

TRANSFORMATION OF AGRICULTURAL AND FOOD WASTE INTO NANOPARTICLES FOR BIOFUEL PRODUCTION

Abstract

The agricultural industry produces a huge amount of waste, the majority of which is not used efficiently and poses a threat to the environment and human health. Agro-residues have a potential future in the agri-food-pharma industries, which has led to the development of numerous bioproducts and novel physiologically active compounds through the application of valorization processes. Development of bioproducts from agro-waste has been the subject of extensive research in recent years. The generation of biofuels is currently improved through the use of nanocapsules. The organic components of food and agricultural waste provides it a large potential to be converted into a form that can be used to make biofuels. Researchers are figuring out how to make biofuels that might be more advantageous. The current review evaluates the potential use of food and agricultural waste in nanocomposites or other nanoparticles for the generation of biofuels.

Keywords: Agro-residue, Food residue, Bioproducts, Biofuels, Nano capsules, Nanocomposites

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I. INTRODUCTION

Once the primary use of the product has been done, the useless, unwanted, and disposed of products that cannot be further used for their primary goal are called wastes. Either dispose of or is intended to degrade or decompose while meeting the standards framed by the national governing authority. [1] High-value products or resources can be derived by implementing optimum innovation that a fuel cell increases the value of the products greater than zero. Not only as a byproduct of the final intended use but also as wastes generated recycling or extraction of raw materials to intermediate or final products [2]. With the traditional thought, wastes are defined as chemically toxic or radioactively harmful or esthetically offensive either in any of the three states of matter including solid, liquid, or gaseous state. Some wastes also orient to repress temporarily and some are indefinitely isolated [3].

With the increase in population growth and industrialization, it has been a continuous demand for a sustainable source of energy with a limited number of resources. 80% of the total global energy demands 80% of this demand has been fulfilling by fossil fuels, which is the primary resource for energy. And from this share of total energy, 58% has been consumed by the transport sector [4, 5]. We all are aware of the fact that this source of energy is not promising and future-oriented. Various questions have been raised on energy security with today's concerns regarding the environment and economics. Researchers are studying various alternatives such as biofuels mainly biodiesel and bioethanol over the traditional source of fossil fuels [6-10].

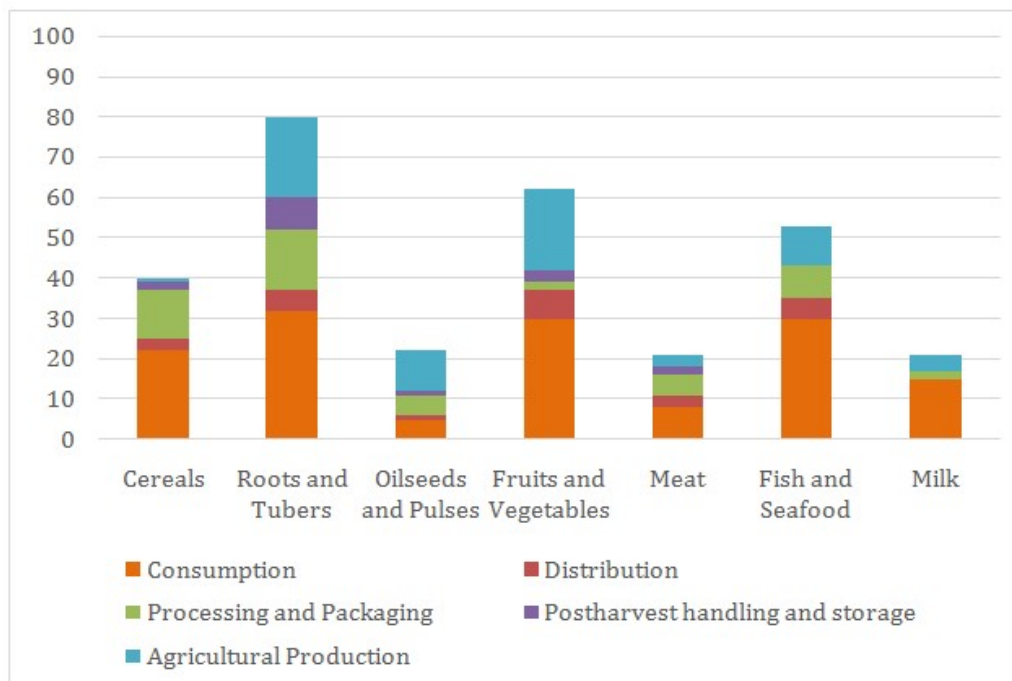


Figure 1: North American Food Losses and waste in percentage for each steps of supply chain for different agricultural commodities [13]

United Nations stated in their Environment Program that there is approximate production of 11.2 billion tons every year, and not only results in degrading environment but also have adverse effects on health, mainly in developing countries, where less than 10% of the total waste is optimized, otherwise openly dumped or burned [11]. Throughout the process from farm to fork, approximately half of the total food is wasted [12, 13]. The following figure discusses food losses at steps of the food supply chain of different commodities (figure 1).

Share of edible food varies on various parameters like geographic conditions, commodity, and step of supply chain and mainly on the quantity of food produced and wasted throughout the process from farm to fork, which remains an unsolvable challenge across the globe. With the estimated population of 9.8 billion by 2050, it is very important to make a breakthrough in technological advancement that possesses the promising solution to tackle this challenge of food waste at different levels throughout the processing levels [14].

The current source of energy that is fossil fuels comprising of coal, oils, and gasoline [15] is limited by the sustainability for the future generation due to the limited amount of fossil fuel which results in the continuous increase in the price along with damaging the environment [16]. The challenges with the current sources of energy include high emission of greenhouse gases, change in climate conditions across the globe and the continuous increases in the energy demand made it important for scientists around the world to find a permanent solution that replaces fossil fuels as the major sources of energy. With recent studies, researchers have come with the solution of using biomass, the renewable source of energy carriers [17] and accounts for approx. 80% of the total renewable energy produced. This helps to generate heat energy, biofuels, and electricity whenever required. This source of energy is termed bioenergy which consists either of solid, liquid, or gaseous fuels originated from the biological source.

Nowadays in developed and some developing countries, the use of biofuels is getting common. For example, in the countries like USA and Brazil, an otto-cycle engine, ethanol (either in pure or mixed with gasoline) is a successful alternative for non-renewable resources of energy. Another important example is biodiesel, and due to its technical, strategic and environmental advantages is a promising fuel to be used in diesel engines [18].

Productions of biodiesel and bioethanol from feedstock have been practiced in different countries and these fuels are called first-generation biofuels [19, 20]. Production of these first-generation biofuels requires a huge amount of feedstock mainly corn, vegetable oil, and animal fats [21]. These ingredients for the production of biofuels are limited due to their common uses and therefore the attention is being drawn to the use of non-feedstock alternatives like wood, food, or agricultural wastes for the production of biofuels [22].

II. WASTES

Sources and Types of Wastes

- 1. Agricultural Wastes:** Leftovers from pre-harvesting, during harvesting and post-harvesting of agricultural products like crops, fruits, vegetables, dairy, meat, poultry, and all the other activities involve or related to the agriculture regardless of being organic or

inorganic either in any of the three states or lubricants depending on the nature of their activity are defined as agricultural wastes. Moreover, these wastes inhibit a vital role in global agricultural productivity [23]. Agricultural wastes altogether sum up to a great share of more than 30% of the total global agricultural production [24]. The recent trend in the production of biofuels from agricultural waste is in-depth research.

Table 1: Chemical Composition of common agricultural residues and wastes

Type of biomass	Lignocellulosic substrate	Cellulose %	Hemicellulose %	Lignin %
Agricultural wastes	Corn cobs	45	35	15
	Wheat straw	30	50	15
	Barley Straw	33-40	20-35	8-17
	Corn Stover	39-42	22-28	18-22
	Nutshell	25-30	25-30	30-40
Industrial Wastes	Waste paper from chemical pulps	60-70	10-20	5-10
	An organic compound from wastewater solids	8-15	0	0
Forestry Crops	Hardwood stems	40-55	24-40	18-25
	Softwood stems	45-50	25-30	25-35
	Leaves	15-20	80-85	0
Energy Crops	Empty fruit bunch	41	24	21.2
	Switchgrass	45	31.4	12

2. Industrial Wastes: One of the major causes of pollution as these are produced in really high amounts, Industrial wastes should be optimized to decrease biological burden [25]. The causative factors of these industrial wastes mainly include recovery from industrial wastes, especially from firms involved in metallurgy and mining, ultimately converted to hydraulic loads, further being disposed of underground [26]. Wastes from industries must be complying with the regulations formed by the governing authority and must be compatible with the flow of sewage pollution without increasing the burden to the same. Industrial wastes must comprise of some particular properties like it should be non-toxic or harmful to the operating protocols of the treatment plant material, to the individual assigned for servicing, or to the surroundings near the septic tank [27] (Table 1). Directly or indirectly affects the flora and fauna of the operational procedure of sewers or treatment plants as these industrial wastes are directly dumped or discharge into the sewers, ultimately connected to the natural water bodies. Targeting these industrial wastes, Municipal wastewater treatment plants are designed in such a way that these discharges are neutralized before being disposed of into nature [28].

Depending on the nature of the wastes, industrial wastes are subcategorized into two types, hazardous and non-hazardous. Mainly produced from cardboard, stone, iron, plastic, glass, and other organic wastes, non-hazardous industrial wastes do not cause any damage to health and the environment. On the other side, wastes such as flammable, biodegradable, and hazardous materials which can cause harm to public health as well as

the environment are hazardous industrial wastes [29]. Moreover, these industrial wastes can either be recyclable or non-recyclable, which is good for landfills [30].

III. ENVIRONMENTAL PROBLEMS CAUSED BY WASTES

- 1. Agricultural Waste Problems:** Emission of greenhouse gases from agricultural machinery and wastes is normal in most of the developing countries causing air pollution, along with the major source of land and water pollution. While talking about water pollution, when this polluted water meets the drinking water, infect it and making it fatal for humans [31]. Not only severe water but also soil pollution is observed in and around regions where agricultural activities are being practiced, with the causative factors mainly include pesticides, insecticides, fungicides, and fertilizers. Along with these as common sources, agricultural activities also increase the level of nitrates in the environment [33]. In the past few decades, agriculture has been one of the main sources of pollution whose effects are last long and possess universal consequences [32].
- 2. Industrial Waste Problems:** The major cause of environmental pollutions is industrial pollution. With many advantages of industrialization, the disadvantage is making it the core source of pollution causing damage to agricultural land as well as the environment. Water released from industries like sugarcane, resin, textiles, oxalic acid, viscous, and latex is more often used for agricultural purposes [34, 35]. Moreover, other than this biogas along with biowastes with other components like sewages, sediments, and muds are used for enhancing plant production and cutting down various other costs including expense on fertilizers [35]. Various other activities are being practiced such as emission and extraction, combustion of fossil and fossil fuels along with the utilization of other inorganic and chemicals which pose risks, to the environment and the living population across the region. Common people must be aware of these risks from industrial wastes have been causing severe damage to the environment whose after-effects can be many years later after the cause [36].

IV. CHARACTERIZATION OF NANOMATERIALS

Nanomaterials are particles very minute in size, whose one dimension is lesser than 100nm or 10^{-9} m, mainly composed of three different layers:

- the outermost layer or surface layer
- the inner layer or shell layer &
- the main core i.e., the nanoparticles themselves.

These layers possess different physiochemical properties at their atomic or molecular level. Few important physio-chemical properties of nanoparticles that make the characterization of these particles more challenging are listed below:

- Minute size
- Easy data interpretation
- The high-quality production of nanoparticles at a laboratory scale
- easier to estimate the concentration of nanoparticles in in-situ and ex-situ reactions

It is quite difficult to compile all these basic properties but unavailability of the sample preparation method and lack of calibration of analytical tools with suitable references make the synthesis a more tedious process. Range of diffractographic and spectroscopic techniques like Raman Spectroscopy, x-ray photoelectron spectroscopy, energy dispersive spectroscopy, dynamic light scattering spectroscopy, UV-visible spectroscopy, and X-ray diffraction are being used to evaluate the characteristics of nanoparticles been synthesized.

V. NANOPARTICLES SYNTHESIS USING DIFFERENT WASTES

Synthesis of nanomaterials using industrial wastes has a broad range of development in special technologies and handling procedures [38]. Many successful types of research are done to synthesize nanoparticles using agricultural waste regardless of being natural or artificial like empty grapes, grapes, corn, cotton, straw, wheat, orange, or banana [37].

- 1. Nano-Cellulose:** Nano-sized cellulose materials are being produced utilizing materials and agricultural-based wastes from durable material industries. Cellular nano-crystals (CNCs) and nano-fibrillated cellulose (NFCs) are two groups of nano-celluloses (NCs), which are generally referred to as the second generation of renewable resources for oil products. High mechanical and low density with being renewability and biogas properties are considerable factors of this second-generation nano-cellulose that draws the attention of the researchers [39]. Inhabiting these futuristic properties, nano-cellulose is being center of attraction of many pieces of research [40]. Many applications are developed in past few years. Two main core studies are (i) to examine the structures of lingo-cellulose-based biomass and their relationship between structure and nano-cellulose properties and (ii) pre-biological treatment and process to extract nano-cellulose [41].

Nano-zulose is produced using the most efficient source as banana bark which is the most abundant and common waste available throughout the globe. Designing the hybrid packaging material, different layers of nano-particles resemble the characteristic features of various layers of the pseudo banana tree as the primary agenda of the study. [42]. Different processes which involve the production of hydrocarbons mostly result in causing environmental damage including sulfur-containing wastewater generation. Therefore, a different alternative approach for the synthesis of nano-cellulose crystals utilizing industrial wastes is made using this common sulfuric acid [43].

- 2. Metals and Metal Oxides Nanoparticles:** Different wastes help in the synthesis and improving the properties of metals and metal oxide nanoparticles. For example, papaya leaves are used as a lingo-cellulosic agricultural waste is used for the production of Fe_3O_4 by the simple thermal decomposition method [44]. Utilizing different plant systems for synthesizing nanoparticles is an easy, environment-friendly, cheap, exciting, and promising way when compared to others. As roots act as the food reservoir for the plants, they are a good source of enzymes, terpenoids, proteins, flavonoids, alkaloids, and other organic- inorganic compounds which plays a vital role as they act as closing and stabilizing agents as well as a decreasing concentration of metal ions in target nanoparticles [45].

Researchers have successfully derived 13.8nm SiO₂ nanoparticles as the source of silica obtained from bamboo leaves; they consider it as a promising and valuable alternative for many medical applications like drug delivery [46].

20nm SiO₂ NPs are obtained as the product of combining banana peel extract to an alkaline solution of tetraethyl orthosilicate in ethanol and then followed by calcination of the solution [47].

TiO₂ powder gel is derived from titanium tetra isopropoxide at 200°C at pH=7 for 5 hours producing TiO₂ solution, whose size is then controlled by using sugarcane baggage [48].

Another example is the utilization of banana peel for enhancing the properties of Mn₃O₄ nanoparticles by preventing the agglomeration of resulting produce by reducing KMnO₄ to Mn₃O₄ formation [49]. Hydrated aluminum nanoparticles are produced by combined precipitation of NaOH and aluminum sulfate in the presence of polyacrylamide and tea wastes. The porosity of these aluminum nanoparticles helps in the exchange of fluoride anions with sulfate to neutralize drinking water [50].

In recent studies, researchers have developed an innovative method for utilizing naturally occurring green and carbon-based wastes including animal wastes, vegetable wastes, and semi-industrial wastes. For example, the newspaper for the synthesis of high-quality graphene oxide and reduced graphene oxide sheets [51].

- 3. Carbon Nanoparticles:** There are few methods for the synthesis of nano-carbons, but the most efficient way is by producing nanotubes from different wastes in a reactor and thermal system. All the materials in the reactor are dispersed into nanoparticles by losing their macroscopicity because of high temperature (more than 700°C) and high pressure along with some specific catalyst for different intervals [52]. On the other hand, the production of nano-carbons is done below a thin sheet of charcoal with the help of some physical activity at high temperature by controlled pyrolysis of residues derived from acrylic fibers [53]. Lactic acid-produced carbon nanotubes have been studied for biodegradability and nano-composite therefore in the end these carbon nanotubes can directly be disposed of into the environment [54].

As the function of laser energy, laser pyrolysis of hydrocarbons in flow reactor for the production of carbon nanoparticles have been studied [55].

Nitrogen-doped porous nano-sheets (N-PCN) are synthesized by utilizing magnesium hydroxide sheets comprehending the use of waste plastics. These nitrogen-doped porous nano-sheets are then improved using zinc and cobalt bimetallic zeolite imidazolate frame nanoparticles including polystyrene whose basic form is carbon [56]. Another example of utilizing plastic wastes is using polyethylene terephthalate (PET) wastes for the production of polygonal carbon nanotubes (MWCNTs) and nano-channeled ultra-fine carbon tubes (NCUFCTs) by spinning cathode technique. At 1700°C, structured in a low-temperature area of an anode, carbon black covers nano-sized ultra-fine individual solid carbon spheres (SCSs) with a mean radius of 110nm and 50nm are manufactured [57].

Supported by groove SiC nanowires, the decomposition of methane into Ni nanoparticles results in the production of Carbon bound nano-fibers, and these nanofibers can grow parallel from a packet of single CNFs [58]. Tea wastes help in the formation of carbon nanoparticles and if they get carbonated, can help to reduce metal oxides, as they comprise a great concentration of potassium, carbon, and nitrogen while limited in phosphorus [59]. Non-biodegradable like propylene, polyethylene, PVCs, polystyrene, etc. have a huge share of municipal wastes contributing millions of tons of them dumped or incinerated into the environment. On the other hand, researchers have found different methods to utilize these agricultural wastes as raw materials for the manufacturing of high valued products like carbon nanotubes, biofuels, and porous carbon emission [60].

- 4. Silica and Graphene Nanoparticles:** Silica nanoparticles are synthesized by using the traditional method is quite tedious and complex, also executed at very high temperature whereas using an easy process of carbothermal reduction in which different sized silica nanoparticles can be produced by disposable boxes, plastic bottles, and other plastic wastes [61]. A researcher also claimed for developing PV cells using silicon produced by utilizing agricultural wastes, and an improved sol-gel method is used to produce agro-based silicon nanoparticles, ultimately reducing the produce to magnesium to produce nanoparticles [62].

As the conventional method for the synthesis of silica nanoparticles is quite tedious and complex because it requires a very high temperature. Silica nanoparticles varying in sizes are obtained from disposal boxes and plastic wastes like water bottles by a simple method of carbothermal reduction [61]. Moreover, another process that utilizes some agricultural waste as an abundant source of silicon that can be used by PV cells for the synthesis of silica nanoparticles is developed by a researcher. The modified soft gel method helps to synthesize agro-based silicon nanoparticles, which are then reduced using magnesium to synthesize silicon nanoparticles [62]. Effective electrical, optical and physical properties of a nano-composite material derived from silver nano-particles and graphene oxide and particle size ranges from 60 to 100nm. The higher electrical conductivity and optical transparency of this material is being reflected by its permeability and electrical resistance when compared with virgin graphene oxide [63]. Various agro-wastes like rice straw, rice husk, and bamboo leaves intend easy synthesis of nanoparticles as these wastes are produced and disposed of in the environment which has been a great concern. To overcome this issue, vermicomposting with *Amelia's (Eisenia foetida)* uses rice husk, sugarcane baggage, and coffee nuts, which helps in the production of silica nanoparticles, which are recovered by calcined of the humus [64].

- 5. Bimetallic Nanoparticles:** Bimetallic nanoparticles have high reactivity when compared to single metal counterparts. Platinum-gold and platinum-bismuth are some common examples of these bound nanoparticles and are used for biomass conversion [65-69]. The distribution of each element and method of synthesis affects the crystal structure of these bimetallic nanoparticles, probably different from bulk alloy. The method used for the production of these nanoparticles is either decomposition, co-reduction, or successive reduction and the method of production controls the morphology of the nanoparticles. Let us discuss in brief these methods of nanoparticle synthesis:

- The process in which a great difference in the reduction potential in metal ion precursor is used for nanoparticles synthesis is called successive reduction.
 - The process in which reduction of two corresponding metals ions takes place simultaneously, as first the metal ion which possesses higher negative reduction potential is reduced and then followed by another metal with lower negative reduction potential in the presence of a stabilizing ligand is called co-reduction.
 - And the process in which metal ions are heated in different ratios, in stabilizer's presence nanoparticles are produced is called thermal decomposition. High temperature and change in nucleation are two important parameters that affect this method [65-69].
 - Production of bimetallic clusters is supported by the reduction in metal salts [68].
- 6. Synthesis of Semiconductor Nanoparticles:** Due to the specific shape and size-dependent properties and reactivity, semiconductor nanomaterials have several industrial applications as the size of the semiconductors greatly affects their band gaps and making it a very important step to control size during the synthesis. The relation between the bandgap and size is inversely proportional thus larger the size of the semiconductor nanomaterial lesser the bandgap is and vice versa. The center of many pieces of research aims for the production of monodisperse crystalline particles, pure form of these semiconductor nanoparticles as the specific method was needed to be identified until a method which involves precipitation from a colloidal solution developed recently [70-73]. Other methods used sol-gel systems or a polymer as a host for the synthesis [70]. Another method discusses the use of high-temperature organometallic anaerobic synthesis of these semiconductor nanoparticles [73].

VI. ENVIRONMENTAL APPLICATIONS OF THE NANOPARTICLES PRODUCED USING DIFFERENT WASTES

Pollution is proved as the biggest origin of many bigger problems posing threat to life on Earth [74]. What would be better than decreasing the environmental pollution while utilizing the wastes generated from different commodities? Nano-cellulose is a very promising option to solve environmental threats and challenges. With a diameter less than 10nm, nano-cellulose claims several unique properties like low visual light scattering, large area, and high mechanical strength. And these main properties of nano-cellulose open the gate for a variety of new gels, films, composites, and materials [74-76].

Membranes, photocatalyst, flocculent, adsorbent are some properties, and the application of cellulose nanoparticles is discussed in the review article [77]. Various engineering and environmental applications such as oil extraction, flame retardation, filtration, and water purification are being carried out using nano-cellulose aerogels [78]. With its unique morphology and characteristics like excellent solubility in most solvents, natural diversity, and low toxicity, this nano-cellulose has proved itself a promising approach for a successful and sustainable way of fighting various challenges. Not only these chemical properties but being environmentally friendly, inexpensive, highly convenient, and easy to use also makes this approach of making nano-lotus for the generation of natural renewable energy storage [79].



Figure 2: Various applications of nanotechnology [80]

VII. APPLICATIONS OF NANOPARTICLES IN BIO-RENEWABLES FORMATION

Many biomass conversions have been catalyzed by metallic nanoparticles along with semiconductor and bimetallic nanoparticles (figure 2). When comparing traditional catalysts with nanoparticles, the latter inhibits a great impact on green technologies because of their size-dependent properties. Production of biodiesel, hydrolysis of cellulosic materials, and decarboxylation of fatty acids, and conversion of sugars are some of the many reactions which can be catalyzed by nanoparticles along with being used in a fuel cells for technological advancement. In other bio-renewable transformations like molecule oxidation and hydrogenation, the type of nanoparticles plays a crucial role [80-100].

- 1. Conversion of Sugars:** In the process of conversion of sugars, ruthenium nanoparticles are found much effective as catalysts. For example, hydrogenolysis to ethylene glycol and propylene glycol from sorbitol, carbon nanoparticles are being supported by Ru (Ruthenium nanoparticles) enhancing the reaction [101,102]. A proposed mechanism is shown in figure 3 [102]. Wet impregnation, calcination, fuel cells, and reduction methods are used to synthesize Ru (Ruthenium nanoparticles) on carbon nanofibers. Studies are still going on assessing the effects of calcination on catalyst properties designated as Ru/CNF- 180°C, Ru/CNF- 240°C, Ru/ CNF-300°C as a catalyst to be led at 180, 240, and 300°C for 5 hours respectively.

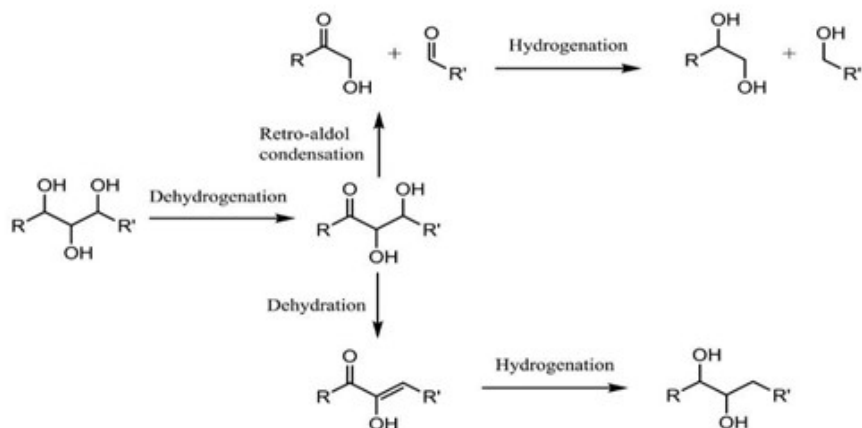


Figure 3: Mechanism showing polyol hydrogenolysis of sorbitol to ethylene glycol and propylene glycol

- 2. Production of Hydrocarbons:** Naturally, hydrocarbons are derived from raw oils and biomass but because of structural differences between the two, it is more difficult yet essential to derive them from biomass, a renewable source. Dumesic's group studies several methods for producing monofunctional hydrocarbons such as hydrophobic alcohols, ketones, carboxylic acids, and heterocyclic compounds by the conversion of sugars and polyols using catalyst Pt-Re, while these catalysts are not to nanoscale, understanding catalyst process and production of nanoparticles. Pt-Re catalyst is produced by controlling the C-O and C-C bond cleavage due to which different monofunctional nanoparticles are created. For the conversion, oxygen atoms need to be eliminated from biomass-derived carbohydrates like sorbitol and glucose and synthesized by controlling the rate of bond cleavage between C-C and C-O atoms, ultimately producing different monofunctional hydrocarbons. Isomerization and C-C coupling process are used to achieve the target as the process increases the weight of jet fuels and diesel by increasing the side hydrocarbons chains.

The remaining fuels are deoxygenated by a sufficient amount of hydrocarbons sources by polyols or sugars. Throughout the process reaction, 90% or even greater amount of energy is contained by the parts of polyols/sugars after the reformation in the presence of Pt-Re catalyst and this reformation leads to the formation of carbon dioxide, which is a crucial factor for the formation of monofunctional hydrocarbons from polyols/sugars as the hydrogen is required for the deoxygenation and also produced during the reaction as a byproduct. Water-gas shift reaction is also led by the reformation process during which catalyst's surface adsorbs the carbon monoxide ultimately reacts to the water to produce hydrogen and carbon dioxide gases. When compared the cleavage of the C-C atom with the C-O atom, the latter one is favored by the oxygenated reactions intermediates resulted from the highly adsorbed carbon monoxide [104]. The hydroxyl groups and oxygen binds strongly to Re, and this oxygen promotes hydrogenolysis

reaction by increasing the rate of C-O bond cleavage [105]. The effect of Re in the Pt-Re-C catalyst mediates the presence of hydroxyl and oxygen in the hydrocarbon [106].

Above 770 K, chemicals and fuels are produced from biomass [107]. Liquid products like olefins, alkenes, and aromatics with appropriate molecular weight for transportation fuels produced from the catalytic conversion of sorbitol and glucose in the presence of Pt-Re.

- 3. Decarboxylation of Fatty Acids:** As bio-renewables are the perfect replacements for fossil fuels which make the hydrocarbons from reduced biofuels, also the process is compatible with current technology advances [108,109]. There are several disadvantages of these oxygenated biofuels containing alkyl esters of long-chain fatty acids including low energy density, high cloud point, high pour point, and the potential for compatibility with the present delivery system [110]. Mechanism of the deoxygenation of fatty acids involves decarboxylation, decarbonylation, and full reduction of hydrogen, further elaborated with the following reaction (figure 4) [111].

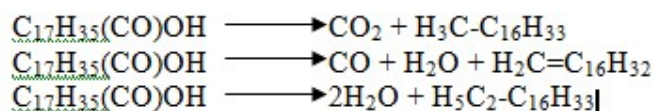


Figure 4: Deoxygenation of fatty acids pathways

- 4. Green Methodologies for Nanomaterials Synthesis:** An area of research has been opened to tackle the disadvantages associated with different physical and chemical methods using green and environmental technologies [112-113].

The idea of utilizing microorganisms such as actinomycetes, yeasts, fungi, algae, protists, and bacteria for the biosynthesis of inorganic materials derives from the efforts of many researchers as the process is simple, cost-effective, and environmentally friendly [114].

Prokaryotic bacteria can also help to synthesize inorganic materials either intracellularly (inside the cells) or extracellularly (outside the cells). For example, calcium carbonate and gypsum can be synthesized by S-layer bacteria, magnetite nanoparticles can be synthesized by magnetotactic bacteria, diatoms and eukaryotic organisms (table 2.) can help to produce siliceous nanoparticles [115-117].

Several factors are affecting the anatomy of the nanoparticles like agitation, reaction time, pH, and nature of biological entities. Various co-factors such as capping and stabilizing agent affects the micro-organism based production of green nanomaterials synthesized in vitro and in-vivo conditions [118].

Table 2: Nanomaterials produced from different sources

Source	Nanomaterials synthesized
Cyanobacteria	
<i>Lyngbyama juscula</i>	Cold NPs
<i>Phormidium tenue</i> NTDM05	CdS NPs
<i>Spirulina platensis</i>	Silver NPs
<i>Microchaete</i> NCCU-342	Silver NPs
<i>Lyngbya majuscule</i>	Silver NPs
<i>Cylindrospermum Stagnale</i> NCCU-104	Silver NPs
<i>Anabaena spp.</i> (SAC 12.82)	Silver NPs
<i>Oscillatoria willei.</i> NTDM01	Silver NPs
Green algae	
<i>Tetraselmis suecica</i>	Cold NPs
<i>Caulerpa sernilata</i>	Silver NPs
<i>Chlorella Vulgaris</i>	Cold NPs
<i>Chlorella Vulgaris</i>	Silver NPs
<i>Chlorella pyrenoidusa</i>	Cold NPs
<i>Ulvaadata</i>	Silver NPs
<i>Chlamydomonas reinhardtii</i>	Ag/Au bimetallic
<i>Chlorella pyrenoidusa</i>	Silver NPs
<i>Spirogyra</i>	Silver NPs
<i>Chlorococcum sp.</i> MM11	Iron NPs
<i>Chlorella vulgaris</i>	Palladium NPs
<i>Chlorococcum humicola</i>	Silver NPs
<i>Scenedesmus-24</i>	CdS NPs
<i>Spirogyra submaxima</i>	Cold NPs
<i>Rhizoclonium fonrinale</i>	Cold NPs
Brown Algae	
<i>Sargassum muticum</i>	Silver NPs
<i>Cystoseira baccata</i>	Cold NPs
<i>Sargassum p/agiophyllum</i>	AgCl NPs
<i>Sargassum tenenimum</i>	Cold NPs
<i>Sargassum muricum</i>	ZnO NPs
<i>Sargassum langifolium</i>	Silver NPs
<i>Turbinaria conoides</i>	Cold NPs
<i>Sargassum bovinum</i>	Palladium NPs
<i>Sargassum muticum</i>	Cold NPs
<i>Turbinariaomata</i>	Silver NPs
<i>Bifurcariabifurcata</i>	CuO NPs
<i>Ecklonia cnva</i>	Cold NPs
<i>Sargassum muricum</i>	Fe ₃ O ₄ NPs
<i>Turbinaria conoides</i>	Silver NPs
Red Algae	
<i>Kappaphycus alvarezii</i>	Cold NPs
<i>Calaxauraelongata</i>	Cold NPs

<i>Amphiroafragilissima</i>	Silver NPs
<i>Lemaneafluviatilis (L)</i>	Cold NPs
<i>Aca111hopharaspesfera</i>	Silver NPs
<i>Cracitaria</i>	Ag/Au bimetallic N Ps
<i>Cracitaria edulis</i>	ZnO NPs
Bacteria	
<i>Klebsiella pneunoniae</i>	Cold NPs
<i>Ceobadllus sp. strain /017</i>	Cold NPs
<i>Escherichia coli K12</i>	Cold NPs
<i>Acinetobacter sp. SW30</i>	Cold NPs
<i>Bacillus stearothennophilus</i>	Cold NPs
<i>Bacillus subr:ilis</i>	Silver NPs
<i>Lactobacillus kimchicus DCYSIT</i>	Cold NPs
<i>Lactobacillus casei</i>	Cold NPs
<i>Ceobacillus stearothermophitus</i>	Silver and Cold NPs
<i>Bacillus species</i>	Silver NPs
<i>Pseudomanas alcaliphila</i>	Selenium NPs
<i>Bacillus Inethylo trophic11.s</i>	Silver NPs
<i>Psychrophilic bacteria</i>	Silver NPs
<i>Brevibacteriun1 casei</i>	Silver and Cold NPs
Fungi	
<i>Alten1aria atternata</i>	Cold NPs
<i>Aspergillus clavatus</i>	Cold NPs
<i>Rhizop11s oryzae</i>	Cold NPs
<i>Penicilliun1 citrinum</i>	Cold NPs
<i>Fusariun1 oxysporum</i>	Silver NPs
<i>Alten1aria sp.</i>	Cold NPs
<i>Arthroderna futvuln</i>	Silver NPs
<i>Alten1aria atternata</i>	Platinum NPs
<i>Penicillium chrysogenum</i>	Cold NPs
<i>Neurospora crassa</i>	Cold NPs
Yeast	
<i>Instant high-sugar dry yeasts</i>	Cold NPs
<i>Hansenulapolyomorpha</i>	Cold NPs
Plant Extracts	
<i>Alfalfa.Plants (Medicago sativa)</i>	Cold NPs
<i>Cymbop-0gon citratus</i>	Cold NPs
<i>Tamarindus indica leaves</i>	Cold NPs
<i>Triticum aestivum</i>	Cold NPs
<i>Sesbonia grandiora</i>	Cold NPs
<i>Aloevera plant extra</i>	Cold Nanotriangles
<i>Emblica officinalis fruit extract</i>	Silver and Cold NPs
<i>Panax ginseng leaves</i>	Silver and Cold NPs
<i>Hibiscus rosa-sinensis</i>	ZnO NPs
<i>Green!ea (Camellia sinensis)</i>	ZnO NPs
<i>Fumariaeherba extract</i>	Platinum NPs

<i>Cacumen Platycadi leaf extract</i>	Cold NPs
<i>Trigonel/afoenum graecum</i>	Cold NPs
<i>Euphorbiahirta L. leaf extract</i>	Cold NPs
<i>Altemanthera dentata leaf extraa</i>	Silver NPs
<i>Mussaenda glabrata leaf extract</i>	Silver and Cold NPs
<i>Geranium leaf aqueous extract</i>	Silver NPs
<i>Trigonel/afoenum-graecum extract</i>	TiO ₂ NPs
<i>Thymbra spicata extraa</i>	Silver NPs
<i>Citrus limon (lemon) aqueous extract</i>	Silver NPs
<i>Chrysanthemum indicum leaf extraa</i>	Silver NPs
<i>Glorioso superbo L. leaf extraa</i>	Cerium oxide NPs
<i>Rosa hybrida petal extract</i>	Cold NPs
<i>Origantmmajorana and Citrus sinensis leaf</i>	Silver NPs
<i>Tree oyscer mushroom Pleurotusostreatus</i>	Silver NPs
<i>Artemisia absinthium aqileous extract</i>	Silver NPs
<i>Blackberry, blueberry, pomegranate, and turmeric extracts</i>	Silver and Cold NPs
ViLS	
<i>Tobacco mosaic vinls</i>	Nanowires
<i>Bacteriophages</i>	Relaxometry

VIII. TECHNIQUES OF NANOMATERIAL IMMOBILIZATION

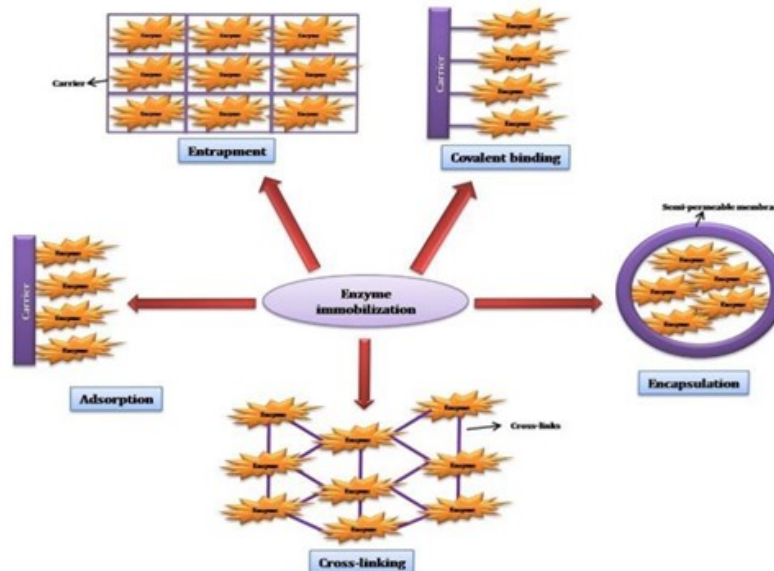


Figure 5: Different enzymes immobilization techniques based on binding capacity

Nanosheets, nanocomposites, nanorods, nanofibers, nanopores, nanoparticles, and various other nanostructures can be used as immobilization catalysts [119-120]. Immobilization techniques can be differentiated based on the binding affinity of the carrier to an enzyme. Different immobilization techniques named cross-linking, covalent bonding, adsorption, encapsulation, and entrapment [121,122] (figure 5), and the efficiency can be improved by any possible combination of these techniques. The various factors that affect the random orientation include the method used for immobilization, nature of biocatalysts, physical properties of support materials, and all these methods have several advantages as well as disadvantages [123].

1. **Adsorption Immobilization:** One of the easiest and conventional technologies used for biocatalyst immobilization is the physical and chemical adsorption of enzymes on the surface support material [124]. The mechanism is based on non-covalent bonding, which is formed by weak electrostatic bonding like hydrogen bond, ionic bond, dipole-dipole bond, and hydrophobic interaction of the enzymes of nanomaterials at optimum pH and ionic strength [125].
2. **Covalent Binding Immobilization:** The linkage via a strong covalent bond, which is formed due to the reactive functional group of the amino acid present on the surface of the enzymes, ultimately binds with the nanoparticles to the carrier, carries out the immobilization [126]. This technique also utilizes unmodified protein.
3. **Entrapment Immobilization:** This technique aims the protection of enzymes from getting denatured and aggregated and takes place in a confined environment through entrapment immobilization, which is based on the reverse Michelle technique and sol-gel chemistry. Entrapment is further subdivided into microencapsulation and gel entrapment is the easiest possible technique [127].
4. **Cross-Linking Immobilization:** As the name suggests the technique uses a multifunctional reagent attached to enzymes and is support-free. There are several reaction conditions under which these are carried out [128]. The advantages and disadvantages of these techniques are also shown in table 3 and the techniques to analyse different nanomaterials has been shown in table 4.

Table 3: Pros and Cons of various immobilization techniques

Immobilization Techniques	Pros	Cons
Adsorption Immobilization	<ul style="list-style-type: none"> • Easy and inexpensive • Reversible • limited or no side effects on biocatalyst • for modification, no additional coupling agent or enzyme is required • k_m values remain substantially unchanged • Increased catalytic activity of mobilized enzymes 	<ul style="list-style-type: none"> • Based on weak reversible interactions between enzymes and carriers. • High profitability in leaching and desorption of enzyme • decreasing rate of enzyme activity • Immobilized enzymes'

		packaging density is not controlled
Covalent binding Immobilization	<ul style="list-style-type: none"> • Strong stable binding • enzyme leaching is prevented • Thermostability is increased 	<ul style="list-style-type: none"> • Low stability • More often, enzymes are deactivated • Immobilized enzymes' substrate affinity is decreased • Conformational Restrictions
Entrapment Immobilization	<ul style="list-style-type: none"> • Damage from mechanical shear, hydrophobic solvents, and gas bubbles is prevented. • Suitability for continuous operation • Simple downstream processing • Integrity and efficiency of protein is retained 	<ul style="list-style-type: none"> • Lower enzyme loading • mass transfer is limited
Cross-Linking Immobilization	<ul style="list-style-type: none"> • No requirement of support matrix • stability of enzyme is high • Decreased desorption • recycling and reuse is easy 	<ul style="list-style-type: none"> • enzyme activity via conformational changes is lost • Diffusion rate is decreased

Table 4: Parameters and corresponding characterization techniques for nanomaterials

Characterization Type	Parameters to study	Techniques suitable
Morphology	Morphology. Dispersion, Shape. 3D visualization	High-resolution transmission electron microscopy. Ferromagnetic resonance 3D-Lomography. Atom makes first-generation force microscopy. UV-visible spectroscopy, polarized optical microscopy, transmission electron microscopy, Scanning electron microscopy.
Structure	Structure and Crystallinity	High-resolution transmission Electron microscopy. Scanning transmission electron microscopy, Electron diffraction. X-ray diffraction spectroscopy, Extended X-ray absorption fine structure
	Particle size	Scanning electron microscopy. Transmission electron microscopy. X-ray diffraction spectroscopy, Dynamic light scattering.

		Nanoparticle tracking analysis, atomic force microscopy. Extended X-ray Absorption fine structure. Small-angle X-ray scattering, High resonance transmission electron microscopy, Ferromagnetic resonance. UV-visible spectroscopy. Matrix-assisted laser desorption/ionization, Differential scanning calorimetry Inductively coupled plasma-mass spectrometry., Liquid nuclear magnetic resonance spectroscopy, Nuclear magnetic resonance spectroscopy. Tunable resistive pulse sensing, Magnetic susceptibility.
	Surface area	Dynamic lights scattering, Small-angle X-ray scattering. Differential scanning calorimetry. Ferronlagnetic resonance, Superparamagnetic relaxometry. Nanoparticle tracking analysis, inductively coupled plasma-mass spectrometry. Scanning electron microscopy. Differential thermal analysis. Tunable resistive pulse sensing,
	Size distribution	Raman spectra analysis, Fourier transform infrared spectroscopy, surface-enhanced relaxometry spectroscopy Energy-dispersive X-ray spectroscopy with field emission electron microscopy. X-ray photoelectron spectroscopy.
	Elemental -chemical composition	Inductively coupled plasma-mass spectrometry, X-ray diffraction spectroscopy. Nuclear magnetic resonance spectroscopy, Magnetic force microscopy. Low-energy on energy ion energy on energy scattering spectroscopy. Inductively coupled plasma - optical emission spectrometry
	Density Nature or bonds	X-ray photoelectron spectroscopy Resonant mass Measurement-Microelectromechanical systems, Differential scanning calorimetry.
Optical	Optical absorption. Transmittance and reflectance. Absorption shift	UV/visible spectroscopy- diffuse reflectance spectrometer
	Absorption or emission capacity Refractive index and extinction	Photoluminescence Null ellipsometer
Magnetic	Magnetic Properties	Value stream Inapping, Magnetic force

		microscopy, Superconducting quantum interference device. Magnetic susceptibility, Ferromagnetic resonance, X-ray magnetic circular dichroism
Others	Growth kinetics	Cryo-Transmission electron microscopy. Liquid- Transmission electron microscopy. Nuclear magnetic resonance spectroscopy, Small-angle x-ray scattering, Transmission electron microscopy. Electron backscatter diffraction, High-resolution transmission electron microscopy.
	Structural detects Concentration	Inductively coupled plasma mass spectrometry. UV-Visible Spectroscopy. Tunable Resistive Pulse Sensing, Resonant mass measurement-Micro electro-mechanical systems.
	Chemical state- oxidation state	Electron energy-loss spectroscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy.

IX. BIOETHANOL AND BIODIESEL PRODUCTION USING NANO IMMOBILIZED CATALYSTS

The demand for advanced feedstock (second and third-generation biofuels) over traditional feedstock (first-generation biofuels) is increasing as the number of biofuels industries increasing. With the high efficiency, advanced feedstocks have little or no adverse effects on the environment [128]. Lack of technology for efficient biomass conversion, commercialization of biofuels is comparable low despite having higher demand, while the combination of nanotechnology with technologies involved in biofuel production gives promising results and effective way to produce biofuel by the breakdown of biomass and also makes the processes cost-effective relaxometry [129-131].

High evaporation enthalpy, high octane number, a wide range of flammability and improved thermal efficiency are some characteristics which makes bioethanol similar to gasoline (table 5) [132] and also makes the blending of bioethanol in gasoline possible. Earlier, first-generation bioethanol was ion synthesized from edible crops like wheat, barley, sugarcane, corn, etc. [133]. As these crops are edible thus pose threat to food security and alternatives need to be found out by researchers. To overcome the issue, the production of bioethanol using naturally available lignocellulose biomass such as forest litters, wood wastes, etc. as a source of sugar for fermentation. Moreover, some energy crops like *Populus*, Switchgrass, etc. are encouraged to cultivate for the specific purpose [134-135] and such manner for the production of bioethanol is called second-generation bioethanol.

Table 5: Applications of different nano-biocatalysts

Nano biocatalysts used	Applications
Perfluoroalkylsulfono (PFS) and alkylsulfono (AS) and acid-functionalized nanoparticles	Improvement in biomass pretreatment and hydrolysis of hemicellulose
Functionalized propyl-sulfonic (PS) acid nanoparticles	Improves pretreatment in biomass
Silver nanoparticles	Enhance sugar yields
Cellulose-coated magnetic nanoparticles	Increased ethanol production rate
Graphene Oxide modified carbon electrode containing copper nanoparticles	For ethanol detection in a fermentation broth
Hetrostructural silver nanoparticles decorated with polycrystalline zinc oxide nanosheets	

Along with bioethanol, the production of biodiesel has been encouraged by the private sectors investor for its better fuel properties and causing minimal damage to the environment [137]. Animal fat and oil crops like canola, mustard, sunflower, soybean, etc. can be used for the production of biodiesel [138], however, it is not economically feasible to use oils for synthesizing biodiesel because of its high production cost and comparably low yield. New researches also claim the utilization of microbial algae as a feedstock for synthesizing biodiesel due to high lipid concentration and higher production rate (figure 6) [139].

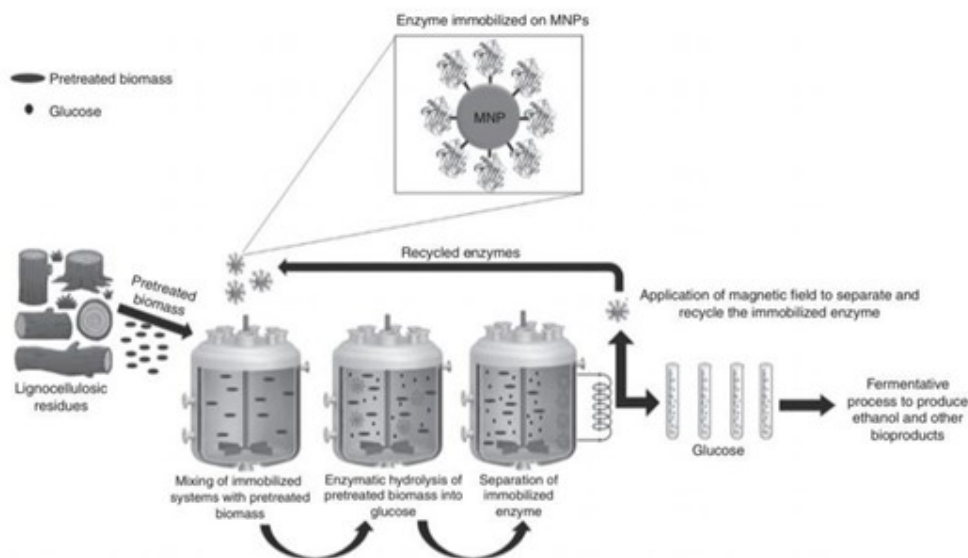


Figure 6: Schematic representation of the production of biofuels by the hydrolysis of cellulose from celluloses immobilized using MNPs

Emerging technologies need to overcome some limitations of high production costs with lesser product recovery. For the conversion of oils to biodiesel, mainly

transesterification is used [140]. During the process, the production of biodiesels or fatty acid methyl esters is carried out by the reaction of alcohol and oil derived from feedstocks. As of now, enzymes, bases, acids, and heterogeneous catalysts are four types of catalyst that are used for the process [141], while it is preferred to use enzyme-catalyzed transesterification involving lipids, which has very high cost limits the commercialization, ultimately getting help from nanoparticles to enhance the biocatalysts' efficiency [142].

X. CONCLUSION

A change toward a greater emphasis on discovering new uses for agricultural waste has been brought on by environmental policy and the rising demand for a wide range of biobased products. Food and agricultural wastes are abundant sources of nutrients and bioactive substances. When discussing their potential use in the creation of bioproducts, it is more accurate to refer to these materials as "feedstock" rather than "waste" because their composition may vary, including the inclusion of sugars, minerals, and proteins. Technology based on nanomaterials can potentially be utilized to expand the industrial applications of bioactive substances. In comparison to conventional resources, the effectiveness and agronomic efficiency have been increased with the introduction of nanoparticles. Development of agro-waste-derived biofuels and bioproducts are widely been researched now a days.

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