

Biomass Valorization for Bioenergy Production



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Abstract Biomass is currently seen as a potential to be used as bioenergy resources. Its high availability and renewability generate extensive interest for further valorization. In Indonesia, research and development of transforming biomass into bioenergy via different pathways is expanding. Conversion of biomass via physical/mechanical, biochemical, and thermochemical offers produces bioenergy in the form of liquid (i.e., biodiesel, bioethanol, and bio-oil), gasses (i.e., biogas and syngas), and solid (i.e., biopellets, biochars, and briquettes). These types of bioenergy are essential for substituting fossil-based fuels, hence have positive impacts on reducing carbon emissions and climate change. Different mechanisms of process occur during the conversion. Specific measures to the influencing factors are crucial to ensure the optimum performance efficacy. This chapter discusses various bioenergy routes from

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biomass substrates from the process' mechanisms to examples, in particular anaerobic digestion, transesterification, fermentation, densification, and thermochemical pathways.

Keywords Anaerobic digestion · Transesterification · Fermentation · Pelletizing · Pyrolysis

1 Introduction

Energy demand continues to increase in line with the increasing rate of population growth and economic growth. For example, according to the Ministry of Energy and Mineral Resources of the Republic of Indonesia (Kementerian ESDM 2021), energy demand in Indonesia is expected to continue to increase until 2030 with an average annual increase of 1.6%. Energy is used in various fields, one of which is as fuel for industrial, transportation, and household activities. The most widely used energy source to date comes from fossil fuels (Ulfa et al. 2021). Fossil fuels are non-renewable fuels and their availability is limited, thus over time there will be scarcity. In addition, fossil fuels can produce emissions (such as NO_x and SO_2), when accumulated, will cause acid rain (Zikri et al. 2018). These problems have an impact on climate change (Istiani et al. 2021).

Also, along with the increasing demand for energy, it is necessary to use renewable energy as an alternative to fossil fuels. Renewable energy can be created from the utilization of biomass including agro-industrial, plantation, agricultural, and forestry wastes. Biomass is an organic material obtained from living things in nature (Calvo-Serrano et al. 2019). Usually, biomass comes from products that are renewable, urban waste, forests, and residues originating from the agricultural sector. Biomass-derived from plants is obtained by the reaction between carbon dioxide and water, air, and the sun through the process of photosynthesis to produce carbohydrates which form a group of biomasses. Biomass is composed of three main components, 40–60%(w), 10–30%(w), and 20–30%(w) (Reyes et al. 2021). Biomass-derived from forest and agricultural plants is generally composed of components of cellulose, hemicellulose, lignin, fat, protein, starch, and sugar. Biomass also contains water and organic components such as nitrogen, sulfur, alkali, alkaline earth, heavy metals, magnesium, chlorine, and potassium.

According to Kusumaningrum and Munawar (2014), biomass has the potential to be used as an energy source as it is abundant, cheap, environmentally friendly, and renewable. While Tursi (2019) defined biomass is organic material produced directly or indirectly by living organisms and is available in a renewable manner. Use of biomass as bioenergy sources can minimize the negative impacts on the environment (Febrianti et al. 2020). Also, the benefits of using biomass-based bioenergy are that it does not emit sulfur that causes acid rain, produces less amount of ash than coal, is abundant in availability, renewable, and relatively fast to produce (Munawar and Subiyanto 2014).

Sources of biomass include agricultural residues such as rice husks, corn cobs, and corn fiber, remaining forest products such as wood, agricultural and plantation industry residues such as palm oil waste including empty oil palm bunches (EFB), shells, fronds, palm tree trunks, wood processing industry sawdust, cocoa shells, sugarcane bagasse, pulp sludge, urban waste such as used paper, and dry leaves (Febrianti et al. 2020). Agricultural industry waste is another source of biomass (Wang et al. 2022). This waste can be detrimental to the environment, like other industrial wastes. The form of this waste can be solids, gases, or liquids. In handling agricultural and industrial waste, it is necessary to group it based on its form and on its raw components, such as carbohydrates, proteins, or fats. Indonesia has potential biomass resources of up to 50,000 MW which are dominated by plants and industrial organic waste. Installed biomass capacity in Indonesia reaches 312 MW (Yana et al. 2022). Biomass is formed by the main lignocellulosic compounds including cellulose, hemicellulose, and lignin. These three compounds function to form complex chemical bonds to become the basic material for plant cell walls. The cellulose content in the biomass varies and ranges from 40 to 50%. Hemicellulose in biomass has a percentage of about 15–35%. Lignin in biomass has a percentage of around 10–25% (Tursi 2019), and is considered as a complex structure that covers the cell walls (Hermiati et al. 2010). The lignocellulosic content contained in biomass can be used to produce energy through the biomass conversion process. Biomass is unique in nature and has different concentration of lignocellulosic compounds, as shown in Table 1 (Hermiati et al. 2010).

Biomass sustainability is critically important to be created in the supply of energy sources. The government's role as a policymaker is vital in developing and implementing renewable energy sources. The support from the Indonesian government is by releasing a Minister of Energy and Mineral Resources Regulation regarding the implementation of co-firing to increase biomass economies of scale and reduce dependence on coal.

Table 1 Lignocellulose content in various biomass

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Cocoa shell	36.47	18.90	60.67
Sugarcane bagasse	50	25	25
Corn cob	41	36	16
Wheat straw	30	50	15
Empty fruit bunches of palm oil	44.21	16.68	35.51
Rice husk	34.4	24.3	19.2

Source Hermiati et al. (2010)

2 Bioenergy from Biomass Resources: Mechanisms and Example

Biomass as a fuel without going through the conversion process has bad properties due to its low density. Direct use of biomass also causes respiratory problems due to carbon monoxide (CO) and sulfur dioxide (SO₂) gases. To reduce this, biomass can be converted into energy such as heat, electricity, liquid, solid, and gaseous fuels (Moura et al. 2022). Various opportunities routes for biomass valorization to bioenergy, either to physical, biochemical, thermal, mechanical, thermal, and thermochemical pathways (Fig. 1). These can be done in several ways including densification, gasification, carbonization, pyrolysis, and anaerobic digestion processes. Each of these conversion principles consists of a specific process that is useful to convert biomass into bioenergy. These routes can produce bioenergy in different forms such as liquids (i.e., biodiesel, bioethanol), gases (biogas, syngas), and solids (biopellet, biochar, briquettes) (Parinduri and Parinduri 2020).

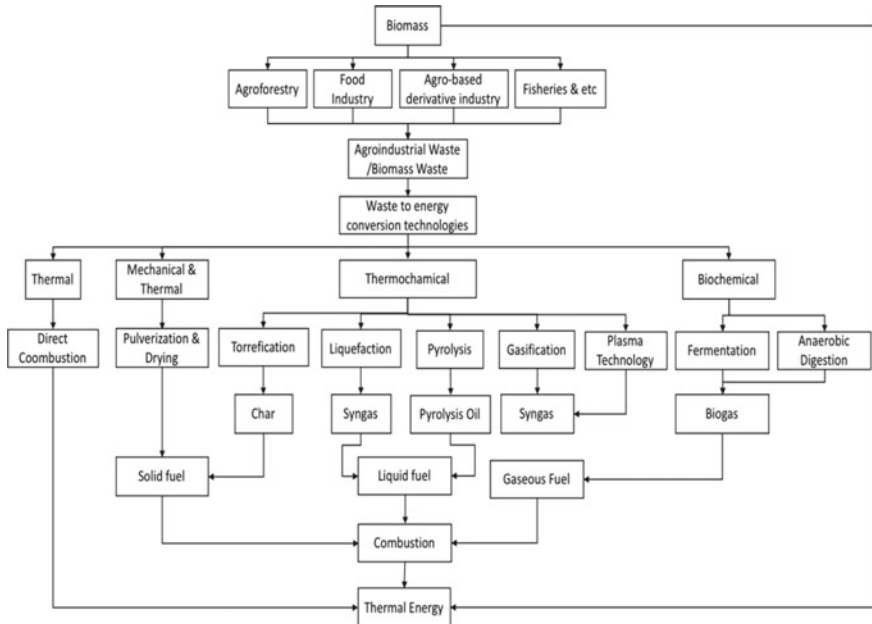


Fig. 1 Biomass conversion to energy pathways

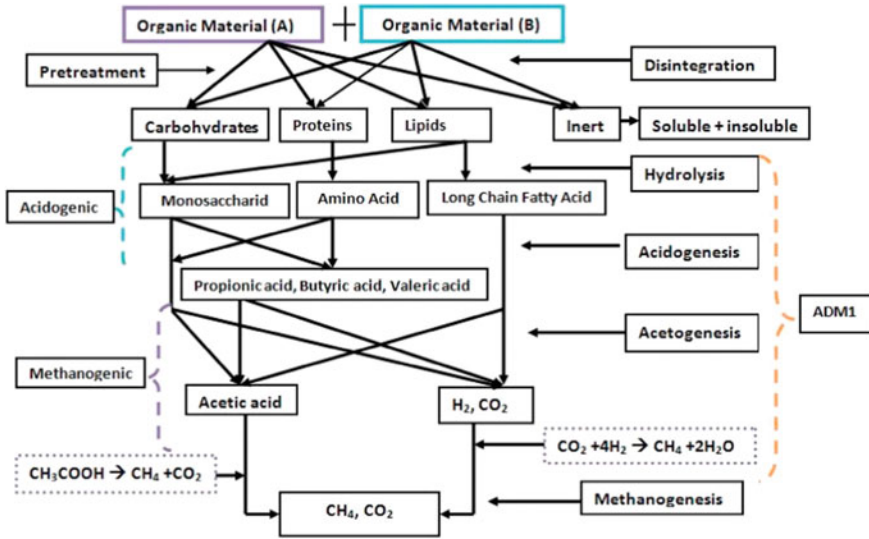


Fig. 2 Stages in the anaerobic digestion process (Hagos et al. 2017)

2.1 Anaerobic Digestion

2.1.1 Definition and Mechanisms

The anaerobic digestion (AD) process consists of four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, where the dominant biogas containing methane gas is produced in the methanogenesis process. The stages of the anaerobic digestion process are shown in Fig. 2. Biogas produced can later be converted into electrical and heat energy or developed into biomethane (Montingelli et al. 2016). Besides biogas, AD also generated organic residues, known as digestate. The AD system enhances the recovery of nutrients (N and P) in the final product. The resulting P composition has the potential to be reused as fertilizer (Li et al. 2022).

2.1.2 Hydrolysis

Hydrolysis as the initial stage of AD is a process of breaking down large and complex polymers such as fats, oils, starch, polysaccharides, and proteins into monomeric or oligomeric components such as amino acids, long-chain fatty acids, and simple sugars. This process is carried out by extracellular enzymes that are owned by microorganisms into the total volume of solution (Thanarasu et al. 2022). This initial stage, known as biological pretreatment, will also produce intermediate products such as ammonia and long-chain fatty acids that can affect the AD process. Thus, the adjustment process in the microbial consortium as well as the bioreactor needs to be

carried out. Operational strategies include co-digestion, pretreatment with enzymes, chemically or mechanically, as well as dividing the AD stages into two major or other stages. Hydrolysis is also known as one of the rate-limiting reactions in which components of complex chemical compounds such as fats, polysaccharides, and proteins are deconstructed into monomers. Hydrolyses are included as individual monomers from suspended solids. The results of this modeling can also determine sufficient exposure time to provide pretreatment as an effort to increase biogas production (Hirmiz et al. 2019). Some preventive steps to avoid biogas production barriers are carried out in several ways, namely, by adding inoculum and adjusting the pH at the hydrolysis–acidogenesis stage. The result of this adjustment can increase bioenergy production two times higher than usual.

2.1.3 Acidogenesis

The acidogenesis stage begins with the absorption of monomer and polymer products into the cell membrane of acidogenic bacteria into volatile fatty acids (VFA), alcohol, and other inorganic compounds such as CO_2 , H_2 , H_2S , and NH_3 (Richard et al. 2019). VFA control is an important factor in biogas production, because the accumulation of these compounds will reduce the effectiveness of biogas production (Thanarasu et al. 2022). Microorganisms involved in this stage include *Acetivibrio*, *Bacteroides*, *Clostridium*, *Eubacterium*, *Lactobacillus*, and *Streptococcus*. One of the syntrophic microorganisms, namely, *C. Cloacimonas*, plays a key role at this stage. This microbial ability is related to the production of methane gas from the hydrogen chain. The coenzyme associated with it is Methanoculleus (Niu et al. 2022). The main challenge in this stage is to avoid VFA conversion to methane gas. The focus of research must emphasize this issue to avoid inhibiting biomethane production. The study of (Al-Sulaimi et al. 2022) showed a negative effect of VFA acidification on production efficiency and biogas biodegradation from waste sludge substrates, especially for bioreactor conditions that use thermophilic reactor conditions. The high concentration of VFA will cause the pH to drop and cause an unfavorable reactor environment for the methanogen process.

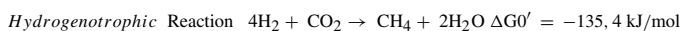
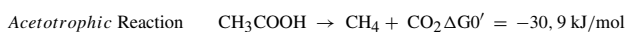
2.1.4 Acetogenesis

Substrate through subsequent breakdown which produces H_2 and CO_2 accompanied by acetate is referred to as the process of acetogenesis. Acetogens are an important step in the biodegradation process of organic matter to maintain the efficiency of the biogas production process. Acetogenic bacteria will use production from hydrolysis and oxidize pyruvate. Pyruvate is part of the intermediate product in the AD process and will be converted to acetate (Thanarasu et al. 2022). Other results such as the hydrogen gas produced will initiate syntrophic relationships in the AD-transfer system between hydrogen species (Meegoda et al. 2018). Acetogen species can be divided into several parts, namely, hydrogen generators and proton-to-hydrogen

reducers. Most of the known homoacetogen species are from the genera *Acetobacterium*, *Acetoanaerobium*, *Acetogenium*, *Butyribacterium*, *Clostridium*, *Eubacterium*, and *Pelobacter* (Borja and Rincón 2017). In a single stage, microorganisms that play a role in acetogenesis and methanogenesis develop simultaneously. The two microorganisms require different environmental conditions. So, currently, another study is being carried out regarding the optimum conditions for both bacteria in single conditions or in two-stage conditions (Qian et al. 2019).

2.1.5 Methanogenesis

The end product of acetogenesis is acetate, H_2 , and the methylated mixture is used by methanogenic bacteria for gas production. Acetate used by methanogens can become a methyl group and CO_2 , and then this group is reduced to methane using electrons provided by the carboxyl group (Thanarasu et al. 2022). This methanogenesis takes place at the end and takes a long retention time between 15 days and 3 months (Tabatabaei et al. 2020). Microorganisms that play a role in this stage are methanogens which are a group of archaeobacteria that are unicellular and very sensitive to the presence of oxygen (Borja and Rincón 2017). One of the inhibiting factors in this stage is the presence of excessive ammonia gas from a high nitrogen content substrate as the main inhibitor. The toxic level of this gas is caused by un-ionized ammonia, due to its ability to enter the bacterial cell membrane to disrupt the balance of potassium and methane protons. The handling practice is to provide additional water, but this also increases operational costs and is inefficient. Because of this, several research and industrial projects have begun to focus on adapting environmental conditions to these methanogenic microbes (Capson-Tojo et al. 2020). There are two pathways involved in this step involving acetic acid and carbon dioxide, the two main products from the previous step to produce methane gas (Kirk and Gould 2020):



The main product resulted from AD is called biogas. Biogas is a mixture of gases produced by methanogenic bacteria through an anaerobic digestion process that transforms complex organic compounds with the help of microorganisms under anaerobic conditions (Gonzalez-Gil et al. 2018). Complex organic compounds can be found in biomass. However, biomass used as raw material for biogas generally has low economic value or is waste, such as industrial agriculture waste (agro-industry), forest product waste, and livestock waste. Many gases contained in biogas include methane (CH_4), carbon dioxide (CO_2), ammonia (NH_3), water vapor (H_2O), hydrogen sulfide (H_2S), methyl siloxane, nitrogen (N_2), oxygen (O_2), volatile components (VOC), carbon monoxide (C.O.), and hydrocarbons. The most extensive content in biogas is 50–80% CH_4 and 20–50% CO_2 from the amount of gas produced. Biogas' energy depends on methane concentration, where the higher the methane content, the greater

the energy content or calorific value (Neves et al. 2004). Physically, methane is colorless, odorless, and flammable. Chemically, methane is composed of one C atom and four H atoms. This compound is very stable due to the presence of C–H bonds and requires an energy of 438.8 kJ/mol to break it down (Park and Lee 2013). A simple purification process can purify biogas by passing the gas through a NaOH solution to bind CO₂ (one impurity) and converting it to precipitate sodium bicarbonate (Na₂CO₃) H₂O. This process will increase the purity of methane (CH₄). Based on research conducted by Lasocki et al. (2015) using 1 M NaOH for 10 min can increase the concentration of CH₄ and remove H₂S and CO₂ altogether.

2.1.6 Enhancing ADProcess: Pathways

As AD technology is primarily dependent on microbial activity, ensuring the feedstock has higher accessibility for the microorganisms is a must. Pretreatment on biomass especially with higher lignocellulosic content should be considered before treated with AD. There are common pretreatment methods, i.e., physical, mechanical, biological, and chemical. Ampese et al. (2022) used the dried apple pomace as AD feedstock VS that through physical pretreatment using a mill to reduce its size resulted in 36.61 L CH₄/kg VS that was predicted to generate electricity, heat, and carbon reduction in 1.92 kWh/ton, 8.63 MJ/ton, 0.62 kg, and CO_{2eq}/ton, respectively. Steam explosion (STEX), as part of physicochemical pretreatment, is being investigated on many energy crops and ecological plants. A lignin-rich macrophyte (*Potamogeton maackianus*) under semi-continuous AD is pretreated via STEX and resulted in enhancing the hydrolysis efficiency from 19% (108 ± 31 L/kg VS) up to 50% (200 ± 36 L/kg VS) (Akizuki et al. 2022). The STEX gives an easier breakdown for the microbial activity and enhances the biomethane yield.

Minimizing the energy input and faster reaction is part of merits of chemical pretreatment, but another consideration that should be noted is the toxicity profile from the materials that has to meet the principle of green chemistry. Lomwongsopon and Aramrueang (2022) seek the biogas potential from cassava pulp pretreated using mild-chemical with concentrations 0.1–0.3 w/v% of H₂SO₄, HCl, NaOH, and KOH. KOH under 2.0 w/v% showed the highest methane yield of 324 ± 4 L/kg VS. Biological pretreatment as one of the favorable methods to explore is generally utilized microorganism activity to degrade and reduce the thickness of cell wall of lignocellulose biomass. For instance, stover as the feedstock is being investigated via AD and given the biological pretreatment using microbial consortium to positively affect the activity of functional microorganisms. A 62.85% increment on the peak phase is shown than the untreated stover and significant methane production is resulted (Zhao et al. 2019).

Along with its development, AD with one feedstock produces low yields and is inefficient (Beniche et al. 2021). The application of Anaerobic co-digestion (AcoD) which is an AD system that uses two or more substrates to improve the process, stability, or production of biogas is preferred because it can increase biogas production by diluting toxic substances and provide a synergistic growing environment

for microorganisms and can also handle multiple wastes at once (Taboada-Santos et al. 2019). For instance, the study of (Wang et al. 2022) the anaerobic co-digestion between excess sludge and chicken manure has effectively increased the methane yield in mesophilic and thermophilic temperatures up to 123.1 L/kg VS and 171.3 L/kg VS, respectively. Proper mixing ratio to have the balance support factor (i.e. pH, C/N) is the main key to enhance the biogas production.

2.1.7 Examples

Commodity of palm oil has been the major crops in some tropical countries, i.e., Indonesia, Thailand, and Malaysia as the three largest producers of biomass. From the industrial process, empty fruit bunches of palm oil (EFB) are the generated waste that could be valorized via AD route to produce biogas. (Suhartini et al. 2020) evaluated the untreated EFB biomass with batch AD under mesophilic temperature for 30 days and the specific methane potential was $0.110 \text{ m}^3/\text{kgVS}_{\text{added}}$. Similarly, (Hidayat et al. 2020) investigated the biomass potential with fungal pretreatment to manage the higher content of lignin which is one of the barriers of AD steps. The pretreatment is capable to disrupt the lignocellulose content and enhance methane production than the untreated along with increment in the organic matter.

Interest in utilizing the macroalgae along with other feedstock has gained more studies with various perspectives either with co-digestion or additional of other bioactive compounds to obtain higher methane yield. In our previous studies, using *G. verrucosa* with the addition of tofu dregs substrate, a higher SMP was produced in a 20% tofu dregs mixture (compared to only 10%) with a value of $120 \text{ L CH}_4/\text{kgVS}$ (Suhartini et al. 2022a).

In line with the synergetic effect from co-digestion, a study by Wickham et al. (2019) showed a positive effect of AcD, with a stable composition of methane gas in the biogas of 60–65%. In this case, AcD does not show any negative implications such as disrupting the stability of the reactor or other toxic gases. However, not all AcoD can provide optimal results, in the study (T.A.S et al. 2020) compared mono and co-digestion substrates and resulted in mono-digestion gave higher yields of $0.61 \text{ m}^3/\text{KgVS}_{\text{reduced}}$ compared to AcoD of $0.39 \text{ m}^3/\text{KgVS}_{\text{reduced}}$. Therefore, AcoD needs to be carried out to see the relation impact on biomethane production either antagonistic or synergetic. Apart from the biomass potential on biogas production and pretreatment work, for the pilot and industrial scales of AD implementation, sometimes the foaming issues are the major concern. This condition could be due to the presence of unwanted microorganisms and other operational factors. Trace element supplementation, adjustment of organic loading rate, addition of anti-foams, and water dilution could be the solution for the foaming issue (Suhartini et al. 2019).

2.2 Transesterification

2.2.1 Definition and Mechanisms

Transesterification as the most common mechanism to produce biodiesel will be discussed in detail in this section. Figure 3 shows the main process that starts from long-chain fatty acids react with alcohol with catalyst and through three stepwise that ultimately produce methyl esters as biodiesel and glycerol as the co-product (Meher et al. 2006). In addition, this reaction is divided into two sections: catalytic or non-catalytic. As shown in Fig. 4, catalytic process could be conducted with homogeneous catalysis, heterogeneous catalysis, or combinatorial catalysis. Acids, alkalis, and enzymes are the materials to be utilized for synthesizing biodiesel under catalytic conditions. FAME produced from various substrates of waste is attracting more researchers to utilize the low cost of feedstock and minimize the waste presence. This study used chicken fat oil and waste cooking oil with acid catalyst and gained the FAME yield of 90.8% and 92.3%, respectively, and categorized as the suitable feedstock for biodiesel feedstock (Shatesh Kumar et al. 2020). Meanwhile, the non-catalytic is carried out with supercritical fluid. This process could be produced more than one product such as other value-added by-products, i.e., triacetin. Under the economic and environment assessment, the supercritical fluid, the progress to address the saponification issue and other unwanted waste generation through other steps, which provides more advantages will have more feasibility if using the glycerol-free process to gain high revenue (Ang et al. 2014).

Table 2 shows the advantages and disadvantages of each process of transesterification under catalytic or non-catalytic process. It should be noted that every process will work effectively under the specific feedstock. The heterogeneous catalytic process emerged to combat drawbacks of homogeneous catalyst role, but if homogeneous catalyst coupling with other methods, i.e., ultrasound-assisted extraction using the *Annona squamosa seed oil* will result in rich oil content of 94.7% yield (Sundaramahalingam et al. 2021). The study revealed that the combined methods seem more feasible from energy balance and have a positive impact on the economic view.

Transesterification of biomass or organic waste results in biodiesel. Biodiesel as a green fuel produced from animal oil, vegetable oil, and algae oil has the physico-chemical similarity with fuel diesel but has low energy density and generates lower

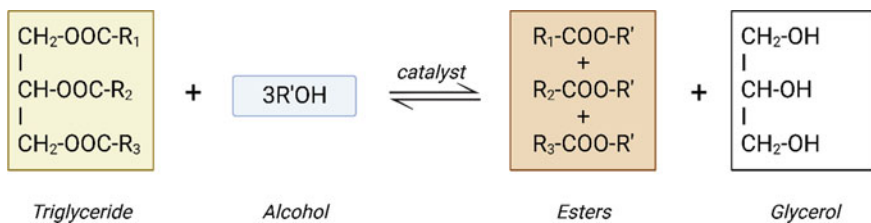


Fig. 3 Transesterification reaction (Meher et al. 2006)

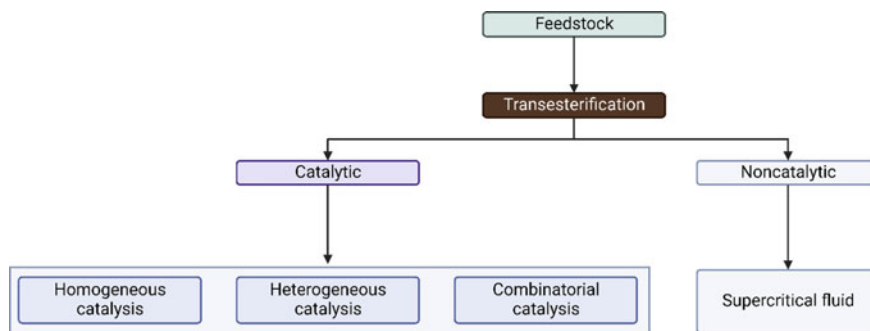


Fig. 4 Overview of transesterification in biodiesel production processes. Adapted from Nayab et al. (2022)

Table 2 Overview of transesterification in biodiesel production processes

Process	Materials	Advantages	Disadvantages	References
Homogeneous catalysis	H ₂ SO ₄ , NaOH, NaOCH ₃ , KOH	<ul style="list-style-type: none"> – Faster reaction rate – Required mild reaction condition – High corrosiveness – Non-reusability – Difficult to be separated 	<ul style="list-style-type: none"> – Contaminated the outcome, affected the separation process – Soap formation – Low purity – Toxic waste generation 	Sakai et al. (2009), Kaur and Ali (2011)
Heterogeneous catalysis	CaO, CaO–KOH, CaMgO, CaZnO	<ul style="list-style-type: none"> – Reusable – Easy separation – Reduces wastewater generation – Lower toxicity 	<ul style="list-style-type: none"> – Partial recoverability and reusability – Energy and waste conservation problem – Longer retention time 	Lee et al. (2014)
Combinatorial catalysis	Mixed catalysis	<ul style="list-style-type: none"> – Increase the yield – Decrease the toxic product 	<ul style="list-style-type: none"> – High expenses 	Kim et al. (2008)
Supercritical fluid	Variance in pressure, temperature, molar ration between alcohol and lipid, and retention time	<ul style="list-style-type: none"> – Shorter duration progress – Efficient conversion step – Catalyst-free operation – Lower quality of feedstock can be used 	<ul style="list-style-type: none"> – Operational cost 	Deshpande et al. (2017), Makareviciene and Sendzikiene (2021)

Table 3 Biodiesel production and major feedstock (OECD-FAO 2021)

Country	Production (%)	Major feedstock
European Union (EU)	32.3	Palm oil, rapeseed oil, used cooking oils
United States	18.1	Soybean oil, used cooking oils
Indonesia	15	Palm oil
Brazil	12.2	Soybean oil
Argentina	5	Soybean oil

GHG emissions (Okechukwu et al. 2022). This substitution could tackle the climate change issues due to reliance on fossil fuel-based sources. Biodiesel or fatty acid methyl ester (FAME) is generated by transesterification and esterification, and is produced of mixed fatty acid esters (biodiesel) and glycerol as the by-products. Global biodiesel production is projected to reach 50 billion L in 2029, which was 53% higher than in 2016 (Rezania et al. 2019). EU has the first position as the largest country in the production of biodiesel followed by the USA and Indonesia. The major feedstock in detail is shown in Table 3. Biomass and its waste utilization in biodiesel production could lead to bioeconomy concept which offers sustainability pathways to generate renewable energy sources.

2.2.2 Pretreatment for Biodiesel Production

In order to enhance the efficient and effective result, biomass is pretreated either with mechanical, physical, chemical, or biological. This pretreatment to assure the extraction will give the maximum result. For instance, the lignocellulose biomass is rich in lignin content, and high crystallinity which will hinder the process of biodiesel production, especially with tolerance to microbe and chemical conditions. Biomass pretreatment for biodiesel production has been investigated in several studies. Biological pretreatment is being sought from other studies. It has been reported that the corn straw is pretreated with *Mycobacterium smegmatis* LZ-K2 to prove the microorganism's capability in reducing the lignin content (Zhang et al. 2019) and the enzyme system shown the possibility further to treat such lignin-rich biomass. In other pretreatment, i.e., dilute acid could produce ethanol and biodiesel. This case of wheat straw valorization under moderate conditions with 140–160 °C and 0.3–0.6% of sulfuric acid concentration could degrade the lignin content more than the other parts. Meanwhile, the physical pretreatment has also been investigated to enhance the yield of FAME. Priyadarshi and Paul (2018) conducted the advanced microwave technology (AMT) pretreatment in regard to achieve high yield of FAME with source from kitchen waste. It resulted to have 96.89 wt% as the maximum FAME yield. A similar pretreatment was also identified from the study to increase the yield of FAME and reported that 93 wt% of the FFA conversion is achieved with AMT as the pretreatment method to reduce water and the viscosity reduction (Idowu et al. 2019).

2.2.3 Bioeconomy Concept on Biodiesel Production

Majority of the world is facing crisis in energy, water, and food nexus. Most of all technology still lack sustainability and viability from the economic and environment view. For instance, in order to produce one renewable energy product, the energy balance resulted in negative values which is not possible to proceed to the pilot scale or industrial scale. This issue is affected by many factors, including feedstock characteristic and technology itself. Hence, implementing bioeconomy concept into the conversion technology is urged to be adopted. Not only produce one product but also more value-added products to balance the energy balance or generate more energy output. Same condition applied for this biodiesel production. Most studies have investigated the chance of producing more products.

Angelaalincy et al. (2023) reported the investigation on managing the environmental contamination from arsenic with phytoremediation and nanoparticle-mediated adsorption while co-produce the biodiesel and increase up to 125% the lipid content and incline the FAME production. This technology combats the pollution issue and provides the new renewable energy outcome which promotes the biorefinery system. Jeyakumar et al. (2022) studied the third generation of biofuel, *Padina tetrastromatica* and *Sargassum swartzii* macroalgae, to produce bioethanol and the solid waste generated is being sought the biodiesel production potential. The result shows that both marine biomasses are capable of extracting ethanol yield and FAME yield more than 80%. Another example of biomass valorization to promote the circular economy is converting *Macaúba* husk into biodiesel and biomethane. The generated waste from biodiesel production is firstly pretreated by subcritical water hydrolysis to breakdown the lignocellulose compound and via anaerobic digestion (AD) to have the clean energy, i.e., biogas (Ampese et al. 2021). The pretreatment successfully improves the biodegradability of feedstock and the biogas production could be further utilized in combined heat and power scenarios to enhance the functionality. Another feedstock being identified with its potential to obtain the same output (biomethane and biodiesel) is the energy crop, sunflower plant. The study result shown the biodiesel yield and biogas production in 96.2% and 342.7 N mL/g VS, respectively (Ebrahimian et al. 2022). This study explored hot water, sodium carbonate, and phosphoric acid as the three physiochemical pretreatments to increase the hydrolysis step that is beneficial for AD technology and showed a positive effect to maintain the recalcitrant content of its biomass.

2.2.4 Examples

A study from Halim et al. (2022) regarding the extraction of oil and protein from the species *Nannochloropsis sp.* (microalgae) developed a hypotonic autolytic and osmotic incubation pretreatment method for easy penetration of microalgae cell walls up to 4.9 times compared to only using conventional methods. After pretreatment, cell disruption (CD) was continued with the mechanical disruption (HPH) or chemical disruption (pH 12) method. From the experiments, the cell walls that did not undergo

pretreatment only experienced 12% CD. The remaining more than 80% indicates that the defense wall of *Nannochloropsis* cells is very thick and difficult to penetrate, so it requires pretreatment to weaken this defense and also increase CD performance (the next process) to maximize liberation products. The results of the pretreatment of autolytic incubation made CD HPH and pH 12 increase, respectively, by 2.4x and 4.9x. The increase in CD performance is due to the high efficiency of disruption which is characterized by the thinning of the cell wall due to its weak defense and makes the biomass more sensitive to the treatment it receives. Other pretreatment results from hypotonic osmotic shock also provide good output. The CD of HPH and PH12 increased by 1.6x and 1.4x, respectively. The low result of this osmotic performance is because this method further increases membrane permeability.

The capability of fixing CO₂ by microalgae is very high and this process can also synergize with each other to produce other energy products such as omega-3, biohydrogen, bioethanol, and biodiesel. The study of Srinuanpan et al. (2018) showed the potential for synergy in the production of biogas and also biodiesel by cultivating the microalgae *Scenedesmus* sp. CO₂ gas reduction of >96% and CH₄ levels obtained >98% are obtained and shown the effective of elaboration of conversion technologies. Another study examining the addition of bacterial culture in microalgae cultivation to increase the FAME yield was carried out by Kumsiri et al. (2021). The use of *Picicocus intestinalis* WA3 bacteria in the cultivation of microalgae *Tetradesmus obliquus* gives a 1.3x increase in biomass production, 1.39x chlorophyll content, and 1.55x lipid productivity. Another way to enhance the biodiesel yield is feedstock valorization. The mixed culture of microalgae (MC) and food waste have been used as a feeding source for the black soldier fly larvae (BSFL) to enrich its nutrients and the BSFL is utilized as the medium to extract biodiesel from it. The result shown that FAME yield of BSFL with MC feeding is higher up to 140% comparing to the food waste feeding (Mahmoud et al. 2022).

2.3 *Densification*

2.3.1 **Introduction and Mechanisms**

Densification, which defined as a way of developing material functions to increase the energy content per unit volume, heat capacity, and reduce combustion ash (Qadry et al. 2018). The densification process is the process of compacting biomass by pressing or pressing thus increasing the potential energy and product mass density (Pradhan et al. 2018). The densification process is mostly carried out on bulk materials or those that have irregular physical forms such as biomass. This is because biomass has a low natural specific energy content. The densification process has several advantages, including facilitating the handling, storage, and transportation processes, controlled particle size distribution for product uniformity and density, improved product composition quality, increased product calorific value per unit volume, and increased energy content (Gong et al. 2021).

The densification is divided into extruding, briquetting, and pelleting. Extruding process involves compressing the material on a screw (screw) or piston to produce a solid and compact product (Istiani et al. 2021). Briquetting process produces a product shaped like a tube with varying dimensions as needed. Pelletizing process involves the flow of material from a rotating roll accompanied by pressure into the holes for the biopellets (dies) (Widjaya et al. 2019). According to Winata (2013), the pelletization process is drying and forming biomass using high pressure to produce cylindrical solid biomass with a maximum diameter of 2.5 cm. Pelletization is carried out to produce denser biomass with a smaller volume and higher density. The quality of solid biomass is influenced by the strength and durability of the particle bonds, die diameter, die temperature, pressure, and preheating of the biomass mixture. The pelleting process can be carried out using the cold method (or without a heating process).

One of the products that resulted from densification is biopellet. Biopellets are a form of renewable energy (Ulfa et al. 2021); in a pellet-shaped made from compressed biomass materials (Munawar and Subiyanto 2014). Biopellets have a cylindrical shape resembling a pipe and have a solid texture, but have a smaller size than briquettes, and generally used for residential stoves, boilers, gasifiers, etc. (Rusdianto and Choiron 2015). Biopellets are widely used by people in American and European countries for space heating in winter and boiler fuel in industry. The size of the biopellets is about 6–10 mm in diameter and about 10–25 mm in length. The physical characteristics of biopellets such as color depend on the raw materials used (Hadiyane et al. 2021). An example of biopellets from coffee waste is shown in Fig. 5.

The advantages of transforming biomass into biopellets include high fuel efficiency and consistency (i.e., reduce NO_x emissions, particulate matters, and volatile organic matters), produce fewer emissions than wood, relatively easy to manufacture, no risk of explosion (Rusdianto and Choiron 2015). Biopellets are a superior fuel due to their higher energy content than the original biomass material. Also, biopellets

Fig. 5 Biopellet from coffee waste (Hadiyane et al. 2021)



have a denser structure, are easy to handle, environmentally friendly, and easy to distribute (Qadry et al. 2018).

According to Frodeson et al. (2019), the two methods commonly used in the manufacture of biopellets are pelletization using screw pressing and hydraulic pressing. Threaded pressing can be done using a single-or twin-screw press. Pressing using a threaded press has several advantages including greater production capacity because the process takes place continuously and saves production time. The way a threaded press works is by applying the screw principle. The material is pressed using the thrust of a rotating screw, then it will be pushed out as a result of the applied pressure. The more the material goes to the end of the screw, the greater the pressure experienced by the material. According to Damayanti et al. (2017), hydraulic pressing is done by applying hydraulic pressure to the material of 2000 lb/in² to allow the material to be molded.

The process of making biopellets generally consists of several stages including preparation of biomass raw materials, pretreatment in the form of initial drying of raw materials and size reduction, densification process (pelleting), final drying of biopellets, and packaging (Istiani et al. 2021). According to Raudhatul Jannah et al. (2022), the size reduction is carried out with a chopping machine to make the size of the raw material range from 3 to 5 mm and then flouring is carried out to transform biomass material into powder. The pelletization process is carried out using a ring die pellet mill. The powdered biomass is put into the machine to be molded into biopellets according to the desired size. Drying of biopellets aimed to reduce the water content to 10–15% before packaging (Damayanti et al. 2017). Factors that affect the characteristics of pellets include characteristics and composition of biomass, adhesive, particle size, moisture content, densification equipment, pressing conditions, and post-production handling (Zikri et al. 2018).

The main parameter in determining the quality of fuel products is the calorific value. The higher the calorific value, the better the quality of the biopellets (Ulfa et al. 2021). High-quality pellets are generally obtained by densification under high pressure with the addition of an adhesive. In the pelletizing process in medium capacity, effective adhesives are derived from natural and cheap ingredients such as sago flour or tapioca flour (Damayanti et al. 2017). The physical criteria for good biopellets include surface structure are smooth dense and solid, no moldy during long-term storage, and do not emit excessive smoke (Lubis et al. 2016). Also, biopellets with good quality must meet predetermined standards as regulated in SNI 8675:2018 (NSA 2018) about biomass pellets for energy, as can be seen in Table 4.

2.3.2 Examples

There are several studies that have examined the manufacture of biopellets from various types of biomass, whether with the addition of adhesive or not. An example is the research by (Damayanti et al. 2017), regarding the effect of sieve size and the addition of tapioca flour adhesive on the characteristics of biopellets from cocoa shells. The research design used was RAK with a factor of sieve size variation and

Table 4 Quality standard for biopellets in Indonesia based on SNI 8675:2018

No	Parameter	Unit	Requirement
1	Density	g/cm ³	Min. 0.8
2	Moisture	%	Max. 12
3	Ash	%	Max. 5
4	Volatile matters	%	Max. 80
5	Bound carbon content	%	Min. 14
6	Calorific value	MJ/kg	Min. 16.5

Source National Standardization Agency (2018)

the percentage of adhesive addition of tapioca starch. Sieve sizes used were 20, 40, 60, and 80 mesh. The percentage of tapioca flour adhesive addition used was 0, 10, and 20%. From the research, it was found that the optimal results were found in the treatment of a 20 mesh sieve size and the addition of 20% adhesive. The resulting quality for the parameters of moisture content and density complies with SNI 8675:2018, while the parameters of ash content and calorific value do not comply with SNI 8675:2018 concerning biomass pellets for energy.

Qadry et al. (2018) study about the characteristics of biopellets from a mixture of palm shells and sawdust. The method in this study is experimental. The composition of the mixed ingredients is 100% palm shells, 100% sawdust, 30% palm shells and 70% sawdust, 70% palm shells and 30% sawdust, 50% palm shells, and 50% sawdust. The sieve size used is 80 mesh. From the research, it was found that the best quality biopellets were found in the combined treatment of a mixture of raw materials 70% palm shell and 30% sawdust. Testing the characteristics of the resulting biopellets complied with SNI 8675:2018 for the parameters of density, moisture content, ash content, volatile matter content, and bound carbon content. Meanwhile, the calorific value parameter does not meet SNI 8675:2018 in several treatments.

Istiani et al. (2021) studied biopellet production from candlenut shell with a different mixture ratio of sago stem and sawdust. The treatment used was the composition of the ingredients including 65% candlenut shell, 5% sago stem, 5% sawdust, 25% tapioca adhesive; 55% candlenut shell, 10% sago stem, 10% sawdust, 25% tapioca adhesive; 45% candlenut shell, 15% sago stem, 15% sawdust, 25% tapioca adhesive; 35% candlenut shell, 20% sago stem, 20% sawdust, 25% tapioca adhesive. From the research results, it was found that the average density of biopellets was 0.29 g/cm³, the average moisture content was 10.31%, the average calorific value was 4181 cal/g, the average ash content was 10.25%, and the average -the average volatile matter content is 71.31%. The best treatment was obtained from a mixture of 55% hazelnut shells, 10% sago bark, 10% sawdust, and 25% tapioca adhesive. The parameters of density and ash content obtained did not meet SNI 8675:2018 for several treatments.

Ulfa et al. (2021) studied the quality of biopellets from rice husk waste. This study used a factorial RAL model with particle size factors and adhesive variations.

Variations in particle size were 40, 60, and 80 mesh, with different adhesive concentrations at 25% and 30% tapioca flour. The results reported that the powder size and the amount of added adhesive and the interaction between the two did not significantly affect the density, moisture content, ash content, volatile matter content, and bound carbon content. However, the powder size, the adhesive concentration, and their interaction had a significant effect on the calorific value. The resulting density values ranged from 0.7 to 0.95 g/cm³, with an average value of ash content (16.5–19.9%), moisture content (13.1–14.5%), volatile matter (57.3–63.6%), bound carbon content (4.7–9.8%), and calorific value (2781–3378 cal/g). The calorific value from the resulting biopellets still did not meet the parameter of SNI 8675:2018. Hence, in-depth studies to improve the quality are required.

A study by Raudhatul Jannah et al. (2022) on biopellets from rattan shavings and mixed sawdust biomass using sago adhesive. The research method uses RAL with factors including powder size and powder composition. The powder sizes used were 20, 40, and 60 mesh. The powder composition (on a wet weight basis) used was rattan (100), sawdust (100), rattan:sawdust (70:30), rattan:sawdust (50:50), and rattan:sawdust (30:70). The best biopellet results were obtained from the treatment with a composition of 100% sawdust and 40 mesh size. The quality of the biopellets produced for the parameters of density, volatile matter content, moisture content, and calorific value complies with SNI 8021:2014, while the parameters of ash content and bound carbon content do not comply with SNI 8021:2014.

2.4 Fermentation

2.4.1 Definition and Mechanisms

Fermentation is one of the main steps critical in the conversion of lignocellulosic or sugars into bioethanol. There are several research methods and conversion design configurations that are economical and environmentally friendly. The fermentation steps of second-generation bioethanol can be carried out in four ways, namely, separate hydrolysis and fermentation (Separate Hydrolysis and Fermentation or SHF), saccharification and simultaneous fermentation (Simultaneous Saccharification and Fermentation or SSF), saccharification and simultaneous co-fermentation (Simultaneous Saccharification and Co-Fermentation or SSCF) and consolidated bioprocessing (CBP) (Cardona and Sánchez 2007; Aditiya et al. 2016).

The Separate Hydrolysis and Fermentation (SHF) method is a method for making bioethanol in which the cellulose hydrolysis and fermentation stages take place in different reactors (Saini et al. 2015). Raw materials containing cellulose are hydrolyzed or saccharified and then followed by pentose fermentation (C5). Ethanol is then distilled and the remaining hydrolysate is flowed into the second reactor to get the hexose component (C6) fermented. Bioethanol is also distilled after hexose fermentation (Balat et al. 2008). This method has the advantage of optimizing the

operating conditions at each stage. The Simultaneous Saccharification and Fermentation (SSF) method is a method for making bioethanol in which the cellulose hydrolysis stage and the pentose fermentation (C5) stage are carried out simultaneously in one reactor. Next, hexose (C6) fermentation will be carried out in another reactor (Cardona and Sánchez 2007). In addition to the lower operating costs of this method compared to the SHF method, the possibility of inhibition of enzyme-related products can also be avoided so that the bioethanol produced is higher (Saini et al. 2015). In this method, the fermentation of pentoses (C5) and hexoses (C6) is separated because microorganisms that utilize both sugars (pentoses (C5) and hexoses (C6)) are slower than microorganisms that only assimilate hexoses (C6). This method also prevents the reduction of monomers formed after the hydrolysis process, so SSF is claimed to produce higher bioethanol yields (Cardona and Sánchez 2007).

In the Simultaneous Saccharification and Co-Fermentation (SSCF) method, different microorganisms are mixed for pentose (C5) and hexose (C6) fermentation in one reactor. This method allows mixed culture microbes to carry out saccharification continuously without separation which is continued by the fermentation process into bioethanol (Cardona and Sánchez 2007). However, the ability to ferment pentoses (C6) together with hexoses (C5) is not widespread among microorganisms and is one of the biggest obstacles in the industrial production of ethanol using this method (Talebniya et al. 2010). The Consolidated Bioprocessing (CBP) method is the conversion of lignocellulose using one or more microorganisms into bioethanol in one unit operation without additional enzymes (Branco et al. 2018). The microorganisms used can produce saccharolytic enzymes (cellulases and hemicellulases) themselves, hydrolyze substrates, and are capable of fermenting both pentoses (C5) and hexoses (C6) so that they are considered the most cost-effective method (Aditya et al. 2016). Despite its advantages that are more efficient in conversion and require less energy, this method has disadvantages, namely, longer conversion times and lower productivity (Miskat et al. 2020).

Bioethanol is a colorless liquid made through a fermentation process from carbohydrates which involves biological processes. As much as 95% of ethanol in the world is made with vegetable-based ingredients and the rest is made synthetically (Lane and Morrissey 2010). In industry, bioethanol is used as a raw material for industrial alcohol derivatives, mixtures of alcohol, basic ingredients for the pharmaceutical industry, and mixtures of vehicle fuels (Ishola et al. 2014). In developed countries, bioethanol is widely used as an ingredient in gasoline mixtures to increase the octane rating of fuel. Bioethanol is mixed with gasoline at volume fractions of 5, 10, and 85% (fuel name E5–E85). E85 fuel is used for vehicles with flexible fuels (flexible fuel vehicles or FFV), while the E5 and E10 fractions can only be used for vehicles without engine modifications (Bušić et al. 2018) According to data from FAO Agricultural Outlook 2015, the two highest bioethanol producers are Brazil and the United States. In Brazil, sales of FFV vehicles are sold consistently every year, indicating that the demand for bioethanol in Brazil is always there.

The production of bioethanol from lignocellulosic biomass is a development of second-generation biofuels. The use of lignocellulosic biomass has advantages and disadvantages. The advantage is that the substrate is not competitive with food

ingredients while the disadvantage is that it requires high efficiency for breaking down lignin as a wrapper for cellulose and hemicellulose. Cellulose is the component most responsible for the production of bioethanol from lignocellulosic biomass (Prasad et al. 2019). In general, there are three main stages in bioethanol production, including pretreatment, hydrolysis, and fermentation. However, the production of bioethanol from biomass, one of which is OPEFB, requires longer stages, namely, pretreatment, hydrolysis, filtration, fermentation, and purification. The stages of the OPEFB conversion process into bioethanol can be seen in Fig. 6. Pretreatment is used to produce monomer from OPEFB which then has the potential to be used as raw material for bioethanol fermentation (Suhartini et al. 2022b). The choice of the pretreatment method can greatly affect the economy because increasing conversion efficiency tends to add significant overall costs (Rabemanolontsoa and Saka 2016). Less significant lignin removal can reduce the rate of hydrolysis and decrease the efficiency of the conversion process, therefore removal of lignin prior to hydrolysis is essential to ensure higher production of C5 and C6 sugars (Wan Azelee et al. 2014).

2.4.2 Pretreatment for Bioethanol Production

Lignin as an aromatic phenolic compound can be attacked by laccase enzymes so that its molecular structure is easily degraded. Laccase enzymes can attack phenolic lignin to form phenoxy radicals but cannot oxidize non-phenolic lignin directly because of its low redox potential. To this end, the laccase enzyme can oxidize low molecular weight mediators which act as electron carriers and diffuse into the insoluble lignin structure to oxidize them. Enzymatic pretreatment of biomass generally uses specific enzymes isolated from certain microbes. This pretreatment tends to be used to degrade lignin which can be carried out by complex lignin enzymes, consisting of lignin-peroxidase (Li-P), manganese-peroxidase (Mn-P), and laccase (Lac). These enzymes are capable of converting and breaking down lignin compounds into their constituent components, namely, conipheryl alcohol, p-cumaryl alcohol, and synapcyl alcohol. After lignin is degraded into its constituents, cellulose, and hemicellulose become more accessible (Ravindran and Jaiswal 2016).

Hendriks and Zeeman (2009) stated that pretreatment of lignocellulosic biomass can also be carried out using combination, thermal, steam, and chemical methods which include alkaline, acidic, and organosolv liquids. Physical pretreatment, i.e., cutting biomass into smaller sizes is widely applied to increase the surface area and reduce the degree of polymerization (Taherzadeh and Karimi 2008). On the other hand, chemical pretreatment, namely, the use of sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), showed excellent results for lignin degradation, reduced crystallinity, and degree of polymerization so as to increase the digestibility of cellulose (Tsabitah et al. 2014). In its application, H_2SO_4 and NaOH are widely applied in pretreatment of biomass to produce biogas and bioethanol although there are drawbacks, namely, the emergence of chemical waste that requires further handling. Biological pretreatments, such as ensiling using EM4 and ensiling using molasses have also been widely studied as alternative options for producing biogas and

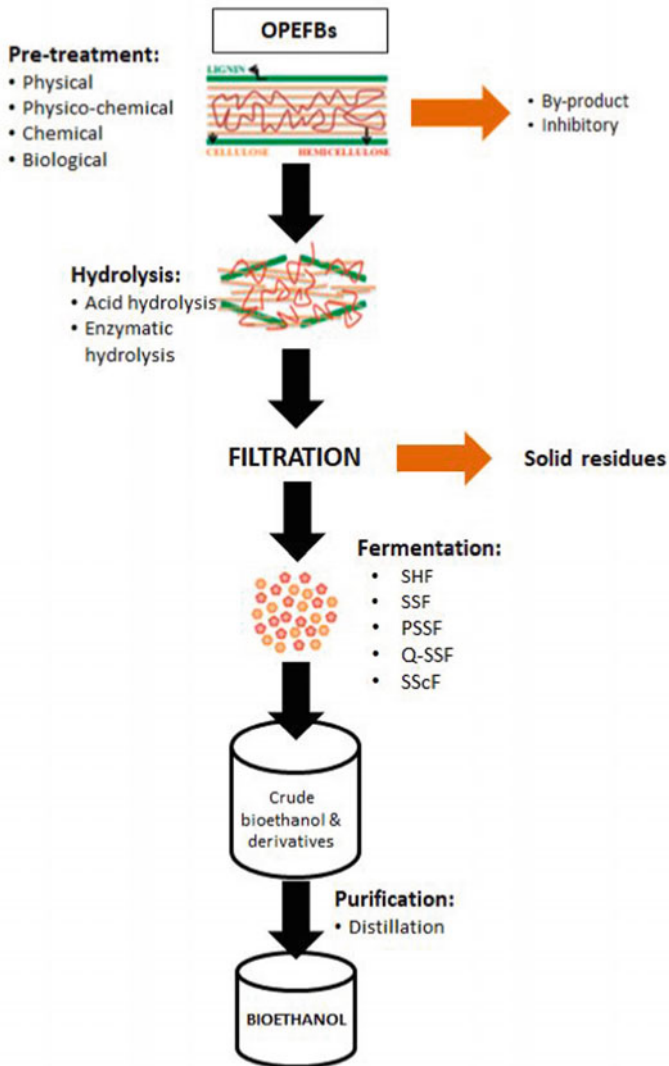


Fig. 6 Stages of the conversion process of OPEFB into bioethanol (Suhartini et al. 2022b)

bioethanol because of their economical and environmentally friendly advantages (Lunsin et al. 2018). The relatively slow rate of biological pretreatment is the main weakness of biological pretreatment. As for the use of the laccase enzyme, as a branch of biological pretreatment, it is proven to be able to degrade lignin in lignocellulosic biomass more effectively (Schroyen et al. 2015). The effectiveness and efficiency of pretreatment in degrading lignin content is highly dependent on the composition of the biomass and operating conditions.

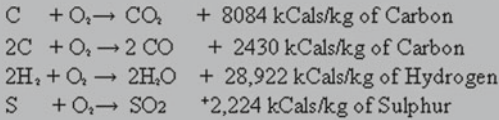
2.4.3 Examples

Releasing the sugar content from its biomass from the complex structure via pretreatment should be facilitated with careful consideration into the economic viability and sustainability regarding the chemical or materials used. Sugarcane bagasse (SB) has been investigated as the feedstock for bioethanol production. Couple pretreatment has been applied with chemical and biological to assure the delignification could be higher. Imidazole, a green solvent, was used to take account for disruption in the complex of cell wall structure of SB. Total bioethanol production of 30%, with ethanol volume of 110.3 L/ton sugarcane has been reached and shows a great correlation between the methods to manage its lignin content (Valladares-Diestra et al. 2022). Following the physicochemical pretreatment, other lignocellulosic biomass, *Miscanthus* as part of energy crops is being exposed to some methods for having much lower lignin content. After pretreated with a novel chemical surfactant, mild chemical (H_2SO_4 or NaOH) in steam explosion was used as the pretreatment for *miscanthus* and these combined methods have demonstrated an increment in lignocellulose accessibility and will promote the enzymatic saccharification in its biomass (Sun et al. 2020). Similarly, a study by Gao et al. (2021) coupling the steam explosion with green-liquor pretreatment and leading to the highest bioethanol yield of 20.3% (%dry biomass) compared with other reported bamboo processes. Conclusively, pretreatment is becoming one of the great strategies to enhance bioethanol production by giving more accessibility to the biomass structure and increasing the hydrolysis activity.

2.5 Thermochemical

2.5.1 Direct Combustion

Combustion is a chemical reaction between flammable matter and oxygen, resulting in the release of heat (Glassman 1977). Direct combustion is one of the oldest methods that is quite simple and is commonly used in thermochemical energy production. Direct combustion is an energy conversion carried out by burning sufficient agro-material in the air to produce heat, steam, or electricity (Mandø 2013). The hydrogen and carbon contained in the fuel will react with oxygen and release energy. During combustion, there are substances that vaporize together with a portion of the carbon in the form of flammable gaseous hydrocarbons and the release of carbon monoxide with thermal degradation. Carbon monoxide is formed due to the reduction reaction of CO_2 with C, with the following chemical formula:



In general, combustion is carried out in a furnace, steam turbine, or boiler (Ye et al. 2022) with a temperature range of 800–1000 °C. Three stages in the direct combustion of agro-materials are evaporation of the water, then distillation and combustion of volatiles occur after which carbon is bound and oxygen reacts at high temperatures (Lackner 2013). Energy is produced in the last two stages; this process is suitable for the conversion of all types of biomass that have a low moisture content (<50%). Several factors affect the direct combustion process, such as the volatile content, water, ash, and tar of the material (Lackner 2013). Direct combustion is considered carbon neutral, although it produces pollutants in the form of nitrogen oxides, sulfur oxides, carbon dioxide, and dioxins.

The heat generated from the direct combustion process is difficult to store, so it must be used immediately. The production cost of the direct combustion process is slightly higher than the pyrolysis and gasification processes. This is because the preparation of raw materials for direct combustion requires drying, cutting, and crushing before being fed into the boiler.

2.5.2 Torrefaction

Torrefaction is basically an improvement process from the direct combustion process on a large scale. Torrefaction is the heat degradation of biomass in inert or nitrogen (Wang et al. 2023). The temperature used for the torrefaction process ranges from 200 to 300 °C without oxygen within a few hours (depending on the condition of the biomass) in non-oxidized conditions with the aim of improving the physicochemical properties of biomass as a solid fuel. Torrefaction is a mild pyrolysis of the fibrous structure of crushed biomass (Han et al. 2022). Its heating value and hydrophobicity are increased to increase the stability of the biomass during storage. The main product produced in this process is charcoal.

Torrefaction can improve the characteristics of the resulting fuel by reducing the water content, increasing the heating value, reducing the oxygen/carbon ratio, and increasing the energy density. There are two kinds of methods used in torrefaction, the wet process and the dry process (Akbari et al. 2021). In wet torrefaction, agro-materials are treated with compressed hot water and produce solid fuel products, aqueous compounds, and gases. However, wet torrefaction has the disadvantage that it is still necessary to separate the excess water contained in the biomass. Dry torrefaction requires intensive drying of agro-materials at higher temperatures. The temperature used for dry torrefaction ranges from 230 to 300 °C in the absence of oxygen.

2.5.3 Pulverization and Drying

In the pulverization and drying process, the biomass is reduced in size and dried with the aim of increasing the quality of the raw material so that it is easy to burn (Sarnavi et al. 2023). Besides that, reducing the size can make it easier for the biomass to be put into the reactor/furnace, and drying can help the next process to be more efficient. The result of this process is solid fuel.

Based on the crushing principle, the biomass pulverizer is classified into hammer, blade, and combined types (Wei et al. 2014). According to the pulverization method and approach, the biomass pulverizer is classified into chopping, rolling cutting, and combined pulverizing types. According to the purpose and particle size of the crushed material, it is classified into coarse, twisted, and fine types.

Drying is a process of removing the water content contained in a material using evaporation to obtain a dry solid product (El-Mesery and El-khawaga 2022). There is a process of transfer of heat and water vapor from the surface of the material to the air without changing the shape of the material. There are two types of drying, namely, natural and artificial drying. Natural drying can be done by placing the material in the free air, and under the heat of the sun, the air is allowed to remove the moisture contained in the biomass, while the sun's heat can help evaporate water from the material. Artificial drying is done by utilizing the heat generated from combustion. This drying can be done using a dryer, such as using a tunnel dryer or oven. The advantage of artificial drying over natural drying is that the temperature and drying rate can be controlled according to needs and will not be affected by climate change. However, artificial drying also has the disadvantage of requiring a higher cost when compared to natural drying.

2.5.4 Liquefaction

Liquefaction is included in the thermochemical agro-material conversion technology (Kavitha et al. 2023). In the process, agro-materials are converted to liquid fuel products through a complex sequence of physical and chemical changes. Agro-materials are decomposed into small molecules. These small molecules are unstable and reactive and can be polymerized into oily compounds. Liquefaction can be done directly or indirectly. Direct liquefaction involves fast pyrolysis to produce tar and pyrolysis oil (Folke Dahl et al. 2011). Indirect liquefaction involves the use of a catalyst to convert non-condensable gaseous products from pyrolysis or gasification into liquid products.

In direct liquefaction (Folke Dahl et al. 2011), the biomass is directly converted into products without drying. Under these conditions, water remains in a liquid state and has a low viscosity and high capacity to dissolve inorganic compounds. Indirect liquefaction involves low temperature (300–350 °C) and high pressure (5–20 MPa) with a residence time of about 30 min and is often carried out using a catalyst in the presence of hydrogen, so this process can also be called catalytic liquefaction. The composition of the resulting pyrolysis oil and char is influenced by the liquefaction

method used. The difference between liquefaction and pyrolysis is that pyrolysis usually occurs at higher temperatures and lower pressures, and it is necessary to dry the raw material first. This liquefaction technology is rarely used because it requires a more expensive reactor. From the liquefaction process, liquid fuels, commonly known as biofuels, such as ethanol and methanol, will be obtained. The most frequently used biofuel is ethanol which can be obtained from sugarcane, corn, and other grains.

2.5.5 Pyrolysis

Pyrolysis is a process in which organic materials containing carbon are decomposed thermochemically (Liu et al. 2022). The pyrolysis process involves little or no oxygen in a closed vessel. Oxygen is only required in small quantities for combustion to occur in order to produce enough heat to start the endothermic pyrolysis process. Then slowly, the oxygen in the vessel will run out because there is no oxygen supply from outside during the process, resulting in incomplete combustion in the vessel, and charcoal is produced. The mechanism of the pyrolysis process of biomass generally consists of hydrolysis reactions, primary reactions, and secondary reactions. Biomass will decompose thermally without oxygen and involves many reactions of biomass biomolecules.

Pyrolysis of biomass can be influenced by four factors, including water content, decomposition of cellulose, lignin, and decomposition of hemicellulose (Vuppaladadiyam et al. 2022). Pyrolysis can be carried out at high temperatures up to 800 °C and low pressures up to 700 kPa. In extreme pyrolysis, carbonization will occur, which will only produce charcoal. If the pyrolysis reactor is equipped with a condenser (Fig. 7), there will be a change in the form of the resulting gas to liquid commonly known as pyrolysis oil. The products produced during the pyrolysis are charcoal, pyrolysis oil, tar, and non-condensable and flammable gases, such as CO, CO₂, CH₄, and H₂ (Samer 2017).

A pyrolysis reactor is an equipment to decompose organic compounds by the heating process without direct contact with outside air at a temperature of 300–600 °C. This reactor is sealed to prevent excessive heat from escaping. The pyrolysis reactor is made of a cylindrical tank made of stainless steel, with rock walls installed between the reactor covers to minimize heat escape. The heat source used is a gas stove with LPG fuel, and there is a thermocouple connected to a pipe in the reactor so that the temperature can be measured and adjusted as desired. The large volume of the reactor will affect the amount of input that will be processed into pyrolysis oil.

The working principle of the pyrolysis reactor is to carry out the process of burning biomass without air (O₂). The decomposition of organic matter will occur as the temperature used increases. There are several types of reactors used in the pyrolysis process, namely, batch/semi-batch, fluidized bed reactors, fixed bed reactors, screw kilns, and spouted beds. Batch/semi-batch-type reactors are the type of reactor that is widely used by researchers because the design is simpler and easier to operate.

There are four stages of the pyrolysis mechanism based on the lignocellulose contained in the material, including removal of water content, decomposition of

Fig. 7 A small pyrolysis reactor



hemicellulose, decomposition of cellulose, and decomposition of lignin. The dewatering step occurs at a temperature of less than 200 °C. If the water content in the material is too high, there will be a risk of producing large amounts of ash. The hemicellulose decomposition stage occurs at a temperature of 200–280 °C at this stage to produce syngas and minor pyrolysis oil. The cellulose decomposition stage occurs at temperatures above 240–350 °C. At this stage, syngas, pyrolysis oil, and minor biochar products are produced. Furthermore, the last stage is the decomposition of lignin which occurs at a temperature of 280–500 °C (Samer 2017). At this stage, the products of pyrolysis oil and biochar are produced.

The mechanism of the pyrolysis process can be seen in Fig. 8. Cellulose and hemicellulose mainly form volatile products on heating due to the thermal splitting of the sugar units. Lignin mainly forms char because it is not easily broken down into smaller molecules.

Some factors that can affect pyrolysis products include temperature, type of agro-material, heating rate, the proportion of oxygen, and equipment design. In general, the resulting charcoal is up to 50% of the dry agro material, the gas product ranges from 5 to 20% depending on the temperature used, while the tar product can be up to 25% by weight percent of the dry agro material. Charcoal has low sulfur and nitrogen content, making it much easier to store and transport than the agro-raw materials used. The resulting tar still contains water and can be separated by distillation or extraction. Pyrolysis oil obtained from the condensation of the resulting gas needs to be acid-neutralized so that it can be used as fuel. The quality and quantity of the product produced are also influenced by the temperature used during the pyrolysis

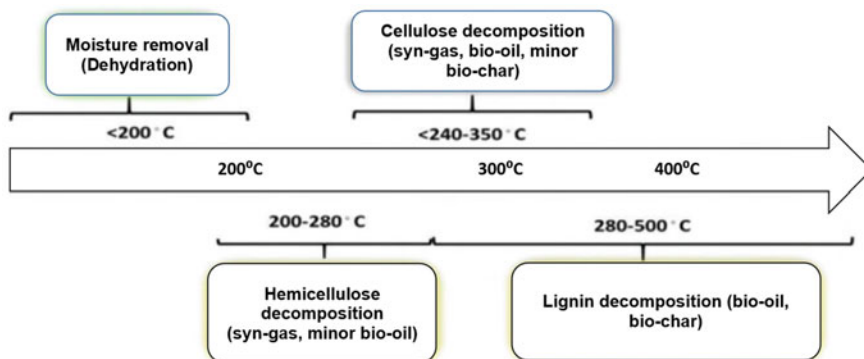


Fig. 7 Biomass degradation temperature (Samer 2017)

process. There are three types of pyrolysis based on temperature levels (Weir et al. 2022), as seen in Table 5.

Slow pyrolysis is a process in which biomass is heated at a slow temperature rate in an inert atmosphere to a maximum temperature (de Almeida et al. 2022). Slow pyrolysis takes place at low heating rates (0.1–0.8 °C/s), longer times (5–30 min or even 25–35 h), and temperatures around 300–550 °C. This pyrolysis process aims to obtain maximum bio-charcoal, syngas, and pyrolysis oil simultaneously.

Table 5 Characteristics of biomass thermochemical conversion technologies

		Pyrolysis		Liquefaction	Gasification
		Slow	Fast		
<i>Feedstock</i>					
Feed Size		Any	Small	Very small	Mixed, large
Moisture content		Low	Very low	Very low	50% max
<i>Parameters</i>					
Temperature °C		400–600	450–900	250–400	1000–1500
Pressure, bar		0.01–1	1	100–200	Up to 20
Maximum throughput achieved to date, dry/year		5	0.05	0.1	40
<i>Product (dry basis on dry feed)</i>					
Gas	Yield, %wt	Up to 40	Up to 70	20	100–250
	HHV, MJ/NM3	5–10	10–20	2–6	May 15
Liquid	Yield, %wt	Up to 30	Up to 70	Up to 50	Up to 3
	HHV, MJ/kg	23	23	30	23
Solid	Yield, %wt	30	Up to 15	Up to 25	Nil (ash)
	HHV, MJ/kg	30	30	30	–

This process can also eliminate the content of smoke production and the formation of solid products. This method can produce a solid uniform product with low water content and higher energy content than the initial biomass. Fast pyrolysis takes place at higher heating rates (10–1000 °C), and very short residence times (0.5–2 s), with temperatures around 850–1250 °C (Hu et al. 2022). This pyrolysis aims to get more pyrolysis oil products than bio-charcoal and syngas. In general, fast pyrolysis produces 60–75% liquid, 15–25% solid, and 10–20% gas. Flash pyrolysis is almost the same as fast pyrolysis, with some modifications and improvements (Cornelissen et al. 2009). This pyrolysis takes place at a very high heating rate of around 1000 °C, a residence time of 0.1–1 s, with a temperature of 800–1000 °C. This pyrolysis aims to get the maximum syngas product.

Pyrolysis technology has several advantages, including, namely, the process is simple, so it does not require high expertise to operate. This technology can eliminate carcinogenic compounds such as PAHs (Polycyclic Aromatic Hydrocarbons). This technology is quite efficient. Namely, it can produce three products with only one process required. The resulting pyrolysis oil product is able to overcome the problem of traditional smoking of fish/meat. The main components of pyrolysis oil are organic compounds and water (15–30%). Therefore, pyrolysis oil has the opportunity to be converted into fuel and chemical sources. The biggest component of bio-oil is hydrocarbons which are traditionally produced from petroleum. Given the dwindling reserves of petroleum, pyrolysis oil has the potential to be developed as a substitute fuel for petroleum. Pyrolysis oil can be used as fuel in furnaces or boilers. However, the high oxygen content in pyrolysis oil components can cause undesirable fuel characteristics, such as increased viscosity, corrosion, low heating value, and unstable during storage (can form a precipitate). Several organic compounds of high economic value found in pyrolysis oil are levoglucosan, toluene, xylene, limonene, and phenol. The constituent components of pyrolysis oil are highly dependent on the composition of the raw materials, the pyrolysis process, and the reaction conditions. Therefore, research on raw materials and pyrolysis process variations is important to extract chemical components with high economic value.

2.5.6 Gasification

Gasification is the partial (imperfect) combustion of solid fuels, which can produce flammable gas and ash (Valizadeh et al. 2022). Gasification of agro-materials belongs to the thermochemical conversion technology, in which solid agro-materials are converted into gaseous fuels. Under controlled conditions, characterized by low oxygen supply and high temperatures, most of the agro materials can be converted into producer gas fuels consisting of carbon monoxide (CO), hydrogen (H₂), carbon dioxide, nitrogen, and methane (CH₄). Producer gas is a mixture of flammable and non-flammable gases. Basically, the gasification process begins with a pyrolysis process at a temperature of around 150–900 °C, followed by an oxidation process of the pyrolysis gas at a temperature of 900–1,400 °C, then a reduction process at a temperature of 600–900 °C (Valizadeh et al. 2022).

The gasification process can produce relatively higher gas, which is around 85%, compared to pyrolysis, which can only produce around 35% gas. Gas fuel from biomass gasification can be used for cooking, both at the household level and in small industries in undeveloped areas. In addition, the gas is used to drive turbines and combustion engines, as fuel in steam boilers, and for lighting. The application of biomass thermal gas is a more efficient alternative and produces lower pollution than direct combustion, although it has the disadvantage of higher investment costs.

There are four different process stages during fuel gasification (Akhtar et al. 2018), among them are:

a. Fuel drying

Agrofuel enters through the top of the gasifier and then moves down during the process. Heat radiation from the combustion zone helps reduce fuel moisture entering the drying zone. Temperatures in this zone range less than 120 °C.

b. Pyrolysis

Dry fuel moves downward and is exposed to heating at higher temperatures, namely, above 200 °C. At this temperature, the fuel begins to lose its volatile content. In this zone, no air is allowed to enter. When the temperature reaches 400 °C, an exothermic reaction occurs, where the structure of the wood material or other organic solids begins to break down.

c. Combustion/Oxidation

The combustion reaction is an exothermic reaction resulting in a theoretical oxidation temperature of up to 1450 °C. The combustible substance of the fuel usually consists of carbon, hydrogen, and oxygen. In complete combustion, carbon dioxide is obtained from carbon in the fuel and water is obtained from hydrogen, usually in the form of water vapour. This heating causes some of the charcoal to be oxidized, and the rest undergoes a reduction process.

d. Reduction

Partial combustion products, such as water, carbon dioxide, and partially cracked pyrolysis products, move through the hot charcoal bed, where subsequent reduction reactions occur. The temperature in the reduction zone ranges from 800 to 1000 °C. The lower the temperature in the reduction zone, the lower the heating value of the gas.

2.5.7 Plasma Technology

Plasma is a gas that undergoes ionization in an electric discharge or a mixture of electrons, radicals, and negative and positive ions. Plasma technology can be used to decompose organic compounds from solid, liquid, or gas waste (Dimitrakellis et al. 2022). This technology is carried out by heating the waste using a device similar to an oven/microwave. The heating principle used in plasma technology is that in

the combustion chamber, two high-voltage electrodes (about 10,000 V) are given, and then the waste is put into the furnace. The electrode is given an electric voltage so that plasma will form, which will decompose the waste. Plasma technology has the advantage that it does not require a large area, takes a short time, and does not involve chemicals.

In wastewater treatment, plasma technology plays a role in various oxidizing processes of the compounds (Dimitrakellis et al. 2022). A reaction occurs on ions and electrons in the plasma in the liquid waste, and then UV light and shockwave are formed. These ions and electrons contain very high energy causing the decomposition of water (H_2O) and producing active species such as OH, O, H, and H_2O_2 . Active specifics are strong oxidants that can oxidize organic compounds and kill bacteria in liquid waste.

3 Conclusion

Biomass can be derived from any organic material including agricultural crop residues, agro-industrial waste, household waste, forestry waste, etc. Different types of biomass has also unique characteristics, which may play a key factor in the selection of the best conversion routes. Lignocellulosic biomass, considered as third-generation sources of bioenergy, is potential to be directly valorized into bioenergy, either via physical/mechanical, biochemical, and thermochemical. However, the results may not be optimum. Hence, pretreatment or other measures are often required to improve the conversion process' efficacy. Specific to anaerobic technology, it is widely adopted in the global world from small to commercial scale. The resulted biogas can be converted into electricity (and heat) or biomethane and the digestate into biofertilizer. Transesterification is the main process to transform biomass into biodiesel, mostly suitable for biomass with high in lipid or oil contents. While fermentation of lignocellulosic biomass to bioethanol remains a challenge, therefore integration with pretreatment and an improved hydrolysis step are necessary. Densification of biomass into biopellets can be one of the alternatives with lower operating cost, however, the risk of carbon emission from burning the fuels need to be considered. Thermochemical pathways offer greater and faster conversion to bioenergy, yet a high cost for the capital investment and operation may hinder the technology for commercial application in Indonesia.

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References

- Abou El-Nour KMM, Eftaiha A, Al-Warthan A, Ammar RAA (2010) Synthesis and applications of silver nanoparticles. *Arab J Chem* 3:135–140
- Ahamed M, AlSaalhi MS, Siddiqui MKJ (2010) Silver nanoparticle applications and human health. *Clin Chim Acta* 411:1841–1848
- Akhavan O, Ghaderi E (2012) Cu and CuO nanoparticles immobilized by silica thin films as antibacterial materials and photocatalysts. *Surf Coat Technol* 205:219–223
- Ali SM, Yousef NMH, Nafady NA (2015) Application of biosynthesized silver nanoparticles for the control of land snail *Eobania vermiculata* and some plant pathogenic fungi. *J Nanomater* 218904
- Ali A, Zafar H, Zia M, Ul Haq I, Phull AR, Ali JS, Hussain A (2016) Synthesis, characterization, applications, and challenges of iron oxide nanoparticles. *Nanotechnol Sci Appl* 9:49–67
- Ali K, Dwivedi S, Azam A, Saquib Q, Al-Said MS, Alkhedhairi AA, Musarrat J (2017) Aloe vera extract functionalized zinc oxide nanoparticles as nanoantibiotics against multidrug resistant clinical bacterial isolates. *J Colloid Interface Sci* 472(2016):145–156
- Anand R, Kulothungan S (2014) Silver mediated bacterial nanoparticles as seed dressing against crown rot pathogen of groundnut. *Arch Appl Sci Res* 6:109–113
- Anjum NA, Adam V, Kizek R, Duarte AC, Pereira E, Iqbal M, Lukatkin AS, Ahmad I (2015) Nanoscale copper in the soil-plant system: toxicity and underlying potential mechanisms. *Environ Res* 138:306–325
- Aqel A, El-Nour KMM, Ammar RAA, Al-Warthan A (2012) Carbon nanotubes, science and technology part (I) structure, synthesis and characterization. *Arab J Chem* 5:1–23
- Arokiyaraj S, Saravanan M, Udaya Prakash NK (2013) Enhanced antibacterial activity of iron oxide magnetic nanoparticles treated with *Argemone mexicana* L. leaf extract: an in vitro study. *Mat Res Bull* 48:3323–3327
- Asanithi P, Chaiyakun S, Limsuwan P (2012) Growth of silver nanoparticles by DC magnetron sputtering. *J Nanomater* 2012:963609
- Asha-Rani PV, Mun GLK, Hande MP, Valiyaveetil S (2009) Cytotoxicity and genotoxicity of silver nanoparticles in human cells. *ACS Nano* 3:279–290
- Astefanei A, Núñez O, Galceran MT (2015) Characterisation and determination of fullerenes: a critical review. *Anal Chim Acta* 882:1–21
- Barrena R, Casals E, Colon J, Font X, Sanchez A, Puentes V (2009) Evaluation of the ecotoxicity of model nanoparticles. *Chemosphere* 75:850–857
- Barrett CS, Cohen JB, Faber J, Jenkins R, Leyden DE, Russ JC, Predecki PK (1986) *Advances in X-ray analysis*, vol 29. Plenum Press, New York, NY, USA
- Bhuyan T, Mishra K, Khanuja M, Prasad R, Varma A (2015) Biosynthesis of zinc oxide nanoparticles from *Azadirachta indica* for antibacterial and photocatalytic applications. *Mater Sci Semicond Process* 32:55–61
- Boro RC, Kaushal J, Nangia Y, Wangoo N, Bhasinc A, Suri CR (2011) Gold nanoparticles catalyzed chemiluminescence immunoassay for detection of herbicide 2,4-dichlorophenoxyacetic acid. *Analyst* 136:2125–2130
- Brice-Profeta S, Arrio MA, Troncet E (2005) Magnetocorderin γ -Fe₂O₃ nanoparticles: a XMCD study. *J Magn Magn Mat* 288:354–365
- Cao YC (2002) Nanoparticles with Raman spectroscopic fingerprints for DNA and RNA detection. *Science* 80:1536–1540
- Chauhan RPS, Gupta C, Prakash D (2012) Methodological advancements in green nanotechnology and their applications in biological synthesis of herbal nanoparticles. *Int J Bioassays* 7:6–10
- Chen Z, Meng HA, Xing GM, Chen C, Zhao Y, Jia G, Wang T, Yuan H, Ye C, Zhao F, Chai Z, Zhu C, Fang X, Ma B, Wan L (2006) Acute toxicological effects of copper nanoparticles in vivo. *Toxicol Lett* 163:109–120
- Chen X, Schluesener HJ (2008) Nanosilver: a nanoparticle in medical application. *Toxicol Lett* 176:1–12

- Chen T, Wong YS, Zheng W, Bai Y, Huang L (2008) Selenium nanoparticles fabricated in *Undaria pinnatifida* polysaccharide solutions induce mitochondria-mediated apoptosis in A375 human melanoma cells. *Coll Surf B* 67:26–31
- Corredor E, Testillano PS, Coronado MJ, González-Melendi P, Fernández-Pacheco R, Marquina C, Ibarra MR, de la Fuente JM, Rubiales D, Pérez-de-Luque A, Risueño MC (2009) Nanoparticle penetration and transport in living pumpkin plants: in situ subcellular identification. *BMC Plant Biol* 9:45
- De Jaeger N, Demeyere H, Finsy R, Sneyers R, Vanderdeelen J, van der Meeren P, van Laethem M (1991) Particle sizing by photon correlation spectroscopy. Part I. Monodisperse latices. Influence of scattering angle and concentration of dispersed material. *Part Part Sys Charac* 8:179–186
- de Oliveira JL, Campos EVR, Bakshi M, Abhilash PC, Fraceto LF (2014) Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: prospects and promises. *Biotechnol Adv* 32:1550–1561
- Doshi R, Braidia W, Christodoulatos C, Wazne M, O'Connor G (2008) Nanoaluminum: transport through sand columns and environmental effects on plant and soil communication. *Environ Res* 106:296–303
- Dubas ST, Pimpan V (2008) Humic acid assisted synthesis of silver nanoparticles and its application to herbicide detection. *Mater Lett* 62:2661–2663
- Duman F, Ismail Ocsoy I, Kup FO (2016) Chamomile flower extract-directed CuO nanoparticle formation for its antioxidant and DNA cleavage properties. *Mat Sci Eng C* 60:333–338
- Ekimov AI, Onuschchenko AA (1981) Quantum size effect in three-dimensional microscopic semiconductor crystals. *JETP Lett* 34:345–348
- El-Rahman AFA, Mohammad TGM (2013) Green synthesis of silver nanoparticle using *Eucalyptus globulus* leaf extract and its antibacterial activity. *J Appl Sci Res* 9:6437–6440
- Embiale A, Hussein M, Husen A, Sahile S, Mohammed K (2016) Differential sensitivity of *Pisum sativum* L. cultivars to water-deficit stress: changes in growth, water status, chlorophyll fluorescence and gas exchange attributes. *J Agron* 15:45–57
- Eric D (1987) Engines of creation: the coming area of nanotechnology. Anchor Library of Science
- Eustis S, El-Sayed MA (2006) Why gold nanoparticles are more precious than pretty gold: noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. *Chem Soc Rev* 35:209–217
- FAO (2009) How to feed the world in 2050. FAO Report Oct. 2009:1–35
- Faraji M, Yamini Y, Rezaee M (2010) Magnetic nanoparticles: synthesis, stabilization, functionalization, characterization, and applications. *J Iran Chem Soc* 7:1–37
- Feynman RP (1960) There's plenty of room at the bottom. *Eng Sci* 23:22–36
- Freestone I, Meeks N, Sax M, Higgitt C (2007) The lycurgus cup—A Roman nanotechnology. *Gold Bull* 40:270–277
- Getnet Z, Husen A, Fetene M, Yemata G (2015) Growth, water status, physiological, biochemical and yield response of stay green sorghum *Sorghum bicolor* (L.) Moench varieties-a field trial under drought-prone area in Amhara regional state. Ethiopia *J Agron* 14:188–202
- Grillo R, Pereira AES, Nishisaka CS, Lima RD, Oehlke K, Greiner R, Leonardo F, Fraceto LF (2014) Chitosan/tripolyphosphate nanoparticles loaded with paraquat herbicide. An environmentally safer alternative for weed control. *J Hazard Mater* 278:163–171
- Gujrati M, Malamas A, Shin T, Jin E, Sun Y, Lu ZR (2014) Multifunctional cationic lipid-based nanoparticles facilitate endosomal escape and reduction-triggered cytosolic siRNA release. *Mol Pharm* 11:2734–2744
- Guo D, Xie G, Luo J (2014) Mechanical properties of nanoparticles: basics and applications. *J Phys D Appl Phys* 47:13001
- Hafez EE, Hassan HS, Elkady M, Salama E (2014) Assessment of antibacterial activity for synthesized zinc oxide nanorods against plant pathogenic strains. *Int J Sci Technol Res* 3:318–324

- Hassan MS, Amna T, Yang OB, El-Newehy MH, Al-Deyab SS, Khil MS (2012) Smart copper oxide nanocrystals: Synthesis, characterization, electrochemical and potent antibacterial activity. *Coll Surf B Biointerf* 97:201–206
- Hirsch LR, Stafford RJ, Bankson JA, Sershen SR, Rivera B, Price RE, Hazle JD, Halas NJ, West JL (2003) Nanoshell-mediated near-infrared thermal therapy of tumours under magnetic resonance guidance. *Proc Natl Acad Sci USA* 100:13549–13554
- Holgate ST (2010) Exposure, uptake, distribution and toxicity of nanomaterials in humans. *J Biomed Nanotechnol* 6:1–19
- Holzinger M, Le Goff A, Cosnier S (2014) Nanomaterials for biosensing applications: a review. *Front Chem* 2:63
- Hossain Z, Mustafa G, Komatsu S (2015) Plant responses to nanoparticle stress. *Int J Mol Sci* 16:26644–26653
- Hou J, Shang J, Jiao C, Jiang P, Xiao H, Luo L, Liu T (2013) A core crosslinked polymeric micellar platinum(IV) prodrug with enhanced anticancer efficiency. *Macromol Biosci* 13:954–965
- Mironava T, Simon M, Rafailovich MH, Rigas B (2013) Platinum folate nanoparticles toxicity: cancer vs. normal cells. *Toxicol in Vitro* 27:882–889
- Husen A, Iqbal M, Aref MI (2014) Growth, water status and leaf characteristics of *Brassica carinata* under drought stress and rehydration conditions. *Braz J Bot* 37:217–227
- Husen A, Iqbal M, Aref IM (2016) IAA-induced alteration in growth and photosynthesis of pea (*Pisum sativum* L.) plants grown under salt stress. *J Environ Biol* 37:421–429
- Husen A (2017) Gold nanoparticles from plant system: synthesis, characterization and application. In: Ghorbanpourn M, Manika K, Varma A (eds) *Nanoscience and plant–soil systems*, vol 48. Springer International Publication, pp 455–479
- Husen A, Iqbal M, Aref IM (2017) Plant growth and foliar characteristics of faba bean (*Vicia faba* L.) as affected by indole-acetic acid under water-sufficient and water-deficient conditions. *J Environ Biol* 38:179–186
- Husen A, Iqbal M, Sohrab SS, Ansari MKA (2018) Salicylic acid alleviates salinity-caused damage to foliar functions, plant growth and antioxidant system in ethiopian mustard (*Brassica carinata* A. Br.) *Agri Food Sec* 7:44
- Husen A, Siddiqi KS (2014a) Carbon and fullerene nanomaterials in plant system. *J Nanobiotechnol* 12:16
- Husen A, Siddiqi KS (2014b) Phytosynthesis of nanoparticles: concept, controversy and application. *Nano Res Lett* 9:229
- Husen A, Siddiqi KS (2014c) Plants and microbes assisted selenium nanoparticles: characterization and application. *J Nanobiotechnol* 12:28
- Hussein M, Embiale A, Husen A, Aref IM, Iqbal M (2017) Salinity-induced modulation of plant growth and photosynthetic parameters in faba bean (*Vicia faba*) cultivars. *Pak J Bot* 49:867–877
- Istiani W, Sribudiani E, Somadona S (2021) Biopellet from waste candlenut shell (*Aleurites moluccana*) with mixture of sago stem biomass (*Metroxylon sago*) and sawdust as an alternative energy source. *Wahana Forestra: Jurnal Kehutanan* 67:170–180
- Iavicoli I, Leso V, Beezhold DH, Shvedova AA (2017) Nanotechnology in agriculture: opportunities, toxicological implications, and occupational risks. *Toxicol App Pharmacol* 329:96–111
- Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354:56–58
- Ibrahim KS (2013) Carbon nanotubes-properties and applications: a review. *Carbon Lett* 14:131–144
- Iravani S (2011) Green synthesis of metal nanoparticles using plants. *Green Chem* 13:2638–2650
- Jaasim B, Thomas R, Mathew J, Radhakrishnan EK (2016) Plant growth and diosgenin enhancement effect of silver nanoparticles in Fenugreek (*Trigonella foenum-graecum* L.). *Saudi Pharm J* 25:443–447
- Jaasim B, Thomas R, Mathew J, Radhakrishnan EK (2017) Plant growth and diosgenin enhancement effect of silver nanoparticles in Fenugreek (*Trigonella foenum-graecum* L.) *Saudi Pharma J* 25:443–447

- Jiang J, Oberdörster G, Biswas P (2009) Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11:77–89
- Jung JH, Cheol OH, Soo NH, Ji JH, Soo KS (2006) Metal nanoparticle generation using a small ceramic heater with a local heating area. *J Aerosol Sci* 37:1662–1670
- Kaida T, Kobayashi K, Adachi M, Suzuki F (2004) Optical characteristics of titanium oxide interference film and the film laminated with oxides and their applications for cosmetics. *J Cosmet Sci* 55:219–220
- Kang T, Wang F, Lu L, Zhang Y, Liu T (2010) Methyl parathion sensors based on gold nanoparticles and Nafion film modified glassy carbon electrodes. *Sens Actuat B* 145:104–109
- Kanhed P, Birla S, Gaikwad S, Gade A, Seabra AB, Rubilar O, Duran N, Rai M (2014) In vitro antifungal efficacy of copper nanoparticles against selected crop pathogenic fungi. *Mater Lett* 115:13–17
- Karnan T, Selvakumar SAS (2016) Biosynthesis of ZnO nanoparticles using rambutan (*Nephelium lappaceum* L.) peel extract and their photocatalytic activity on methyl orange dye. *J Mol Struct* 1125:358–365
- Khadri H, Alzohairy M, Janardhan A, Kumar AP, Narasimha G (2013) Green synthesis of silver nanoparticles with high fungicidal activity from olive seed extract. *Adv Nanopart* 2:241–246
- Khodakovskaya M, Dervishi E, Mahmood M, Xu Y, Li Z, Watanabe F, Biris AS (2009) Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. *ACS Nano* 3:3221–3227
- Khot LR, Sankaran S, Maja JM, Ehsani R, Schuster EW (2012) Applications of nanomaterials in agricultural production and crop protection: a review. *Crop Prot* 35:64–70
- Kim DY, Saratale RG, Shinde S, Syed A, Ameen F, Ghodake G (2018) Green synthesis of silver nanoparticles using *Laminaria japonica* extract: characterization and seedling growth assessment. *J Clean Prod* 172:2910–2918
- Klug HP, Alexander LE (1974) X-ray diffraction procedures for poly-crystallite and amorphous materials, 2nd edn. Wiley, New York, NY, USA
- Kneipp K, Wang Y, Kneipp H, Perelman LT, Itzkan I, Dasari RR, Fela MS (1997) Single molecule detection using surface-enhanced Raman scattering (SERS). *Phys Rev Lett* 78:1667–1670
- Kot M, Major Ł, Lackner JM, Chronowska-Przywara K, Janusz M, Rakowski W (2016) Mechanical and tribological properties of carbon-based graded coatings. *J Nanomater* 2016:1–14
- Laware S, Raskar S (2014) Influence of zinc oxide nanoparticles on growth, flowering and seed productivity in onion. *Int J Curr Microbiol Appl Sci* 3:874–881
- Lee CW, Mahendra S, Zodrow K, Li D, Tsai YC, Braam J, Alvarez PJ (2010) Developmental phytotoxicity of metal oxide nanoparticles to *Arabidopsis thaliana*. *Environ Toxicol Chem* 29:669–675
- Leonhardt U (2007) Optical metamaterials: Invisibility cup. *Nat Photon* 1:207–208
- Lidén G (2011) The European Commission tries to define nanomaterials. *Ann Occup Hyg* 55:1–5
- Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. *Environ Pollut* 150:243–250
- Liu J, Qiao SZ, Hu QH (2011) Magnetic nanocomposites with mesoporous structures: synthesis and applications. *Small* 7:425–443
- Liu R, Lal R (2015) Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. *Sci Tot Environ* 514:131–139
- Luo M, Liu D, Zhao L, Han J, Liang Y, Wang P, Zhou Z (2014) A novel magnetic ionic liquid modified carbon nanotube for the simultaneous determination of aryloxyphenoxy-propionate herbicides and their metabolites in water. *Anal Chim Acta* 852:88–96
- Mahmoud WMM, Rastogi T, Kümmerer K (2017) Application of titanium dioxide nanoparticles as a photocatalyst for the removal of micropollutants such as pharmaceuticals from water. *Curr Opin Green Sust Chem* 6:1–10
- Mallakpour S, Sirous F (2015) Surface coating of α -Al₂O₃ nanoparticles with poly(vinyl alcohol) as biocompatible coupling agent for improving properties of bio-active poly(amide-imide) based nanocomposites having l-phenylalanine linkages. *Prog Org Coat* 85:138–145

- McWilliams A (2018) Nanocomposites, nanoparticles, nanoclays and nanotubes: global markets to 2022. BCC Research Report Overview, pp 1–7
- Min Y, Li J, Liu F, Yeow EK, Xing B (2014) NIR light mediated photoactivation pt based antitumor prodrug and simultaneous cellular apoptosis imaging via upconversion nanoparticles. *Angew Chem Int Ed Engl* 53:1012–1016
- Mishra S, Keswani C, Abhilash PC, Fraceto LF, Singh HB (2017) Integrated approach of agri-nanotechnology: challenges and future trends. *Front Plant Sci* 8:471
- Morsy MK, Khalaf HH, Sharoba AM, El-Tanahi HH, Cutter CN (2014) Incorporation of essential oils and nanoparticles in pullulan films to control foodborne pathogens on meat and poultry products. *J Food Sci* 79:M675–M682
- Mucalo MR, Bullen CR, Manley-Harris M, McIntire TM (2002) Arabinogalactan from the Western larch tree: a new, purified and highly water-soluble polysaccharide-based protecting agent for maintaining precious metal nanoparticles in colloidal suspension. *J Mat Sci* 37:493–504
- Murugan K, Labeeba MA, Panneerselvam C, Dinesh D, Suresh U, Subramaniam J, Madhiyazhagan P, Hwang J, Wang L, Nicoletti M, Benelli G (2015) *Aristolochia indica* green synthesized silver nanoparticles: a sustainable control tool against the malaria vector *Anopheles stephensi*. *Res Vet Sci* 102:127–135
- Nagajyothi PC, Muthuraman P, Sreeknath TVM, Kim DH, Shim J (2017) Anticancer activity of copper oxide nanoparticles against human cervical carcinoma cells. *Arab J Chem* 10:215–225
- Naseem T, Farrukh MA (2015) Antibacterial activity of green synthesis of iron nanoparticles using *Lawsonia inermis* and *Gardenia jasminoides* leaves extract. *J Chem* 2015:912342
- Nasrollahzadeh M, Sajadi SM, Maham M (2015) Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaf extract and their catalytic activity for the Suzuki-Miyaura coupling in water. *J Mol Catal A Chem* 396:297–303
- Nava OJ, Soto-Robles CA, Gómez-Gutiérrez CM, Vilchis-Nestor AR, Castro-Beltrán A, Olivás A, Luque PA (2017) Fruit peel extract mediated green synthesis of zinc oxide nanoparticles. *J Mol Struct* 1147:1–6
- Nel AE, Mädler L, Velegol D, Xia T, Hoek EM, Somasundaran P, Klaessig F, Castranova V, Thompson M (2009) Understanding biophysicochemical interactions at the nano-bio interface. *Nat Mater* 8:543–557
- Ngo QB, Dao TH, Nguyen HC, Tran XT, Nguten TV, Khuu TD, Huynh TH (2014) Effects of nanocrystalline powders (Fe, Co and Cu) on the germination, growth, crop yield and product quality of soybean (Vietnamese species DT-51). *Adv Nat Sci Nanosci Nanotechnol* 5:1–7
- Nhan LV, Ma C, Rui Y, Liu S, Li X, Xing B, Liu L (2015) Phytotoxic mechanism of nanoparticles: destruction of chloroplasts and vascular bundles and alteration of nutrient absorption. *Sci Rep* 5:11618
- Nhan LV, Ma C, Rui Y, Cao W, Deng Y, Liu L, Xing B (2016) The effects of Fe₂O₃ nanoparticles on physiology and insecticide activity in non-transgenic and Bt-transgenic cotton. *Front Plant Sci* 6:1263
- O'Brien SC, Heath JR, Curl RF, Smalley RE (1988) Photophysics of buckminsterfullerene and other carbon cluster ions. *J Chem Phys* 88:220
- Ocsoy I, Paret ML, Ocsoy MA, Kunwar S, Chen T, You M, Tan W (2013) Nanotechnology in plant disease management: DNA-directed silver nanoparticles on graphene oxide as an antibacterial against *Xanthomonas perforans*. *ACS Nano* 7:8972–8980
- Ojha NK, Zyryanov GV, Majee A, Charushin VN, Chupakhin ON, Santra S (2017) Copper nanoparticles as inexpensive and efficient catalyst: a valuable contribution in organic synthesis. *Coord Chem Rev* 353:1–57
- Ouda SM (2014) Antifungal activity of silver and copper nanoparticles on two plant pathogens, *Alternaria alternata* and *Botrytis cinerea*. *Res J Microbiol* 9:34–42
- Pandey A, Kulkarni A, Roy B, Goldman A, Sarangi S, Sengupta P, Phipps C, Koppam J, Oh M, Basu S, Kohandel M, Sengupta S (2014) Sequential application of a cytotoxic nanoparticle and a PI3 K inhibitor enhances antitumor efficacy. *Cancer Res* 74:675–685

- Park HJ, Kim SH, Kim HJ, Choi SH (2006) A new composition of nanosized silica-silver for control of various plant diseases. *Plant Pathol J* 22:295–302
- Pereira AES, Grillo R, Mello NFS, Rosa AH, Fraceto LF (2014) Application of poly(epsilon-caprolactone) nanoparticles containing atrazine herbicide as an alternative technique to control weeds and reduce damage to the environment. *J Hazard Mater* 268:207–215
- Periasamy VS, Alshatwi AA (2013) Tea polyphenols modulate antioxidant redox system on cisplatin-induced reactive oxygen species generation in a human breast cancer cell. *Basic Clin Pharmacol Toxicol* 112:374–384
- Poinern GEJ (2014) A laboratory course in nanoscience and nanotechnology, 1st edn. CRC Press Taylor & Francis, Boca Raton, FL, USA
- Puri A, Loomis K, Smith B, Lee JH, Yavlovich A, Heldman E, Blumenthal R (2009) Lipid-based nanoparticles as pharmaceutical drug carriers: from concepts to clinic. *Crit Rev Ther Drug Carrier Syst* 26:523–580
- Qi M, Zhang K, Li S, Wu J, Pham-Huy C, Diao X, Xiao D, He H (2016) Superparamagnetic Fe₃O₄ nanoparticles: synthesis by a solvothermal process and functionalization for a magnetic targeted curcumin delivery system. *New J Chem* 4480:4480–4491
- Qian H, Peng X, Han X, Ren J, Sun L, Fu Z (2013) Comparison of the toxicity of silver nanoparticles and silver ions on the growth of terrestrial plant model *Arabidopsis thaliana*. *J Environ Sci* 25:1947–1955
- Rao JP, Geckeler KE (2011) Polymer nanoparticles: preparation techniques and size-control parameters. *Prog Polym Sci* 36:887–913
- Rastogi A, Zivcak M, Sytar O, Kalaji HM, He X, Mbarki S, Brestic M (2017) Impact of metal and metal oxide nanoparticles on plant: a critical review. *Front Chem* 5:78
- Rawat MK, Jain A, Singh S, Mehert W, Thunemann AF, Souto EB, Mehta A, Vyas SP (2011) Studies on binary lipid matrix based solid lipid nanoparticles of repaglinide: in vitro and in vivo evaluation. *J Pharm Sci* 100:2366–2378
- Risom L, Møller P, Loft S (2005) Oxidative stress-induced DNA damage by particulate air pollution. *Mutation Res* 592:119–137
- Roldán MV, Pellegrini N, de Sanctis O (2013) Electrochemical method for Ag-PEG nanoparticles synthesis. *J Nanopart* 2013:524150
- Rui M, Ma C, Hao Y, Guo J, Rui Y, Tang X, Zhao Q, Fan X, Zhang Z, Hou T, Zhu S (2016) Iron oxide nanoparticles as a potential iron fertilizer for peanut (*Arachis hypogaea*). *Fron Plant Sci* 7:815
- Rui M, Ma C, Tang X, Yang J, Jiang F, Pan Y, Xiang Z, Hao Y, Rui Y, Cao W, Xing B (2018) Phytotoxicity of silver nanoparticles to peanut (*Arachis hypogaea* L.): physiological responses and food safety. *ACS Sustain Chem Eng* 5:6557–6567
- Sadiq IM, Pakrashi S, Chandrasekaran N, Mukherjee A (2011) Studies on toxicity of aluminum oxide (Al₂O₃) nanoparticles to microalgae species: *Scenedesmus* sp. and *Chlorella* sp. *J Nanopart Res* 13:3287–3299
- Salata OV (2004) Applications of nanoparticles in biology and medicine. *J Nanobiotechnol* 2:3
- Shaalan M, Saleh M, El-Mahdy M, El-Matbouli M (2016) Recent progress in applications of nanoparticles in fish medicine: a review. *Nanomed Nanotechnol Biol Med* 12:701–710
- Shankamma K, Yallappa S, Shivanna MB, Manjanna J (2016) Fe₂O₃ magnetic nanoparticles to enhance *Solanum lycopersicum* (tomato) plant growth and their biomineralization. *Appl Nanosci* 6:983–990
- Shao W, Nabb D, Renevier N, Sherrington I, Luo JK (2012) Mechanical and corrosion resistance properties of TiO₂ nanoparticles reinforced Ni coating by electrodeposition. *IOP Conf Ser Mater Sci Eng* 40:12043
- Siddiqi KS, Husen A (2016a) Fabrication of metal nanoparticles from fungi and metal salts: scope and application. *Nano Res Lett* 11:98
- Siddiqi KS, Husen A (2016b) Fabrication of metal and metal oxide nanoparticles by algae and their toxic effects. *Nano Res Lett* 11:363

- Siddiqi KS, Husen A (2016c) Engineered gold nanoparticles and plant adaptation potential. *Nano Res Lett* 11:400
- Siddiqi KS, Husen A (2016d) Green synthesis, characterization and uses of palladium/platinum nanoparticles. *Nano Res Lett* 11:482
- Siddiqi KS, Rahman A, Tajuddin HA (2016e) Biogenic fabrication of iron/iron oxide nanoparticles and their application. *Nano Res Lett* 11:498
- Siddiqi KS, Husen A (2017a) Recent advances in plant-mediated engineered gold nanoparticles and their application in biological system. *J Trace Elements Med Biol* 40:10–23
- Siddiqi KS, Husen A (2017b) Plant response to engineered metal oxide nanoparticles. *Nano Res Lett* 12:92
- Siddiqi KS, Husen A, Rao RAK (2018a) A review on biosynthesis of silver nanoparticles and their biocidal properties. *J Nanobiotechnol* 16:14
- Siddiqi KS, Rahman A, Tajuddin HA (2018b) Properties of zinc oxide nanoparticles and their activity against microbes. *Nano Res Lett* 13:141
- Siddiqi KS, Husen A, Sohrab SS, Osman M (2018c) Recent status of nanomaterials fabrication and their potential applications in neurological disease management. *Nano Res Lett* 13:231
- Sigmund W, Yuh J, Park H, Maneeratana V, Pyrgiotakis G, Daga A, Taylor J, Nino JC (2006) Processing and structure relationships in electrospinning of ceramic fiber systems. *J Am Ceram Soc* 89:395–407
- Soares C, Branco-Neves S, de-Sousa A, Pereira R, Fidalgo F (2016) Ecotoxicological relevance of nano-NiO and acetaminophen to *Hordeum vulgare* L.: combining standardized procedures and physiological endpoints. *Chemosphere* 165:442–452
- Sondi I, Salopek-Sondi B (2004) Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. *J Colloid Interface Sci* 275:177–182
- Song G, Hou W, Gao Y, Wang Y, Lin L, Zhang Z, Niu Q, Ma R, Mu L, Wang H (2016) Effects of CuO nanoparticles on *Lemna minor*. *Bot Stud* 57:3
- Sotiriou GA, Pratsinis SE (2010) Antibacterial activity of nanosilver ions and particles. *Environ Sci Technol* 44:5649–5654
- Sotiriou GA, Teleki A, Camenzind A, Krumeich F, Meyer A, Panke S, Pratsinis SE (2011) Nanosilver on nanostructured silica: antibacterial activity and Ag surface area. *Chem Eng J* 170:547–554
- Soundarrajan C, Sankari A, Dhandapani P, Maruthamuthu S, Ravichandran S, Sozhan G, Palaniswamy N (2012) Rapid biological synthesis of platinum nanoparticles using *Ocimum sanctum* for water electrolysis applications. *Bioproc Biosys Eng* 35:827–833
- Stoimenov PK, Klinger RL, Marchin RL, Klabunde KJ (2002) Metal oxide nanoparticles as bactericidal agents. *Langmuir* 18:6679–6686
- Sukirtha R, Priyanka KM, Antony JJ, Kamalakkannan S, Thangam R, Gunasekaran P, Krishnan M, Achiraman S (2012) Cytotoxic effect of green synthesized silver nanoparticles using *Melia azedarach* against in vitro HeLa cell lines and lymphoma mice model. *Process Biochem* 47:273–279
- Syu Y, Hung J, Chen JC, Chuang H (2014) Impacts of size and shape of silver nanoparticles on *Arabidopsis* plant growth and gene expression. *Plant Physiol Biochem* 83:57–64
- Thatoi P, Kerry RG, Gouda S, Das G, Pramanik K, Thatoi H, Patra JK (2016) Photo-mediated green synthesis of silver and zinc oxide nanoparticles using aqueous extracts of two mangrove plant species, *Heritiera fomes* and *Sonneratia apetala* and investigation of their biomedical applications. *J Photochem Photobiol B Biol* 163:311–318
- Thomas S, Harshita BSP, Mishra P, Talegaonkar S (2015) Ceramic nanoparticles: fabrication methods and applications in drug delivery. *Curr Pharm Des* 21:6165–6188
- Tien DC, Tseng KH, Liao CY, Huang JC, Tsung TT (2008) Discovery of ionic silver in silver nanoparticle suspension fabricated by arc discharge method. *J Alloys Compd* 463:408–411
- Tippayawat P, Phromviyo N, Boueroy P, Chompoosor A (2016) Green synthesis of silver nanoparticles in *Aloe vera* plant extract prepared by a hydrothermal method and their synergistic antibacterial activity. *Peer J* 4:e2589

- Tran PA, Webster TJ (2011) Selenium nanoparticles inhibit *Staphylococcus aureus* growth. *Int J Nanome* 6:1553–1558
- Uddin I, Poddar P, Kumar U, Phogat N (2013) A novel microbial bio-milling technique for the size reduction of micron sized Gd_2O_3 particles into nanosized particles. *J Green Sci Tech* 1:48–53
- Umar S, Anjum NA, Ahmad P, Iqbal M (2018) Drought-induced changes in growth, photosynthesis, and yield traits in mungbean: role of potassium and sulfur nutrition. In: Ozturk M, Hakeem KR, Ashraf M (eds) *Crop production technologies for sustainable use and conservation: physiological and molecular advances*. Apple Academic Press, Waretown, NJ, USA, pp 79–89
- Venkatachalam P, Priyanka N, Manikandan K, Ganeshbabu I, Indiraarulsevi P, Geetha N, Muralikrishna K, Bhattacharya RC, Tiwari M, Sharma N, Sahi SV (2016) Enhanced plant growth promoting role of phycomolecules coated zinc oxide nanoparticles with P supplementation in cotton (*Gossypium hirsutum* L.). *Plant Physiol Biochem* 110:118–127
- Vesenska J, Manne S, Giberson R, Marsh T, Henderson E (1993) Colloidal gold particles as an incompressible atomic force microscope imaging standard for assessing the compressibility of biomolecules. *Biophys J* 65:992–997
- Vimala K, Sundarraj S, Paulpandi M, Vengatesan S, Kannan S (2014) Green synthesized doxorubicin loaded zinc oxide nanoparticles regulates the Bax and Bcl-2 expression in breast and colon carcinoma. *Process Biochem* 49:160–172
- Vinković T, Novák O, Strnad M, Goessler W, Jurašin DD, Paradiković N, Vrček IV (2017) Cytokinin response in pepper plants (*Capsicum annuum* L.) exposed to silver nanoparticles. *Environ Res* 156:10–18
- Wang J, Wang X, Song Y, Zhu C, Wang K, Guo Z (2013) Detecting and delivering platinum anticancer drugs using fluorescent maghemite nanoparticles. *Chem Commun (Camb)* 49:2786–2788
- Wang JJ, Sanderson BJ, Wang H (2007) Cyto- and genotoxicity of ultrafine TiO_2 particles in cultured human lymphoblastoid cells. *Mutat Res* 628:99–106
- Wang Z, Xie X, Zhao J, Liu X, Feng W, White JC, Xing B (2012) Xylem- and phloem-based transport of CuO nanoparticles in maize (*Zea mays* L.). *Environ Sci Technol* 46:4434–4441
- Weir A, Westerhoff P, Fabricius L, Hristovski K, von Goetz N (2012) Titanium dioxide nanoparticles in food and personal care products. *Environ Sci Technol* 46:2242–2250
- Wolf R, Matz H, Orion E, Lipozencic J (2003) Sunscreens—the ultimate cosmetic. *Acta Dermatovenerol Croat* 11:158–162
- Yousuf PY, Ahmad A, Hemant GAH, Aref IM, Iqbal M (2015) Potassium and calcium application ameliorates growth and oxidative homeostasis in salt-stressed Indian mustard (*Brassica juncea*) plants. *Pak J Bot* 47(5):1629–1639
- Yu J, Xu D, Guan HN, Wang C, Huang LK, Chi DF (2016) Facile one-step green synthesis of gold nanoparticles using *Citrus maxima* aqueous extracts and its catalytic activity. *Mat Lett* 166:110–112
- Yu Z, Sun X, Song H, Wang W, Ye Z, Shi L, Ding K (2015) Glutathione-responsive carboxymethyl chitosan nanoparticles for controlled release of herbicides. *Mater Sci Appl* 6:591–604
- Zhang H, Chen G (2009) Potent antibacterial activities of Ag/TiO_2 nanocomposite powders synthesized by a one-pot sol-gel method. *Environ Sci Technol* 43:2905–2910
- Zhang Q, Li N, Goebel J, Lu Z, Yin Y (2011) A systematic study of the synthesis of silver nanoplates: is citrate a “magic” reagent? *J Am Chem Soc* 133:18931–18939
- Zhao G, Song S, Wang C, Wu Q, Wang Z (2011) Determination of triazine herbicides in environmental water samples by high-performance liquid chromatography using graphene-coated magnetic nanoparticles as adsorbent. *Anal Chim Acta* 708:155–159
- Zheng Y, Sache L (2009) Gold nanoparticles enhance DNA damage induced by anti-cancer drugs and radiation. *Radiat Res* 172:114–119
- Zur Mühlen A, Zur Mühlen E, Niehus H, Mehnert W (1996) Atomic force microscopy studies of solid lipid nanoparticles. *Pharma Res* 13:1411–1416