (carbohydrate and lignin).

Hence, the main objectives of this review are to reassess the various methods used for the treatment of agricultural wastes, their products, advantages and disadvantages in comparison with non-renewable fuels, and the benefits of using second generation biomasses. The production of biofuels is shown in Figure 1.

**Table 1.** Composition of crops<sup>29-31</sup>

Crop type	Residue/crop ratio	Carbohydrate %	Lignin %
Barley Barley straw	1.2	67.10 70.00	2.90 9.00
Oat Oat straw	1.3	58.29 65.60	4.00 13.75
Corn Corn straw	1	73.70 58.29	0.60 18.69
Rice Rice straw	1.4	87.50 49.33	7.13
Wheat Wheat straw	1.3	35.85 54.00	16.00
Sugar cane Bagasse	0.6	67.00 67.15	14.50

**Figure 1.** Transformation of agricultural waste to biofuels

This study centers on the aspects of energy security and climate change as well as the desired shift in the direction of biofuels from food waste as a renewable energy source providing opportunities for the substitution of fossil fuels, thus contributing to better waste conversion in a more sustainable manner. Furthermore, this study reports on the current situation of biofuel production.

The key focus of this review is the recent diminution in the area of waste management with energy development processes/techniques. This review addresses the significance of organic substances for the production of clean and renewable energy, including alternate solutions for non-renewable fuels. The need for appropriate and renewable alternatives to fossil fuels is discussed.

## 2. Current status of biofuel production

Recent advancements in integrated biorefineries have significantly improved the conversion of waste lignocellulosic components into a diverse array of bioproducts. These include biofuels, platform chemicals, resins, bioplastics, additives, and various other biobased materials, catering to a wide range of applications.<sup>18</sup> It has taken a while for the US and Europe's second generation biofuels industry to create a sizable amount of liquid fuel. The second generation biodiesel produced by Nest Oil ranged in volume from 770 million to 600 million liters. In 2012, Europe produced 41,000 to 82 million liters of ethanol. In 2012, the USA produced 49.3 billion liters of ethanol and 3.67 billion liters of biodiesel, respectively, while the EU produced 4.39 billion liters of ethanol.<sup>32</sup> A recent article illustrating the present use of oil palm wastes from palm oil mill activities highlighted some of the promising advancements and research on the treatment of oil palm solid wastes. Due to its high production yearly compared to other palm solid wastes and its high organic matter and nutrient contents, empty fruit bunches (EFB) is the most often used waste in the palm oil industry. EFB, a bio-organic fertilizer mostly composed of nitrogen, phosphorus, potassium, magnesium, and carbon, is used to preserve soil moisture, raise soil pH, and prevent soil erosion. Bunch ash is an excellent source of chemical fertilizer, providing 41.4% of potassium nutrients on a dry basis.<sup>33</sup> Current studies suggest that biofuels are improving the quality of output and decreasing the power of CO<sub>2</sub> pollution. The manufacturing of bio-diesel production and bioethanol are:

1. For biodiesel production steps involved in the extraction of biodiesel, a single or two-stage transesterification of triglycerides.

2. For bioethanol production, three main steps are involved:<sup>34</sup>

- a) Pretreatment b) Fermentation and c) Distillation.

According to the international energy agency (IEA), the production of transport biofuels increased by 6% from 89 Mtoe in 2018 to 96 Mtoe in 2019. The analysis also predicted an increase of 3% annually in Iran's environmental costs associated with using fossil fuels for transportation.<sup>35</sup>

## 3. Methods of biofuel production from agricultural wastes

### 3.1 Biofuel production via hydrothermal carbonization

Wet torrefaction, also known as hydrothermal carbonization (HTC), has recently emerged as the most popular method for treating wet waste.<sup>36</sup> By using core reaction pathways such as the HTC is an exothermic process that lowers the oxygen and hydrogen content of biomass by hydrolysis, dehydration, decarboxylation, polymerization, poly-condensation, and aromatization.<sup>37</sup> HTC is a process of conversion of wet biomass into biofuel at a range low temperature (180-350 °C) and autogenous pressure, i.e. the pressure generated by the reactor itself during the carbonization activity.<sup>38</sup> Whereas microwave-assisted hydrothermal carbonization operates at even lower temperatures i.e. 160 to 200 °C.<sup>39</sup> Additionally, HTC can be efficiently performed via decoupled temperature and pressure hydrothermal (DTPH) reaction at 200 °C and 20 MPa pressure.<sup>40</sup> HTC has been shown to be a reliable technology for converting biomass into a variety of bio-products, including solid fuel or hydrochar, bio-oil, soil conditioner to improve soil fertility and maximize crop yields, carbon catalyst that can be used to make fine chemicals, affordable carbon adsorbents used for water purification or as a chemical barrier for different heavy metals or CO<sub>2</sub> sorption, and, finally, carbon material for effective fuel cells.<sup>41</sup> Nevertheless, it is primarily used for hydrochar production.<sup>39</sup> Three key phases make up the carbonization reaction: (a) dehydration of the carbohydrate to produce hydroxymethyl furfural; (b) polymerization of these furfurals to create polyfurans; and (c) further carbonization through intermolecular dehydration.<sup>42</sup>

The biomass is placed in a process reactor with an appropriate biomass-to-water ratio during conventional HTC, and the solution is then heated for a predetermined amount of time at a subcritical temperature (between 180 and 350 °C).<sup>38</sup> The characteristics of the produced solid fuel (hydrochar) may be managed, stored, and transported with a great deal less effort when HTC and densification are combined.<sup>43</sup> HTC process requires a few perquisites with regard to biomass preparation and treatment (primarily, unlike other thermal treatment procedures the wet waste does not require pre-drying).<sup>44</sup> HTC is more favorable than other modern thermo-chemical transformation processes (such as pyrolysis, combustion, and gasification) because it can change wet feedstock into solid carbonaceous biochar at comparatively

higher yields without pre-dehydration.<sup>45</sup> Compared to other biological treatment technologies HTC requires less time and compact reactor arrangements; additionally it is an effective technology for carbon fixation and CO<sub>2</sub> sequestration.<sup>42</sup> HTC is used for biofuel production from lignocellulose agricultural residues such as barley, maize,<sup>46</sup> rice husk, corn straw<sup>47</sup> and energy crops such as corn and grass silage.<sup>41</sup> Co-hydrothermal carbonization of dry agricultural biomasses, grape marc and corn stover, with cow manure leads to the production of high-quality hydrochar that can be used as a fuel and for soil amendment.<sup>48</sup> The properties of hydrochar produced depend on the precursor sources.<sup>49</sup>

### 3.2 Biofuel production through anaerobic digestion

The technology of anaerobic digestion (AD) is used to break down organic material without the use of oxygen and produce biogas. Numerous minerals, including phosphate and ammonium, are present in high concentrations in the leftover effluent from this digestive process. If excessive amounts of wastewater are applied to agricultural land, there may be worries about pollution or financial hardship if more treatment is required before discharge. The nutrient-rich wastewater can be used to cultivate photosynthetic microalgae, though. In order to reduce the cost of effluent treatment, conventional AD techniques may be combined with microalgae cultivation.<sup>50</sup>

As a result, anaerobic digestion provides a clever alternative to obtain additional energy like as methane (CH<sub>4</sub>) and recover nutrients from biomasses with low energy availability (LEA). Numerous kinds of algae are sufficiently suitable for anaerobic digestion and are somewhat rich in lipids, carbohydrates, and proteins. They lack lignin, making them more easily biodegradable in anaerobic settings than lignocellulosic biomass. Studies demonstrate that pretreatments, such as those characterized by lipid mining that is energy-intensive, break down cell walls and cell membranes to aid anaerobic breakdown by liberating intracellular material. Anaerobic digestion produces CH<sub>4</sub>, which can either be burned to provide power or converted into renewable transportation fuels. The liquid digestate, which includes water and fertilizers like phosphate (PO<sub>4</sub><sup>3-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>), can be utilized to produce algae in the future and the digested solids can be composted.<sup>51</sup>

The lack of food and energy on a worldwide scale is one of the major issues affecting socioeconomic activities and threatening sustainable development. By switching to biofuels instead of fossil fuels, you can reduce your impact on the environment while still getting the renewable and sustainable energy you need. As a result, adopting cutting-edge technologies to exploit renewable resources has gained more attention recently. Due to their renewability and lower greenhouse gas (GHG) emissions when compared to fossil fuels, biofuels are probably a significant factor. Oilseed plants, which are imperfect, fairly expensive, and in competition with human food, are currently the primary source of biodiesel production. Finding non-edible feedstocks is therefore crucial for the manufacture of biofuel. Crop leftovers are the most readily available and economically viable renewable feedstocks for the development of second-generation biofuels, without disrupting the food chain.<sup>51-52</sup>

The most popular and well-established method for producing biogas from organic waste is anaerobic digestion, which is used in municipal and industrial settings. The “first generation of biofuels” that have been created recently utilized anaerobic digestion. The “first generation biofuels” have mostly concentrated on producing biofuel from domestic plant sources. In these plans, solar energy is used to stimulate the carbon dioxide-photosynthetic attachment of organic materials. The energy crop is harvested, consumed as a flammable fuel right away, or converted into another substance like ethanol, hydrogen, or methane. These “first generation biofuels” have received much criticism for using priceless food crops as feedstocks for the production of fuel.<sup>53</sup>

Agricultural waste is transformed into energy through the method of AD by utilizing a significant amount of energy. Thus, for this biological treatment to make sense, input energy must be less than output energy.<sup>54</sup>

AD is one of the most widely held waste-to-energy conversion technologies among the different biofuel production routes because of its benefits over other technologies. For instance, the production of biodiesel requires lipid-enriched biomass, but this requires a lot of energy because harvesting and drying biomass require significant energy inputs.<sup>55</sup>

### 3.3 Biofuel production through pyrolysis

Six new conversion approaches have recently been added to the two main procedure categories for biomass transformation, thermochemical and biochemical conversion. While only pyrolysis can provide a number of high-value products, including chemicals, charcoal, bio-oil, and biogas.<sup>56</sup> The existing pyrolysis process can be modified by co-



pyrolysis with various materials, successfully promoting the qualities of the resulting bio-oil.<sup>57</sup> In addition to Second-generation biofuels are mostly made from municipal, industrial, and agricultural waste, including lignocellulosic biomass, plastic waste, food waste, and medical waste. This has the potential to produce lucrative items as well as spark some economic, social, and environmental interest. Second-generation biofuels have faced a number of challenges, most notably high transportation and pretreatment costs, which have prevented their research, promotion and commercialization.<sup>58</sup> Assuming the many advantages waste oil pyrolysis is probable to have a significant impact on the energy market in the near future.<sup>59</sup>

By heating organic compounds to high temperatures in an inert atmosphere or without oxygen, the pyrolysis method converts them into the desired products. The distribution of products from pyrolysis varies depending on the feedstocks and heating rates; these products can be used in industries as chemicals (biogas, bio-oil, and char) or as an energy source. Research has demonstrated that traditional pyrolysis yields both desired products, like bio-oil, and less desirable products, like char. This is problematic because these by-products encourage the production of coke and clog the filter's pores. The pyrolysis process can be made more efficient by adding an appropriate catalyst, which will increase the yield of bio-oil and decrease tar products.<sup>60</sup>

### 3.4 Biofuel production through acid catalysis

The usage of fossil fuels can have negative effects on the environment and national security. Rising ground temperature, climate change, acid rain and other consequences are indirect results of air pollution, foggy cities and water contamination from oil spills. To stop environmental damage and assure food security, clean energy must be employed.<sup>61</sup> Energy security and climate change issues will start to be addressed by the efficient product of biofuels from renewable resources.<sup>62</sup> It is becoming more and more clear that biofuels might be a workable form of renewable energy, as opposed to the finite supply, geopolitical instability, and detrimental global effects of fossil fuel energy. The quality of living for the expanding global population must be improved. Biofuels are one alternative that might be used to address the world's energy demands. Although fossil fuels have long been the main source of energy, their use is unsustainable and their burning causes environmental issues.<sup>6</sup> It was determined that promising alternatives to finite fossil fuels existed. However, the conversion of edible vegetable oils to biodiesel using homogeneous acid and base catalysts is now considered as being untenable for the future due to competition between food and fuel as well as other environmental difficulties connected to the catalyst system and feedstock.<sup>63</sup>

Both the benefits of using biodiesel as an alternative fuel and the issues with its manufacture are discussed. There are numerous studies on the benefits and drawbacks of producing biodiesel by esterifying fatty acids with solid acid catalysts. An alternative fuel made from the monoalkyl ester of fatty acids is called biodiesel. Vegetable oils, animal fats, and even recycled fat from the food industry can all be used to make it.<sup>64</sup> Activated Carbon, hydrous zirconia, silica, and tungsten phosphosphoric acid (TPA) impregnates were used to study the production of biodiesel from low-quality canola oil containing up to 20 weight percent free fatty acids.<sup>65</sup> Solid acid catalyzed biodiesel production is quite fascinating. Solid acid catalysts (both Lewis type, such as mixed and sulfated oxides, and Bronsted type, like sulfonic acid-containing materials) combine the advantages of heterogeneous base catalysts with mineral acids.<sup>66</sup> Homogeneous acid catalysts like  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{BF}_3$ , and  $\text{H}_3\text{PO}_4$  have been proposed to promote simultaneous esterification of free fatty acids and transesterification of triglycerides in a single catalytic step, skipping the preconditioning phase, when using low cost feedstock with a high free fatty acid content. Since these catalysts are less effective for transesterification than alkaline catalysts, higher pressure, temperature, methanol to oil molar ratios, and catalyst concentrations are required to produce suitable transesterification reaction rates. Acid catalyzed transesterification has thus received less attention despite being insensitive to free fatty acid in the feedstock due to its comparably slower reaction rate.<sup>67</sup> The up-gradation of reaction parameters has demonstrated that the highest yield of biodiesel (98% wt.) can be obtained at 200 °C, 3% wt. catalyst loading and 1:18 oil to alcohol molar ratio. Nonetheless the oil-to-alcohol molar ratio widely depends upon the amount or percentage of free fatty acid present in the oil.<sup>68</sup> Due to their simplicity and simultaneous promotion of esterification and transesterification from low grade, highly acidic and water containing oils without soap formation, processes for making biodiesel that relies on acid catalysts are preferable to traditional methods. For this process, highly reactive homogeneous Brönsted acid catalysts are effective, but they have significant contamination and corrosion issues, making it crucial to undertake effective separation and purification processes.<sup>69</sup> Interest in the development of solid acid catalysts has increased significantly as a result of recent developments in various nano-based

materials, particularly those based on metal oxides and various magnetic nanoparticles. Solid acid catalysts based on metal oxides seem promising for the transesterification and esterification reactions of different oils and waste products for the manufacture of biodiesel.<sup>70</sup> Strong liquid acid catalysts are less vulnerable to free fatty acids and can perform transesterification and esterification simultaneously. However, they take longer and call for hotter reaction temperatures. To manufacture biodiesel, however, low-cost feedstocks might be employed in acid catalyzed methods, which would reduce production costs.<sup>71</sup>

### 3.5 Biofuel production through trans-esterification

The chemical process of converting one ester into another ester such as alkyl monoester that makes up biodiesel, is known as Trans-esterification.<sup>72</sup> The primary synthetic methods have been employed in the production of biodiesel, encompassing non-catalytic conversion, nano-fibers (such as ZnO/Ni-SBA-16@GO, SiO<sub>2</sub>-Cu@Fe<sub>2</sub>O<sub>3</sub> nanofibers), acid-catalyzed transesterification (use of H<sub>2</sub>SO<sub>4</sub>, HCl, HSO<sub>3</sub> and many others) and alkali-catalyzed trans-esterification.<sup>73-77</sup> In the trans-esterification process, acid catalysts produce extremely high yields.<sup>78</sup> Moreover, nano-fiber catalysts are proven to produce 98% of biodiesel at 70 °C and 7 h reaction time.<sup>76,77</sup> Fatty acid and alkyl esters can be produced by trans-esterifying triglycerides to alcohols, primarily methanol and ethanol.<sup>79</sup> The process of turning sunflower oil into biodiesel using transesterification has been studied. Sunflower oil must go through trans-esterification in order to be converted into biodiesel. This process involves changing the glycerol in triglycerides with a short-chain alcohol while a catalyst is present. To perform this process, the catalyst is dissolved in methanol in an alkaline medium at a low temperature and atmospheric pressure.<sup>80</sup> The most common process for creating biodiesel is trans-esterification, particularly alkali-catalyzed trans-esterification.<sup>81</sup> Although for the production of biodiesel alternative methods exist, however, trans-esterification using alkali-catalysis converts high amounts of triglyceride to the appropriate methyl esters in a minimum time period. The amount of glycerides with somewhat high water and free fatty acid content increases even though trans-esterification with acid catalysis is significantly slower than with alkali catalysis.<sup>82</sup> Alkaline, acidic and enzymatic catalysts can all be used to transesterify used frying oil. Each catalyst has pros and cons that vary depending on unwanted chemicals, particularly free fatty acids and water.<sup>83</sup> Lately, the applications of homogeneous base catalyst (KOH, CH<sub>3</sub>OK, NaOH, and CH<sub>3</sub>ONa) has demonstrated their specialty, showcasing notable advantages like a high rate of reaction, and favorable reaction conditions. A particularly remarkable effect of this process is that it makes saponification much easier.<sup>84,85</sup> Addressing the drawbacks of homogeneous base catalysts in transesterification, the heterogeneous acid catalyst has emerged as a viable option since it prevents saponification and is impervious to water and Free Fatty Acids (FFA) present in the feedstock.<sup>84</sup>

### 3.6 Biofuel production through simultaneous saccharification

Because these types of feedstock are typically not used for human consumption, second generation biofuels are referred to as “Advanced biofuels”. According to recent studies, second generation biofuels will generally outperform first generation biofuels in terms of sustainability.<sup>32</sup> Lignocellulosic agricultural wastes, their sources, and cost-effective pretreatment techniques for enzymatic hydrolysis and fermentation to produce bioethanol.<sup>86</sup> Numerous researchers have emphasized the creation of biofuel using agricultural and biological wastes. Nutshells are the source for the microorganisms that ferment to make bioethanol. In the process of converting biomass, cellulose is collected and used by bacteria to produce ethanol through the cellulolytic process. Combination of *saccharomyces cerevisiae* and *Bacillus stearothermophilus*. Through simultaneous saccharification and fermentation, yeast and bacteria generate bioethanol. Which displays the approximately 16.11+/-0.4962 (g/L) ethanol produced throughout the course of 14 days of incubation.<sup>87</sup> The method of simultaneous saccharification and fermentation (SSF) is a superior alternative to Heat Shock transcription Factor (HSF) because it uses simultaneous saccharification and fermentation, which helps produce ethanol by removing waste products and does not require a separate reactor, in the fermentation of lignocellulosic hydrolysate.<sup>32</sup> There are two ways to convert second-generation biofuels: one involves thermochemical processing, the other involves biochemical processing. In contrast, thermochemical refers to the conversion of a range of products through chemical reformation and thermal degradation. The terms direct combustion, gasification, liquefaction, and pyrolysis all refer to thermochemical conversion. Synthesis gas, also known as syngas, is produced when biomass is cooked in the absence of oxygen and consists largely of hydrogen and carbon monoxide.<sup>15</sup> The best temperature for *Saccharomyces cerevisiae*

is only 30 °C for their use in biofuel production, but since most fermentations do not permit temperatures as elevated as 50 °C, we treasured to recognize the finest saccharification situations at temperatures more appropriate for an SSF process. To find the maximum conditions for hydrolysis, relative experiments employing cellulosic emulsions and Microcrystalline Cellulose (MCC) samples at temperatures fluctuating from 30 to 50 °C were performed.<sup>88</sup> The main factors affecting the SSF process are temperature, enzyme loading, yeast concentration, pH, solid content and yeast strain. Temperature is a critical factor for SSF because of the contrast between the optimum temperatures for enzymatic hydrolysis (45-50 °C) and fermentation (30-35 °C)<sup>89</sup> to keep the process conditions within the pH range of 5.5-6.5.<sup>90</sup> Thereupon main drawback to simultaneous saccharification and fermentation (SSF) processes is the incompatibility of the temperature and pH climax for the hydrolysis and fermentation steps-with the anterior optimum at 50-55 °C and pH 4.5-5.5.<sup>91</sup>

#### 4. Advantages of biofuel production from agricultural wastes

Biofuels, used as an alternative energy source, provide a significant amount of energy and reduce pollution,<sup>92</sup> since biofuels have relatively less harmful carbon(CO<sub>2</sub>, CO, THC) emission.<sup>93</sup> More advantages of biofuel over fossil fuels are given in Table 2. First-generation biofuels are often made from animal fats or edible crops with high fat, sugar, and starch content, such as potato, corn, sugarcane, sorghum, and fish oil. However, the usage of first-generation biofuels has led to a number of issues, including cultivated land occupancy, water shortages, and a conflict between fuel and food.<sup>94</sup> A more sustainable alternative to first generation biomasses is agricultural wastes. Farms produce garbage, but instead of dumping it in landfills, they use cost-effective methods that lower the cost of waste management, protecting the farmers' income.<sup>95</sup> Similar to value-added hydrocarbons produced in petrochemical businesses, lignin found in lignocellulosic biomass may be removed using ultrasonic techniques, is a source of numerous aromatics, and can be transformed into highly oxygenated and polar molecules that may be used in large industries.<sup>96</sup>

**Table 2.** Advantages of biofuels over fossil fuels

Impact	Biofuels	Fossil fuels
Emission	Because all of the carbon in a biofuel has already been removed from the atmosphere, they are carbon neutral	Fossil fuels emit greenhouse gases and ultimately lead to global warming
Renewability	It is expected that biomass resources needed to make biofuels will be produced repeatedly	In the next few decades fossil fuel will not be available at affordable prices
Economic enhancement	Creating a biofuels business reduces imports, boosts employment, and keeps the economy independent of global trends	Imports of fossil fuels have a negative impact on security and economic progress
Safety	Producing biofuels from agricultural wastes is highly safe. Biofuel spills can be broken down, and absorbed naturally	Extracting some fossil fuels from the Earth is a dangerous process. Spills of oil have a serious effect on environment because they are not biodegradable

#### 5. Disadvantages of biofuel

There are several drawbacks to using biofuels as a transportation fuel in four areas: cost, nitrogen oxide emission, viscosity, and corrosion resistance. On the other hand, reclaiming land through predatory means and cultivating annual crops like maize would lead to increased soil erosion and a reduction in soil fertility. Large-scale irrigation will further



exacerbate the water deficit and limit the lifespan of rivers. The process can cause ecosystem deterioration, regional and larger-scale soil erosion, as well as various health issues.<sup>97</sup> Due to high production costs and a lack of technological validation, second generation biofuels are not yet produced commercially. The harvesting, storing, and delivery methods in use today are insufficient for processing and distributing biomass on a broad scale. The usage of these fuels is linked to less concern, which could result in a food crisis in developing nations or negatively affect consumer prices in rich countries.<sup>92</sup>

## 6. Conclusion

In recent decades, the advancement and encouragement of industrialization, modernization, urbanization, and globalization have greatly increased the use of fossil fuels and the true resource outflow, causing enormous amounts of CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub> release as well as significant carbon dioxide growth in the atmosphere.<sup>98</sup> Pakistan's government allocates over \$3.7 billion each year for the import of fossil fuels, exerting a substantial influence on an economy that is already fragile.<sup>99</sup> Additionally, Pakistan ranks as the fifth most susceptible nation globally to the impacts of climate change.<sup>100</sup> As Pakistan experiences a rise in population and simultaneous urbanization, the resulting impacts of climate change are anticipated to have severe and devastating consequences.<sup>101</sup> After coal and oil, biomass is the third-largest major energy source in the world.<sup>102</sup> Currently, biomass in all of its forms contributes roughly 1,250 million Tones or 14% of the world's yearly energy consumption.<sup>103</sup> Estimates indicate that Kenya relies on biomass for approximately 68% of its total energy, India for 47%, Pakistan for 27%, Brazil for 25%, and China for 13%. Despite a decline in the overall contribution of biomass due to increased industrialization and economic growth, there is a noticeable upward trend in the utilization of biomass resources in developing countries, growing at an annual rate exceeding 2%.<sup>104</sup>

The compositions of different biomasses demonstrated in detail, in several studies are evident that biofuel (especially those produced from non-food plant sources) are more sustainable than fossil fuel.<sup>105-108</sup> Agricultural residues account for 33% of the total biomass used worldwide.<sup>93</sup> Biomasses produced from agricultural residues reduce the cost of waste management, contrarily they require pretreatment and costly and complex separation processes; since they comprise 33%-51% cellulose, 19%-34% hemicellulose, and 20%-30% lignin 99,<sup>8,9</sup> which might increase the production cost. Although there are myriad methods of converting agricultural wastes into fuel in order to commercialize this globally researchers ought to track down easier and cost-effective methods of pretreatment and separation. Furthermore, the most feasible methods used for the generation of biofuels from agricultural residues include hydrothermal carbonization, anaerobic digestion, simultaneous saccharification, pyrolysis and trans-esterification via acid or alkaline catalysis. It is reasonable to infer that the waste produced from agricultural activities and processes is valuable and can be utilized to achieve the global renewable energy target in an affordable and accessible manner.

## Author's contributions

Abida Nisar, Mahgul Bashir, Nazia Mubeen and Sabagul Younus collected the data for different parts of the review papers. Kiya Hashum and Muhammad Haroon helped in rephrasing the paper and provided guideline for writing review paper, and Sahid Mehmood and Fazal Haq helped in revising the paper before and after submission.

## Conflict of interest

The authors declare no conflicts of interest.

## References

- [1] Alaswad, A.; Dassisti, M.; Prescott, T.; Olabi, A. G. J. R.; Reviews, S. E. Technologies and developments of third generation biofuel production. *Renew. Sust. Energ. Rev.* **2015**, *51*, 1446-1460.

- [2] He, S.; Barati, B.; Hu, X.; Wang, S. Carbon migration of microalgae from cultivation towards biofuel production by hydrothermal technology: A review. *Fuel Process. Technol.* **2023**, *240*, 107563.
- [3] Malode, S. J.; Prabhu, K. K.; Mascarenhas, R. J.; Shetti, N. P.; Aminabhavi, T. M. Recent advances and viability in biofuel production. *Energy Convers. Manag.: X.* **2021**, *10*, 100070.
- [4] Tashtoush, G. M.; Al-Widyan, M. I.; Albatayneh, A. M. Factorial analysis of diesel engine performance using different types of biofuels. *J. Environ. Manage.* **2007**, *84*, 401-411.
- [5] Padmaja, K.; Atheya, N.; Bhatnagar, A.; Singh, K. J. F. Conversion of calotropis procera biocrude to liquid fuels using thermal and catalytic cracking. *Fuel.* **2009**, *88*, 780-785.
- [6] Rodionova, M. V.; Poudyal, R. S.; Tiwari, I.; Voloshin, R. A.; Zharmukhamedov, S. K.; Nam, H. G.; Zayadan, B. K.; Bruce, B. D.; Hou, H. J.; Allakhverdiev, S. I. Biofuel production: challenges and opportunities. *Int. J. Hydrog. Energy.* **2017**, *42*, 8450-8461.
- [7] Alalwan, H. A.; Alminshid, A. H.; Aljaafari, H. A. Promising evolution of biofuel generations. Subject review. *Renewable Energy Focus* **2019**, *28*, 127-139.
- [8] Suali, E.; Suali, L. Impact assessment of global biofuel regulations and policies on biodiversity. In *Environmental Sustainability of Biofuels*; Elsevier, 2023; pp 137-161.
- [9] Das, P. K.; Das, B. P.; Dash, P. Potentials of postharvest rice crop residues as a source of biofuel. In *Refining Biomass Residues for Sustainable Energy and Bioproducts*; Elsevier, 2020; pp 275-301.
- [10] Robak, K.; Balcerek, M. Review of second generation bioethanol production from residual biomass. *Food Sci. Biotechnol.* **2018**, *56*, 174.
- [11] Hsu, T.-A. Pretreatment of biomass. In *Handbook on Bioethanol*; Routledge, 2018; pp 179-212.
- [12] Keller, F. A.; Hamilton, J. E.; Nguyen, Q. A. In *Microbial Pretreatment of Biomass: Potential for Reducing the Severity of Thermochemical Biomass Pretreatment*; Biotechnology for Fuels and Chemicals: The Twenty-Fourth Symposium, Springer, 2003; pp 27-41.
- [13] Kuldeep, A.; Bhosale, A.; Garadkar, K. Enhanced photocatalytic performance of TiO<sub>2</sub>-carbon nanocomposite. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 9006-9017.
- [14] Amin, F. R.; Khalid, H.; Zhang, H.; Rahman, S. U.; Zhang, R.; Liu, G.; Chen, C. Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express* **2017**, *7*, 1-12.
- [15] Naik, S. N.; Goud, V. V.; Rout, P. K.; Dalai, A. K. Production of first and second generation biofuels: a comprehensive review. *Renew. Sust. Energ. Rev.* **2010**, *14*, 578-597.
- [16] Battaglia, M.; Thomason, W.; Fike, J. H.; Evanylo, G. K.; von Cossel, M.; Babur, E.; Iqbal, Y.; Diatta, A. A. The broad impacts of corn stover and wheat straw removal for biofuel production on crop productivity, soil health and greenhouse gas emissions: A review. *Gcb Bioenergy* **2021**, *13*, 45-57.
- [17] Dahman, Y.; Dignan, C.; Fiayaz, A.; Chaudhry, A. 13-An introduction to biofuels, foods, livestock, and the environment. In *Biomass, Biopolymer-Based Materials, and Bioenergy*; Verma, D.; Fortunati, E.; Jain, S.; Zhang, X., Eds.; Woodhead Publishing, 2019; pp 241-276.
- [18] Mujtaba, M.; Fernandes Fraceto, L.; Fazeli, M.; Mukherjee, S.; Savassa, S. M.; Araujo de Medeiros, G.; do Espírito Santo Pereira, A.; Mancini, S. D.; Lipponen, J.; Vilaplana, F. Lignocellulosic biomass from agricultural waste to the circular economy: a review with focus on biofuels, biocomposites and bioplastics. *J. Clean. Prod.* **2023**, *402*, 136815.
- [19] Carriquiry, M. A.; Du, X.; Timilsina, G. R. Second generation biofuels: Economics and policies. *Energy Policy* **2011**, *39*, 4222-4234.
- [20] Saha, S.; Sharma, A.; Purkayastha, S.; Pandey, K.; Dhingra, S. Bio-plastics and biofuel: is it the way in future development for end users? In *Plastics to Energy*; Elsevier, 2019; pp 365-376.
- [21] Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* **2007**, *25*, 294-306.
- [22] Mat Aron, N. S.; Khoo, K. S.; Chew, K. W.; Show, P. L.; Chen, W. H.; Nguyen, T. H. P. Sustainability of the four generations of biofuels-a review. *Int. J. Energy Res.* **2020**, *44*, 9266-9282.
- [23] Abdullah, B.; Syed Muhammad, S. A. F.; Shokravi, Z.; Ismail, S.; Kassim, K. A.; Mahmood, A. N.; Aziz, M. M. A. Fourth generation biofuel: A review on risks and mitigation strategies. *Renew. Sust. Energ. Rev.* **2019**, *107*, 37-50.
- [24] Shokravi, Z.; Shokravi, H.; Aziz, M. A.; Shokravi, H. The fourth-generation biofuel: a systematic review on nearly two decades of research from 2008 to 2019. *Fossil Free Fuels* **2019**, 213-251.
- [25] Hoang, A. T.; Sirohi, R.; Pandey, A.; Nizetić, S.; Lam, S. S.; Chen, W.-H.; Luque, R.; Thomas, S.; Arıcı, M.; Pham, V. V. Biofuel production from microalgae: challenges and chances. *Phytochemistry Reviews* **2023**, *22*, 1089-1126.
- [26] Brinegar, K.; K. Yetisen, A.; Choi, S.; Vallillo, E.; Ruiz-Esparza, G. U.; Prabhakar, A. M.; Khademhosseini, A.; Yun, S.-H. The commercialization of genome-editing technologies. *Crit. Rev. Biotechnol.* **2017**, *37*, 924-932.

- [27] Shokravi, H.; Shokravi, Z.; Heidarrezaei, M.; Ong, H. C.; Koloor, S. S. R.; Petru, M.; Lau, W. J.; Ismail, A. F. Fourth generation biofuel from genetically modified algal biomass: Challenges and future directions. *Chemosphere* **2021**, *285*, 131535.
- [28] Calise, F.; Cappiello, F. L.; Cimmino, L.; Dentice d'Accadia, M.; Vicidomini, M. A comparative thermoeconomic analysis of fourth generation and fifth generation district heating and cooling networks. *Energy* **2023**, *284*, 128561.
- [29] Miller, D. F. *Composition of Cereal Grains and Forages*; National Academy of Sciences, 1958.
- [30] Doe, U. Emissions of Greenhouse Gases in the United States, 1995. Energy Information Administration, US Department of Energy Report DOE/EIA-0573 (95), Washington, DC, 1996.
- [31] Riahi, E.; Ramaswamy, H. S. Structure and composition of cereal grains and legumes. *Handbook of Postharvest Technology* **2003**, *1*.
- [32] Janssen, R.; Turhollow, A. F.; Rutz, D.; Mergner, R. Production facilities for second-generation biofuels in the USA and the EU-current status and future perspectives. *Biofuel. Bioprod. Biorefin.* **2013**, *7*, 647-665.
- [33] Sukiran, M. A.; Abnisa, F.; Daud, W. M. A. W.; Bakar, N. A.; Loh, S. K. A review of torrefaction of oil palm solid wastes for biofuel production. *Energy Convers. Manag.* **2017**, *149*, 101-120.
- [34] Malode, S. J.; Prabhu, K. K.; Mascarenhas, R. J.; Shetti, N. P.; Aminabhavi, T. M. Recent advances and viability in biofuel production. *Energy Convers. Manag.: X* **2021**, *10*, 100070.
- [35] Yazdanparast, R.; Jolai, F.; Pishvae, M. S.; Keramati, A. Second-generation biofuel development in iran: current state and future directions. *Energy Sources, Part B: Economics, Planning, and Policy* **2021**, *16*, 258-278.
- [36] Sharma, H. B.; Sarmah, A. K.; Dubey, B. Hydrothermal carbonization of renewable waste biomass for solid biofuel production: A discussion on process mechanism, the influence of process parameters, environmental performance and fuel properties of hydrochar. *Renew. Sust. Energ. Rev.* **2020**, *123*, 109761.
- [37] Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuel. Bioprod. Biorefin.* **2010**, *4*, 160-177.
- [38] Lu, X.; Jordan, B.; Berge, N. D. Thermal conversion of municipal solid waste via hydrothermal carbonization: Comparison of carbonization products to products from current waste management techniques. *Waste Manage.* **2012**, *32*, 1353-1365.
- [39] Deng, C.; Lin, R.; Kang, X.; Wu, B.; Ning, X.; Wall, D.; Murphy, J. D. Co-production of hydrochar, levulinic acid and value-added chemicals by microwave-assisted hydrothermal carbonization of seaweed. *Chem. Eng. J.* **2022**, *441*, 135915.
- [40] Yu, S.; Yang, X.; Li, Q.; Zhang, Y.; Zhou, H. Breaking the temperature limit of hydrothermal carbonization of lignocellulosic biomass by decoupling temperature and pressure. *Green Energy Environ.* **2023**, *8*, 1216-1227.
- [41] Oliveira, I.; Blöhs, D.; Ramke, H.-G. Hydrothermal carbonization of agricultural residues. *Bioresour. Technol.* **2013**, *142*, 138-146.
- [42] Liu, F.; Yu, R.; Guo, M. Hydrothermal carbonization of forestry residues: influence of reaction temperature on holocellulose-derived hydrochar properties. *J. Mater. Sci.* **2017**, *52*, 1736-1746.
- [43] Kambo, H. S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sust. Energ. Rev.* **2015**, *45*, 359-378.
- [44] Waqas, M.; Aburizaiza, A. S.; Miandad, R.; Barakat, M. A.; Nizami, A. S. Development of biochar as fuel and catalyst in energy recovery technologies. *J. Clean. Prod.* **2018**, *188*, 477-488.
- [45] Libra, J. A.; Ro, K. S.; Kammann, C.; Funke, A.; Berge, N. D.; Neubauer, Y.; Titirici, M.-M.; Fühner, C.; Bens, O.; Kern, J.; Emmerich, K.-H. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 71-106.
- [46] Seyedsadr, S.; Al Afif, R.; Pfeifer, C. Hydrothermal carbonization of agricultural residues: A case study of the farm residues-based biogas plants. *Carbon Resources Conversion* **2018**, *1*, 81-85.
- [47] Raheem, A.; He, Q.; Ding, L.; Dastyar, W.; Yu, G. Evaluating performance of pyrolysis and gasification processes of agriculture residues-derived hydrochar: Effect of hydrothermal carbonization. *J. Clean. Prod.* **2022**, *338*, 130578.
- [48] Mariuzza, D.; Lin, J.-C.; Volpe, M.; Fiori, L.; Ceylan, S.; Goldfarb, J. L. Impact of Co-Hydrothermal carbonization of animal and agricultural waste on hydrochars' soil amendment and solid fuel properties. *Biomass and Bioenergy* **2022**, *157*, 106329.
- [49] Sharma, R.; Jasrotia, K.; Singh, N.; Ghosh, P.; Srivastava, S.; Sharma, N. R.; Singh, J.; Kanwar, R.; Kumar, A. A comprehensive review on hydrothermal carbonization of biomass and its applications. *Chemistry Africa* **2020**, *3*, 1-19.
- [50] Cai, T.; Park, S. Y.; Racharaks, R.; Li, Y. Cultivation of nannochloropsis salina using anaerobic digestion effluent as

a nutrient source for biofuel production. *Appl. Energy* **2013**, *108*, 486-492.

- [51] Ayala-Parra, P.; Liu, Y.; Field, J. A.; Sierra-Alvarez, R. Nutrient recovery and biogas generation from the anaerobic digestion of waste biomass from algal biofuel production. *Renew. Energ.* **2017**, *108*, 410-416.
- [52] Abomohra, A. E.-F.; Shang, H.; El-Sheekh, M.; Eladel, H.; Ebaid, R.; Wang, S.; Wang, Q. Night illumination using monochromatic light-emitting diodes for enhanced microalgal growth and biodiesel production. *Bioresour. Technol.* **2019**, *288*, 121514.
- [53] Ward, A.; Lewis, D. M.; Green, F. B. Anaerobic digestion of algae biomass: a review. *Algal Res.* **2014**, *5*, 204-214.
- [54] Li, Y.; Chen, Y.; Wu, J. Enhancement of methane production in anaerobic digestion process: A review. *Appl. Energy* **2019**, *240*, 120-137.
- [55] Bhandari, M.; Kumar, P.; Bhatt, P.; Simsek, H.; Kumar, R.; Chaudhary, A.; Malik, A.; Prajapati, S. K. An integration of algae-mediated wastewater treatment and resource recovery through anaerobic digestion. *J. Environ. Manage.* **2023**, *342*, 118159.
- [56] Salama, E.-S.; Hwang, J.-H.; El-Dalatony, M. M.; Kurade, M. B.; Kabra, A. N.; Abou-Shanab, R. A.; Kim, K.-H.; Yang, I.-S.; Govindwar, S. P.; Kim, S.; Jeon, B.-H. Enhancement of microalgal growth and biocomponent-based transformations for improved biofuel recovery: A review. *Bioresour. Technol.* **2018**, *258*, 365-375.
- [57] Su, G.; Ong, H. C.; Ibrahim, S.; Fattah, I. R.; Mofijur, M.; Chong, C. T. Valorisation of medical waste through pyrolysis for a cleaner environment: Progress and challenges. *Environ. Pollut.* **2021**, *279*, 116934.
- [58] Ong, H. C.; Chen, W.-H.; Singh, Y.; Gan, Y. Y.; Chen, C.-Y.; Show, P. L. A state-of-the-art review on thermochemical conversion of biomass for biofuel production: A TG-FTIR approach. *Energy Convers. Manag.* **2020**, *209*, 112634.
- [59] Su, G.; Ong, H. C.; Mofijur, M.; Mahlia, T. I.; Ok, Y. S. Pyrolysis of waste oils for the production of biofuels: A critical review. *J. Hazard. Mater.* **2022**, *424*, 127396.
- [60] Zaidi, A. A.; Khan, A.; AlMohamadi, H.; Anjum, M. W.; Ali, I.; Naqvi, S. R.; Kokuryo, S.; Miyake, K.; Nishiyama, N. Catalytic pyrolysis of rice husk over defect-rich beta zeolites for biofuel production. *Fuel* **2023**, *348*, 128624.
- [61] Azadbakht, M.; Safieddin Ardebili, S. M.; Rahmani, M. A study on biodiesel production using agricultural wastes and animal fats. *Biomass Convers. Biorefin.* **2021**, 1-7.
- [62] Peralta-Yahya, P. P.; Keasling, J. D. Advanced biofuel production in microbes. *Biotechnol. J.* **2010**, *5*, 147-162.
- [63] Mansir, N.; Taufiq-Yap, Y. H.; Rashid, U.; Lokman, I. M. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Convers. Manag.* **2017**, *141*, 171-182.
- [64] Kiss, A. A.; Dimian, A. C.; Rothenberg, G. Solid acid catalysts for biodiesel production-towards sustainable energy. *Advanced Synthesis & Catalysis* **2006**, *348*, 75-81.
- [65] Kulkarni, M. G.; Gopinath, R.; Meher, L. C.; Dalai, A. K. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chem.* **2006**, *8*, 1056-1062.
- [66] Sani, Y. M.; Daud, W. M. A. W.; Aziz, A. A. Activity of solid acid catalysts for biodiesel production: a critical review. *APPL. CATAL. A-GEN.* **2014**, *470*, 140-161.
- [67] Melero, J. A.; Iglesias, J.; Morales, G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chem.* **2009**, *11*, 1285-1308.
- [68] Jacobson, K.; Gopinath, R.; Meher, L. C.; Dalai, A. K. Solid acid catalyzed biodiesel production from waste cooking oil. *Appl. Catal. B-Environ.* **2008**, *85*, 86-91.
- [69] Su, F.; Guo, Y. Advancements in solid acid catalysts for biodiesel production. *Green Chem.* **2014**, *16*, 2934-2957.
- [70] Vasić, K.; Hojnik Podrepšek, G.; Knez, Ž.; Leitgeb, M. Biodiesel production using solid acid catalysts based on metal oxides. *Catalysts* **2020**, *10*, 237.
- [71] Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; Goodwin, J. G. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353-5363.
- [72] Canakci, M.; Van Gerpen, J. Biodiesel production via acid catalysis. *Trans. ASABE* **1999**, *42*, 1203-1210.
- [73] Gerçel, H. F.; Pütün, A. E.; Pütün, E. Hydropyrolysis of extracted *Euphorbia rigida* in a well-swept fixed-bed tubular reactor. *Energy Sources* **2002**, *24*, 423-430.
- [74] Ma, F.; Hanna, M. A. Biodiesel production: a review. *Bioresour. Technol.* **1999**, *70*, 1-15.
- [75] Kusdiana, D.; Saka, S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel* **2001**, *80*, 693-698.
- [76] Ul Haq, Z.; Tahir, K.; Aazam, E. S.; Almarhoon, Z. M.; Al-Kahtani, A. A.; Hussain, A. A.; Nazir, S.; Khan, A. U.; Subhan, A.; Ur Rehman, K. Surfactants assisted SiO<sub>2</sub>-Cu@Fe<sub>2</sub>O<sub>3</sub> nanofibers: Ultra efficient photocatalyst for photodegradation of organic compounds and transesterification of waste edible oil to biodiesel. *Environ. Technol.*



*Innov.* **2021**, *23*, 101694.

- [77] Athar Hussain, A.; Nazir, S.; Ullah Khan, A.; Tahir, K.; Albalawi, K.; Ibrahim, M. M.; Almarhoon, Z. M.; Al-Shehri, H. S.; Mersal, G. A. M.; Mohammed Aldawsari, A. Preparation of zinc oxide graphed nickel incorporated mesoporous SBA-16 doped graphene oxide: An efficient catalyst for transesterification of waste edible oil to biodiesel and photocatalytic degradation of organic dyes. *Inorg. Chem. Commun.* **2022**, *139*, 109379.
- [78] Guan, G.; Kusakabe, K.; Sakurai, N.; Moriyama, K. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. *Fuel* **2009**, *88*, 81-86.
- [79] Cheirsilp, B.; Aran, H.; Limkatanyu, S. Impact of transesterification mechanisms on the kinetic modeling of biodiesel production by immobilized lipase. *Biochem. Eng. J.* **2008**, *42*, 261-269.
- [80] Antolin, G.; Tinaut, F.; Briceno, Y.; Castano, V.; Perez, C.; Ramirez, A. Optimisation of biodiesel production by sunflower oil transesterification. *Bioresour. Technol.* **2002**, *83*, 111-114.
- [81] Leung, D. Y.; Wu, X.; Leung, M. K. H. A review on biodiesel production using catalyzed transesterification. *Appl. Energy* **2010**, *87*, 1083-1095.
- [82] Fukuda, H.; Kondo, A.; Noda, H. Biodiesel fuel production by transesterification of oils. *J. Biosci. Bioeng.* **2001**, *92*, 405-416.
- [83] Kulkarni, M. G.; Dalai, A. K. Waste cooking oil an economical source for biodiesel: a review. *Ind. Eng. Chem. Res.* **2006**, *45*, 2901-2913.
- [84] Lam, M. K.; Lee, K. T.; Mohamed, A. R. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnol. Adv.* **2010**, *28*, 500-518.
- [85] Pisarello, M. L.; Querini, C. A. Catalyst consumption during one and two steps transesterification of crude soybean oils. *Chem. Eng. J.* **2013**, *234*, 276-283.
- [86] Saini, J. K.; Saini, R.; Tewari, L. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. *3 Biotech* **2015**, *5*, 337-353.
- [87] Duc, P. A.; Dharanipriya, P.; Velmurugan, B. K.; Shanmugavadivu, M. Groundnut shell-a beneficial bio-waste. *Biocatal. Agric. Biotechnol.* **2019**, *20*, 101206.
- [88] Hoffman, S. M.; Alvarez, M.; Alfassi, G.; Rein, D. M.; Garcia-Echauri, S.; Cohen, Y.; Avalos, J. L. Cellulosic biofuel production using emulsified simultaneous saccharification and fermentation (eSSF) with conventional and thermotolerant yeasts. *Biotechnol. Biofuels* **2021**, *14*, 157.
- [89] Zhang, W.; Lin, Y.; Zhang, Q.; Wang, X.; Wu, D.; Kong, H. Optimisation of simultaneous saccharification and fermentation of wheat straw for ethanol production. *Fuel* **2013**, *112*, 331-337.
- [90] Diah, K.; Joni, P.; Endang, S.; Sumi, H. Biohydrogen production through separate hydrolysis and fermentation and simultaneous saccharification and fermentation of empty fruit bunch of palm oil. *Res. J. Chem. Environ.* **2018**, *22*, 193-197.
- [91] Chacón, M. G.; Ibenegbu, C.; Leak, D. J. Simultaneous saccharification and lactic acid fermentation of the cellulosic fraction of municipal solid waste using *Bacillus smithii*. *Biotechnol. Lett.* **2021**, *43*, 667-675.
- [92] Datta, A.; Hossain, A.; Roy, S. An overview on biofuels and their advantages and disadvantages. *Asian J. Chem.* **2019**, *31*, 1851-1858.
- [93] Viesturs, D.; Melece, L. Advantages and disadvantages of biofuels: observations in Latvia. Latvia University of Agriculture, 2014.
- [94] Sipra, A. T.; Gao, N.; Sarwar, H. Municipal solid waste (MSW) pyrolysis for bio-fuel production: A review of effects of MSW components and catalysts. *Fuel Process. Technol.* **2018**, *175*, 131-147.
- [95] Cappelli, G.; Yamaç, S.; Stella, T.; Francone, C.; Paleari, L.; Negri, M.; Confalonieri, R. Are advantages from the partial replacement of corn with second-generation energy crops undermined by climate change? A case study for giant reed in northern Italy. *Biomass and Bioenergy* **2015**, *80*, 85-93.
- [96] Clark, J. H. Green chemistry for the second generation biorefinery-sustainable chemical manufacturing based on biomass. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 603-609.
- [97] He, C. W. The current situation of the development of biofuels and main technical problems. *Adv. Mat. Res.* **2014**, *827*, 244-249.
- [98] Mofijur, M.; Masjuki, H.; Kalam, M.; Atabani, A. E. Evaluation of biodiesel blending, engine performance and emissions characteristics of *Jatropha curcas* methyl ester: Malaysian perspective. *Energy* **2013**, *55*, 879-887.
- [99] Asghar, R.; Sulaiman, M. H.; Mustaffa, Z.; Ullah, N.; Hassan, W. The important contribution of renewable energy technologies in overcoming Pakistan's energy crisis: Present challenges and potential opportunities. *Energy Environ.* **2022**, *34*, 3450-3494.



- [100]Ahmad, A.; Ashfaq, M.; Rasul, G.; Wajid, S. A.; Khaliq, T.; Rasul, F.; Saeed, U.; Rahman, M. H.; Hussain, J.; Ahmad Baig, I. Impact of climate change on the rice-wheat cropping system of Pakistan. In *Handbook of Climate Change and Agroecosystems*; World Scientific, 2015; pp 219-258.
- [101]Anwar, A.; Younis, M.; Ullah, I. Impact of urbanization and economic growth on CO<sub>2</sub> emission: a case of far east Asian countries. *Int. J. Environ. Res. Public Health* **2020**, *17*, 2531.
- [102]Bapat, D.; Kulkarni, S.; Bhandarkar, V. *Design and Operating Experience on Fluidized Bed Boiler Burning Biomass Fuels with High Alkali Ash*; American Society of Mechanical Engineers: New York, NY (United States), 1997.
- [103]Hall, D.; Rosillo-Calle, F.; Woods, J. In *Biomass, its importance in balancing CO<sub>2</sub> budgets*, Biomass for energy, industry and environment, 6th EC Conference, Elsevier Science London: 1991; pp 89-96.
- [104]Shukla, P. In *Biomass energy future for India*, Proceedings of International Workshop, Rio De Janeiro, Brazil, 1997.
- [105]Pattanaik, L.; Naik, S. N.; Hariprasad, P. Valorization of waste *Indigofera tinctoria* L. biomass generated from indigo dye extraction process-potential towards biofuels and compost. *Biomass Convers. Biorefin.* **2019**, *9*, 445-457.
- [106]Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G.; Morgan, T. J. An overview of the organic and inorganic phase composition of biomass. *Fuel* **2012**, *94*, 1-33.
- [107]Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40-76.
- [108]Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel* **2013**, *105*, 19-39.