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Aruna TN
Ph.D. Scholar, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Utkarsh Dwivedi
Assistant Professor, College of Agricultural Engineering, UAS-GKVK, Bengaluru, Karnataka, India

Ramya CS
Ph.D. Scholar, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Swapnaja K Jadhav
Scientist, ICAR-Central Institute of Agricultural Engineering, Bhopal, Madhya Pradesh, India

Gaddamwar Rohith Bhojyareddy
Ph.D. Scholar, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Amit Kumar Gupta
SRF, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Kishan Kumar
Ph.D. Scholar, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Corresponding Author:
Aruna TN
Ph.D. Scholar, ICAR-Indian Agricultural Research Institute, New Delhi, Delhi, India

Application of nanotechnology in bioethanol production and its effects on engine performance

Aruna TN, Utkarsh Dwivedi, Ramya CS, Swapnaja K Jadhav, Gaddamwar Rohith Bhojyareddy, Amit Kumar Gupta and Kishan Kumar

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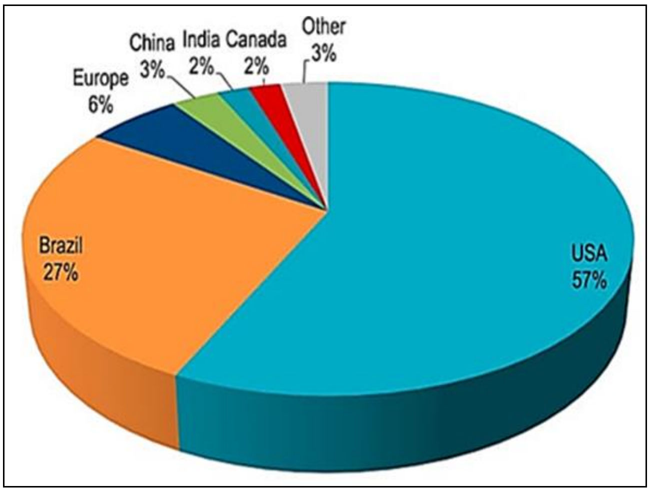
Abstract
Bioethanol is recognized as a highly promising alternative to conventional fossil fuels, offering potential solutions for both energy security and pollution challenges. However, its large-scale production from lignocellulosic biomass faces several limitations, including the feedstock complexity, the raw materials' nature, the enzymatic hydrolysis cost, and the lack of efficient co-fermenting yeast strains, all of which contribute to reduced bioethanol yields. Studies involving numerical simulations of Spark Ignition (SI) engines operating on ethanol-gasoline blends have revealed increased emissions of nitrogen oxides (NOx) and Carbon Dioxide (CO_2), alongside reductions in Carbon Monoxide (CO) and unburned hydrocarbons (HC). The integration of nanotechnology into bioethanol has shown significant promise in enhancing the efficiency of biomass pretreatment, conversion to fermentable sugars, and fermentation processes. Furthermore, incorporating nanoparticles as fuel additives has led to notable improvements in engine performance and a reduction in harmful exhaust emissions. Specifically, the use of metallic nano catalysts facilitates oxidation reactions, thereby improving air-fuel mixture quality, which results in higher torque, increased engine power, and improved brake thermal efficiency. When metallic nano-oxides are added to ethanol-gasoline blends, they contribute to reduced fuel consumption and lower emissions of CO, unburned hydrocarbons (UHC), and NOx, while slightly increasing CO_2 output. Thus, nanoparticles play a crucial role in enhancing fuel characteristics, optimizing engine efficiency, and minimizing pollutant emissions.

Keywords: Bioethanol, lignocellulosic biomass, enzymes, nanoparticles and nano-catalyst

1. Introduction
The increasing global population and rapid economic growth have significantly escalated energy demand, which continues to be primarily met by fossil fuels. This heavy reliance on non-renewable sources presents two major challenges: the rapid price depletion of fossil fuel and the environmental impact caused by GHGs (greenhouse gases) [1]. Volatile fuel prices and elevated GHG levels remain key issues hindering the sustainable use of fossil fuels. The swift decline in fossil fuel supplies has markedly heightened the need for renewable and sustainable energy resources [2].
The exhaustion of fossil fuel reserves and the rise in global temperatures due to GHG emissions from fossil fuel combustion are currently motivating researchers to seek alternative and eco-friendly energy sources. Consequently, it is essential to seek an alternative fuel that can effectively supplant standard gasoline without considerable alteration to the engine design and vehicle operation. To tackle these difficulties, the utilization of renewable energy sources, such as biofuels, has been extensively contemplated globally [3, 4].
Biofuels, derived from renewable biological sources, offer a sustainable alternative to fossil fuels by addressing both environmental concerns and resource depletion [5]. These fuels can be produced from a range of feedstocks, including agricultural residues, woody and herbaceous biomass, and various types of organic waste. Although the combustion of biofuels does emit carbon dioxide, this emission is partially offset as the CO_2 is reabsorbed during the growth cycle of the biomass used in their production, making the process comparatively carbon neutral.

Currently, biofuels such as bioethanol, biodiesel, biogas, and biohydrogen are gaining significant attention from researchers and industry sectors due to their environmental advantages, cost-effectiveness, and potential for production from non-edible biomass sources [6, 7].

Bioethanol is regarded as a highly viable alternative to fossil fuels, offering the dual benefits of enhancing energy security and mitigating environmental pollution [8]. Globally, the United States and Brazil dominate bioethanol production, relying primarily on corn and sugarcane juice as feedstock's, respectively. The United States contributes about 14 billion gallons annually, while Brazil produces nearly 7 billion gallons each year. According to the Renewable Fuels Association (2015), the total global production of bioethanol reaches approximately 25 billion gallons per year. A comparative overview of ethanol production across various countries is presented in Figure 1.



Source: Global bioenergy statistics 2020

Fig 1: Worldwide Bioethanol Production

Replaced just 10% of the global gasoline consumption with bioethanol derived from sugarcane juice could potentially reduce carbon emissions by as much as 66 million tons annually. Hence, the present review explains about the production of bioethanol, need of nanotechnology in the enhancement and the ethanol effects in the engine operations.

2. Bioethanol Production Process

Bioethanol is produced through various technological pathways, categorized into three primary generations: first-generation (1G), second-generation (2G), and third-generation (3G) biofuels [9]. First-generation bioethanol is obtained from edible feedstocks such as sugarcane and corn, which are traditionally used for food and have high fermentable sugar content. In contrast, second-generation bioethanol is synthesized from lignocellulosic biomass, which includes non-food materials such as agricultural residues (e.g., corn stover, wheat straw), forestry byproducts, energy crops like switchgrass and certain woody or herbaceous plants, as well as industrial and municipal wastes. This biomass is composed primarily of cellulose, hemicellulose and lignin, along with minor components such as ash, proteins, and other extractives [10].

Lignocellulosic feedstock's are increasingly preferred due to their abundance, sustainability, and low procurement cost. These materials offer a promising route for scaling up global bioethanol production, with an estimated potential to contribute approximately 442 billion liters annually. Additionally, 2G bioethanol has a greater environmental benefit compared to 1G bioethanol, particularly in terms of reducing greenhouse gas emissions.

Third-generation bioethanol refers to ethanol derived from algae. This emerging category is attracting considerable interest due to algae's high carbohydrate content and the minimal presence of lignin, which significantly reduces the need for complex and costly pretreatment processes [11, 12]. The simplified processing requirements and high productivity make algal biomass a highly promising feedstock for future bioethanol production. Figure 2 illustrates the classification of bioethanol by generation and respective feedstock sources.

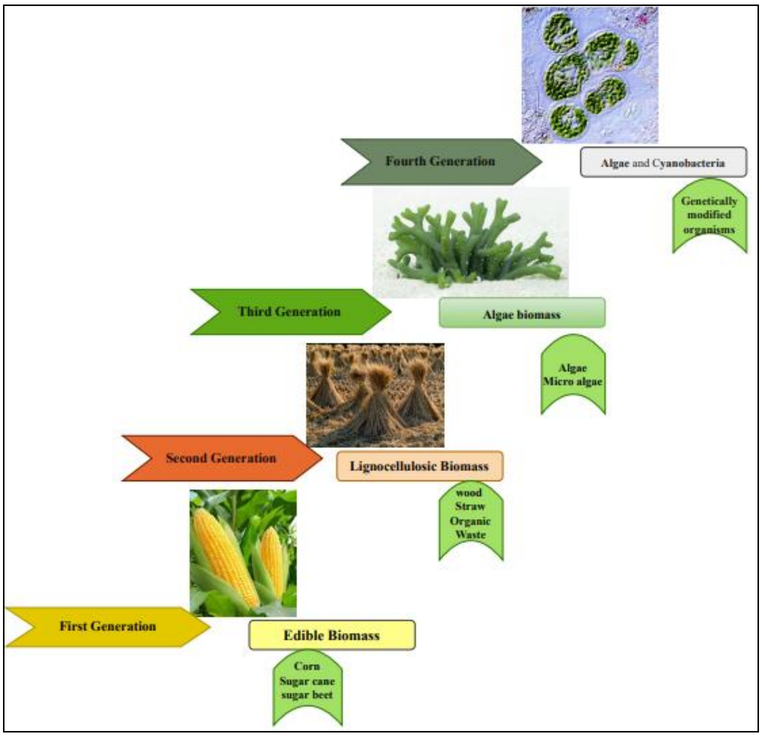


Fig 2: Different Bioethanol production generations and their resources

The conversion of various feedstock's into bioethanol generally involves four major steps: pretreatment, hydrolysis, fermentation, and ethanol recovery. Pretreatment is a crucial step, particularly for lignocellulosic biomass, as it breaks down the rigid structure of the material to release cellulose that is otherwise bound within a complex matrix of lignin and hemicellulose. This structural alteration enhances the accessibility of cellulose for subsequent enzymatic hydrolysis. When the crystalline structure of cellulose is effectively disrupted during pretreatment, it becomes significantly more susceptible to enzymatic action, often resulting in sugar yields exceeding 90% of the theoretical maximum, especially when feedstocks like grasses, corn residues, or woody biomass are used [13]. This improvement occurs because the enzymatic enzymes can then directly interact with cellulose chains, rather than being hindered by binding to lignin surfaces. Moreover, effective pretreatment minimizes sugar degradation (particularly of pentose sugars), supports efficient reactor sizing, reduces overall energy input for heating, and limits the formation of inhibitory compounds that could interfere with both hydrolysis and fermentation. These combined effects contribute to higher ethanol yields and more cost-effective production.

Following the pre-treatment of lignocellulosic biomass, the next step is the hydrolysis of polymeric carbohydrates (cellulose and hemicellulose) to produce sugar monomers. This stage is essential because the enzymes required for the subsequent fermentation stage can only digest sugar monomers. The hydrolysis process can be catalyzed by either acids or enzymes. Acid-catalyzed hydrolysis involves using either concentrated or dilute acid. Acid hydrolysis of the lignocellulose is conducted in two phases: in the first phase, dilute acid is used to hydrolyze hemicellulose, while in the second phase, cellulose is hydrolysed using concentrated acid. Alternatively, enzyme-catalyzed hydrolysis uses enzymes to convert polymeric carbohydrates into sugar monomers under mild operating conditions generally temperature between 45-50°C and at a pH of 4.8-5.0. This approach is efficient, leading to high sugar yields without forming inhibitors or causing corrosion.

After the pretreatment stage, the hydrolysis of lignocellulosic biomass is carried out to convert complex carbohydrates, mainly cellulose and hemicellulose, into simple sugar monomers. It is critical, as only monomeric sugars can be utilized in the fermentation process to produce ethanol. Hydrolysis can be achieved through either acid-based or enzyme-based methods. Acid hydrolysis is typically performed in two stages: initially, dilute acid is applied to break down hemicellulose, followed by the use of concentrated acid to hydrolyze the more resistant cellulose fraction. On the other hand, enzymatic hydrolysis employs specific enzymes to degrade the polymeric carbohydrates into fermentable sugars under relatively mild conditions typically at temperatures between 45°C and 50°C and a pH range of 4.8 to 5.0. This enzymatic method is advantageous due to its high efficiency in sugar release, minimal formation of inhibitory compounds, and the absence of equipment corrosion, making it suitable for sustainable and scalable bioethanol production.

The hydrolysis of lignocellulosic biomass into glucose involves three key steps. The first step involves the formation of shorter-chain cellodextrins and free chains, achieved by catalyzing cellulose with water molecules using endoglucanase (MetaCyc, 2014). The second step involves degrading cellodextrin into cellobiose (a two-unit glucose molecule) using exoglucanase (MetaCyc, 2014). Finally, β-glucosidase hydrolyzes cellobiose into individual glucose molecules [14]. The generation of glucose is crucial, as it serves as the primary substrate for the fermentation stage that follows.

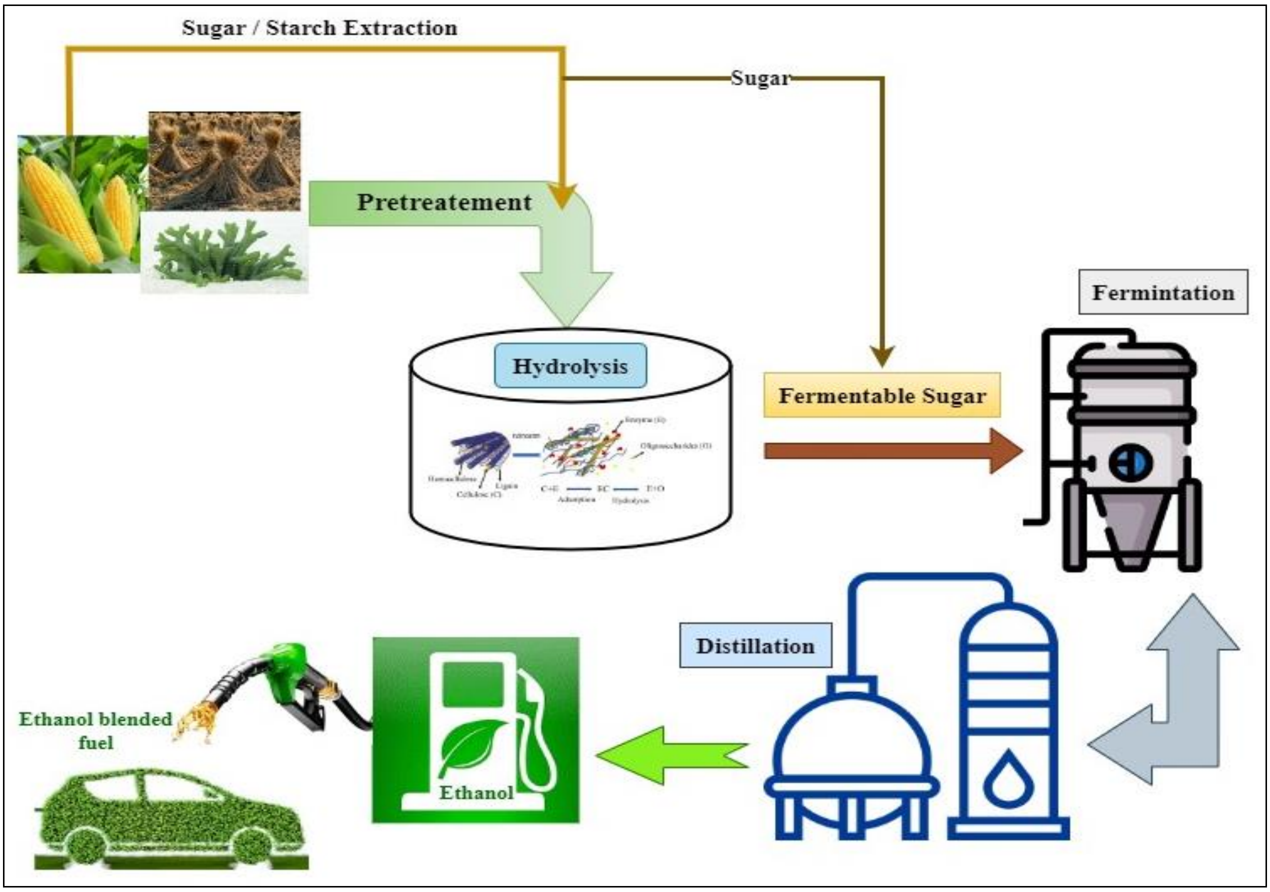


Fig 3: Bioethanol Production Process

Fermentation is the next critical phase in ethanol production, where microorganisms such as yeast, fungi, or specific bacterial strains convert these simple sugars into ethanol, along with minor by-products like organic acids and gases [15]. Among these microbes, Saccharomyces cerevisiae is the most commonly used yeast due to its efficiency in ethanol production and its strong tolerance to ethanol concentration [16]. This yeast efficiently ferments hexose sugars such as glucose, fructose, and mannose produced primarily from cellulose hydrolysis into ethanol. In contrast, hemicellulose-derived sugars like xylan must first be converted into xylose, which may require alternative or genetically modified microbial strains for efficient fermentation.

After the fermentation of monomeric sugars, the next step is the recovery of ethanol from the fermentation broth. This is typically achieved by reducing the water content of the broth to around 0.5% by volume, which enables the production of ethanol with a purity of at least 99.5% by volume. However, the recovery process is hindered by the azeotropic nature of the ethanol-water mixture, which means that the two components form a constant boiling point mixture. As a result, the ethanol separation is primarily carried out through distillation, a method that capitalizes on the difference in boiling points of the ethanol and water to separate the two [17].

3. Pros and Cons of Bioethanol

Bioethanol is utilized as an alternative fuel for transportation, replacing gasoline, as well as in power generation through thermal combustion, thermochemical reactions in fuel cells, cogeneration processes, and as a raw material in the chemical industry. Ethanol-blended fuels can reduce net greenhouse gas emissions by up to 37.1%, which represents a substantial environmental benefit. The exhaust gases from ethanol combustion are significantly cleaner due to more efficient burning. Bioethanol can be derived from any plant that contains starch or sugar, and it is considered to be carbon-neutral. This means that the carbon dioxide released during its production is offset by the amount absorbed by the crops during photosynthesis. Furthermore, ethanol helps reduce ozone formation, as its emissions are less reactive with sunlight compared to those from gasoline, thereby lowering the potential for ozone damage. Ethanol spills also biodegrade or dilute to non-toxic levels more readily. Additionally, ethanol has a higher-octane rating than gasoline, which enhances its anti-knock properties and improves engine fuel efficiency. The oxygen content in ethanol contributes to a cleaner combustion process, especially at relatively low temperatures.

However, the commercial production of bioethanol from lignocellulosic biomass faces several challenges, including the complex nature of the feedstocks, high enzyme costs, and the lack of co-fermenting yeasts [18]. These factors contribute to the higher production costs and make it difficult to standardize operational conditions for bioethanol production. Moreover, bioethanol has a lower energy content compared to gasoline, providing about 34% less energy per liter. In other words, bioethanol offers approximately 70% of the energy content found in gasoline. The Reid vapor pressure of ethanol is also lower than that of gasoline, which results in slower evaporation and challenges in engine startup at temperatures below 20°C. Additionally, due to its high octane number, engines designed to run on bioethanol cannot use gasoline or diesel, although they can operate in engines with higher compression ratios. Studies on spark ignition engines fueled by a gasoline-ethanol blend have shown increased concentrations of NOx and CO2, while levels of CO and HC were reduced [12]. Despite these challenges, nanotechnology presents a promising solution, potentially improving feedstock properties and boosting engine performance.

4. Need of Nanotechnology

Nanomaterials [19] can be modified on their surfaces to improve stability, control their reactivity, and enable them to dissolve in various solvents. They can be used directly or indirectly in the processes involved in the manufacture of biofuels due to their diverse range of sizes, shapes, surface reactivity, and adsorption capacities. Metallic nanoparticles, nanofibers, and nanotubes can speed up the metabolic process. Various nanoparticles, such as nanocrystals, nanodroplets, and nanomagnets, are incorporated into gasoline and diesel blends to enhance their performance. Additionally, nanomaterials can act as catalysts, boosting the anaerobic microbial communities, facilitating electron transfer, & reducing the impact of inhibitors during the fermentation phase of biofuel production.

5. Application of nanotechnology in biofuel

The implementation of nanotechnology in the business of biofuel industry has become an interesting way to make biofuel production better in a way that saves money and time.

Table 1: Application of nanotechnology in Biofuel

Biogas	• Biodegradation of substrate • Increase biogas and methane production • Increase activity of methanogens • Increase accumulation of volatile fatty acids • Enhanced methanation process
Bioethanol	• Pre-treatment of biomass • Improved feedstock • Better crop production • Improve enzymatic degradability of cellulose • Increase the feasibility of immobilization of enzymes • Increase sugar and ethanol production • Enhanced fermentation
Biodiesel	• High yield of microalgal biomass • Enhanced cell density • Improve the efficiency of lipid extraction • Trans esterification process • Increase bio catalytic efficiency • As immobilization carriers • Enhanced biodiesel production
Bio-hydrogen	• Enhance the rate of electron transfer • Lower the concentration of dissolved oxygen in the culture • Enhance the functionality of oxygen-sensitive hydrogenase • Supply essential nutrients for microbial growth • Pre-treatment of biomass • Immobilization of enzymes • Dark fermentation. • Enhance the yield of bio-hydrogen.

Source: Kamla *et al*., 2021[1]

6. Nanotechnology in bio-ethanol production

Nano-technology application in bioethanol production can enhance plant biomass pre-treatment, conversion to fermentable sugars, and the fermentation process [4]. The recalcitrance of most agro-industrial wastes, particularly lignocellulosic biomass, remains a significant obstacle to its conversion into second-generation biofuels. Nanomaterials aid in the fermentation and recovery of bioethanol and can enhance the effectiveness of pre-treatment. Bioethanol production primarily uses nanoparticles for biomass pretreatment, enzyme immobilization, fermentation, recovery, and inhibitor removal. Additionally, the ability to reuse nanomaterials is a key advantage for the economic feasibility of biofuels [20].

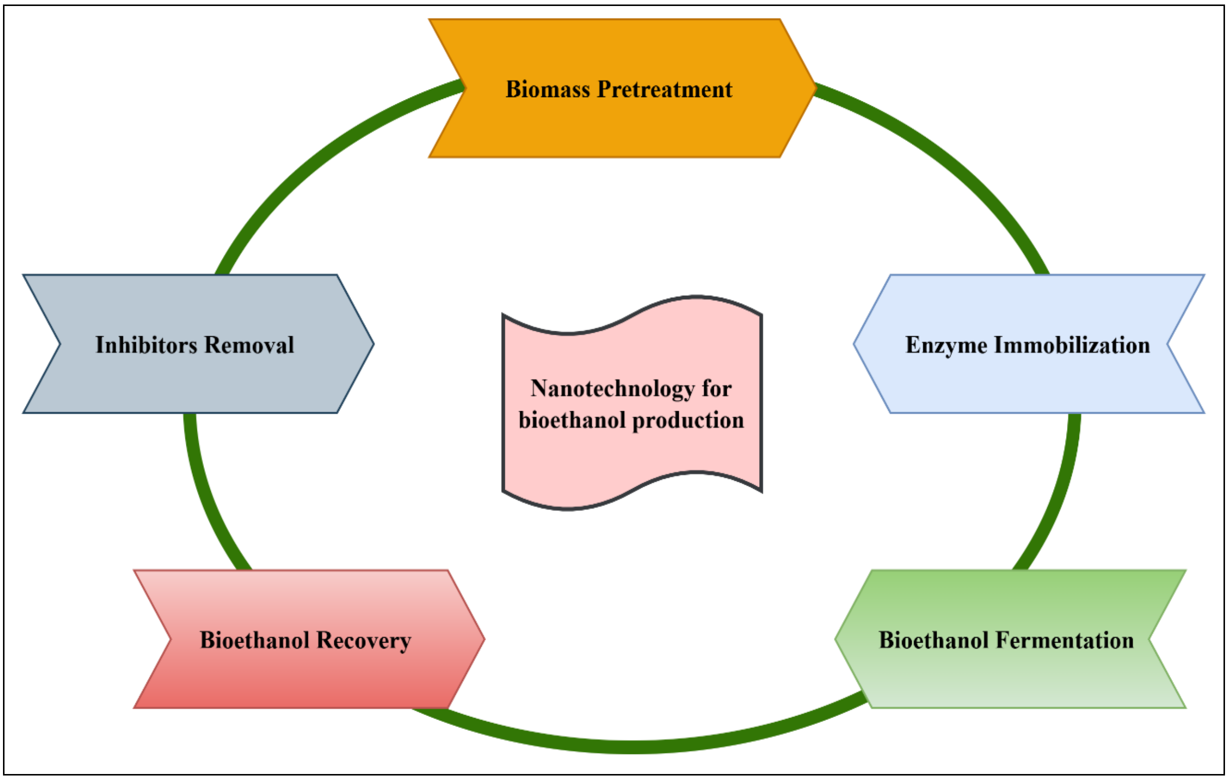


Fig 4: Nanotechnology in bioethanol production

6.1 Biomass pre-treatment

Pre-treatment is crucial in the production process as it significantly impacts the quality and value of the final product. Different conventional methods are there for the pre-treatments. Nevertheless, the conventional pre-treatment procedures have limitations in terms of decreasing the polymerization rate and reducing the crystallinity of cellulose. The enzymatic hydrolysis of lignocellulosic biomass (LB) continues to face challenges due to the formation of inhibitory compounds, incomplete digestion of LB, and the generation of monomeric lignin compounds. Also, Conventional methods consume more time, cause environmental pollution, and require a high cost of chemical catalyst. The primary obstacle is the complete and cost-effective removal of lignin compounds while preserving the integrity of carbohydrates, which are subsequently used in the production of biofuels [21]. To address these challenges, the integration of nanotechnology has a profound effect on the biorefinery industry due to its remarkable properties. Nanotechnology-based pre-treatment methods are being extensively studied for their potential benefits [22]. The effectiveness of this technique mostly hinges on the nanoparticles' ability to pierce the LB cell membrane. This approach reduces the recalcitrance of lignocellulosic biomass (LB) by inducing a high level of shear in the reactor, thereby enhancing the effectiveness of the chemical catalyst [23]. In addition to being a good pre-treatment procedure for LB, the usage of magnetic nanoparticles may have further advantages. This procedure is economical since the immobilized enzyme is easily retrieved and reused.

Various nanoparticles were explored for the production of bioethanol and applied in biomass pre-treatment to extract sugars from different lignocellulosic feedstocks. Rivera *et al.* [24] studied the effects of acid-functionalized nanoparticles on the pre-treatment of wheat straw and corncob. Similarly, Ingle *et al.* [14] evaluated the pre-treatment of sugarcane bagasse and sugarcane straw using two types of acid-functionalized magnetic nanoparticles (alkyl sulfonic acid-Fe_3O_4 MNPs and butyl carboxylic acid-Fe_3O_4 MNPs), both of which showed optimal xylose recovery.

6.2 Enzyme immobilization

Enzymes are essential in biocatalysis since their high substrate specificity, ease of synthesis, and reduced environmental impact. Despite their significance, the widespread application of enzymes in industrial development is constrained by their high production costs and limited ability to be reused. In biochemical processes, enzymes often lose functionality when exposed to harsh conditions such as elevated temperatures, organic solvents, or extreme pH levels. These factors can lead to structural degradation, preventing their recovery and reuse from the reaction environment [25].

To overcome these challenges, enzyme immobilization presents a more straightforward approach for enhancing operational efficiency and stability, even though it may involve higher initial costs. Immobilized biocatalysts often use whole cells and enzymes [26]. Immobilized enzymes are catalysts that are restricted to some degree, while their catalytic activity remains intact [27]. Immobilized enzymes are crucial due to their reusability, ability to sequester enzymes, enhanced stability under varying temperature and pH conditions, and prolonged activity enzyme immobilization can be accomplished by entrapping the enzyme within a support matrix. It is essential that both the enzyme substrates and the resulting products are able to move freely into and out of the immobilized region. The carrier material used should be biocompatible and insoluble, featuring a high surface area along with functional groups that facilitate effective enzyme attachment [28].

In recent years, multiple carrier-supported strategies have been adopted to enhance the performance and durability of enzymes, while also lowering costs for industrial-scale applications. These methods include enzyme aggregation, microwave-assisted immobilization techniques, and the utilization of materials such as mesoporous structures and nanoparticles. Enzymes and proteins have been successfully embedded within polymeric silica matrices and gold-based nanoparticles [29]. Notably, the emergence of nanotechnology has amplified the focus on magnetic nanoparticles due to their promising properties.

The unique physical and chemical characteristics of nanoparticles have made them valuable tools across various biotechnological fields, offering improved functionality and performance. Nanoparticles, due to their high surface-area-to-volume ratio, enable a greater loading of immobilized enzymes. These immobilized enzymes tend to remain functional across broader pH and temperature ranges compared to their free counterparts. Nanoparticles are typically uniform in size and shape, often featuring a distinct core-shell structure. They can be synthesized easily without relying on surfactants or harmful chemicals and are engineered to meet precise size specifications for practical applications. Additionally, they offer the potential for simultaneous immobilization of multiple enzymes on a single particle [30]. The super magnetic property of nanoparticles helps to easily separate an immobilized enzyme, increasing reusability.

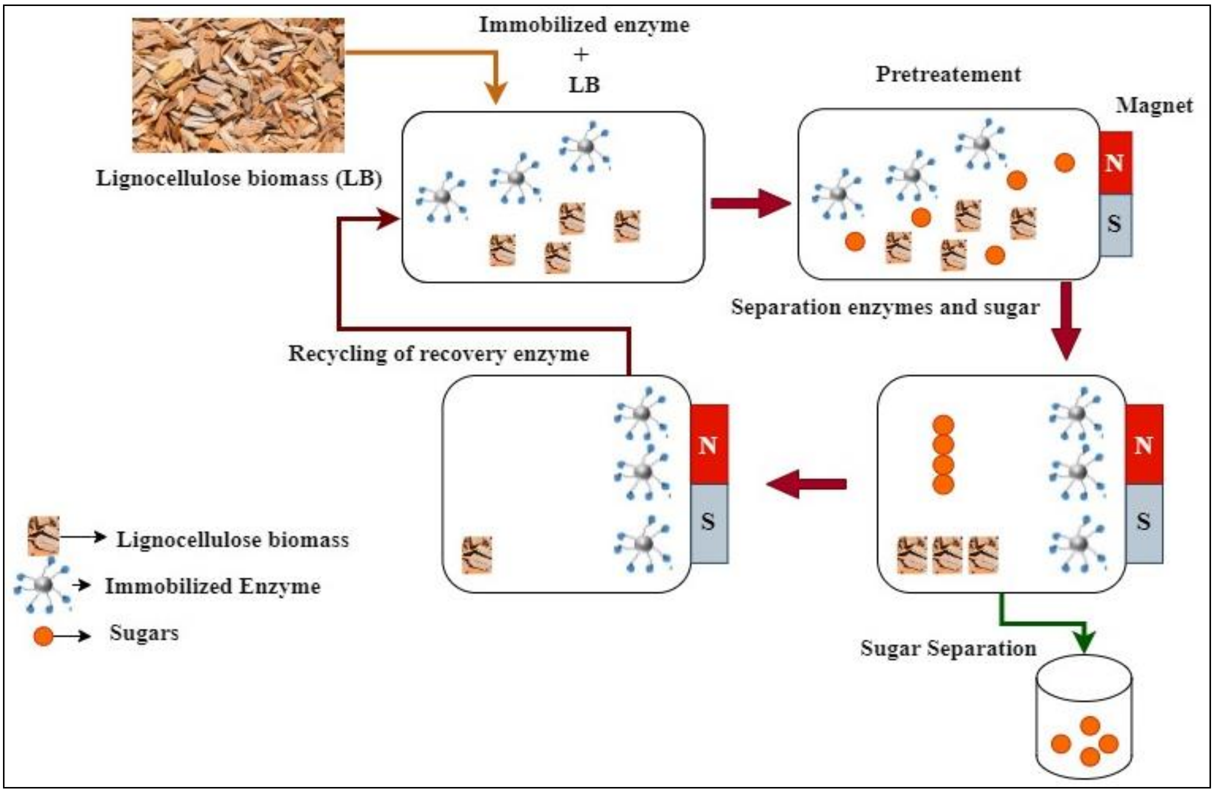


Fig 5: Lignocellulosic biomass hydrolysis using cellulase bound to magnetic nanoparticles (MNPs)

Magnetic Nanoparticles (MNPs) offer a practical advantage in biomass processing post-pre-treatment, as they enable easy recovery of catalysts via an external magnetic field, allowing for repeated use in subsequent cycles [31]**.** A study by Poorakbar *et al.* [32] highlighted enhanced catalytic performance and thermal resistance of cellulases derived from *Penicillium* funiculosum when supported on magnetic gold-silica nanostructures. The system achieved a 76% enzyme immobilization efficiency and maintained functional stability over five reuse cycles.

Enzyme immobilization presents a sustainable strategy for enzyme utilization, providing protection against the inhibitory effects of organic acids and alcohols formed during fermentation, while also improving ethanol yield and allowing for multiple reuse cycles [33]**.** A variety of nanomaterials including silica, titanium dioxide (TiO_2), polymer-based nanoparticles, fullerenes, graphene, and carbon nanotubes, have been explored for enzyme immobilization in the context of bioethanol production [34].

6.3 Bioethanol fermentation

Due to high costs associated with free enzyme systems, immobilizing microorganisms has become essential. The increased surface-area-to-volume ratio of nanomaterials enhances their catalytic performance, reusability, and overall bioethanol yield. Studies on enzyme and yeast immobilization using various nanoparticles (NPs) have demonstrated that these nanomaterials offer a stable, efficient, and economically viable approach for converting lignocellulosic biomass into bioethanol.

However, while nanoparticles can improve the efficiency of bioethanol production, their application must be carefully optimized, as excessive concentrations may inhibit microbial growth and activity. Microbial cells function as biological factories, producing enzymes necessary for industrial processes. In addition to facilitating enzyme immobilization, nanomaterials are also utilized to support the immobilization of whole microbial cells. Beyond enhancing fermentation yields, nanoparticles have also shown potential to improve ethanol production via the syngas route.

7. Bioethanol recovery

During fermentation, the accumulation of bioethanol can inhibit cell growth and viability, which in turn reduces overall ethanol production. Pervaporation has emerged as a promising method for bioethanol recovery because it allows for the simultaneous fermentation and in-situ extraction of biofuels. While yeast cells can clog membranes during this process, the incorporation of carbon nanotubes into membrane filters has proven to enhance bioethanol recovery while improving the antifouling properties of the system. Additionally, a nanofiltration membrane combined with a forward osmosis system has demonstrated success in removing fermentation inhibitors and concentrating fermentable sugars from rice straw hydrolysates.

Table 2: Nano catalysts in bioethanol production

Nano-particle	Application
NiO	• Bioethanol production increased by 59.96%. • The inclusion of nanoparticles resulted in a 145% boost in bioethanol productivity and a 110% rise in acetic acid concentration.
NiO and Fe_3O_4	• Achieved a maximum ethanol yield of 0.26 g/g, an ethanol productivity of 0.22 g/L/h, and a fermentation efficiency of 51% at 0.01 wt. %. • Enhanced performance by 1.60-fold and 1.13-fold using NiO and Fe3O4 nanoparticles, respectively.
ZnO	• A maximum ethanol yield of 0.0359 g/g based on dry weight of plant biomass was achieved at a concentration of 200 mg/L of ZnO nanoparticles.
Magnetic nanoparticles	• Ethanol productivity achieved 264 g/L·h. • The immobilized cells remained stable in saline at 4°C for over one month.
Fe_3O_4	• Bioethanol yield upto 93% • Bioethanol yield upto 53.7 %
GO-PtRu NPs	• Increases the chlorophyll content in C. minutum biomass and boosts bioethanol production.
Silica, TiO_2, polymeric NPs, fullerene, grapheme and CNTs	• Immobilization of enzymes for bioethanol production
Cobalt-ferrite-silica	• Improve production
Magnetic nanoparticles	• Pre-treatment of straw
Fe3O4/Alginate Nano composite	• Improve enzymatic hydrolysis
Fe_3O_4	• Thermal stability for 8 h
$FeCl_3$	• Bioethanol yield
MnO_2	• Cellulase binding efficiency • Bioethanol yield

8. Nano additives blended with fuel

To mitigate greenhouse gas emissions and reduce gasoline consumption, bioethanol is being investigated as a potential alternative to traditional gasoline. It may be mixed with gasoline or used directly in automobiles (EERE, 2015). The timing of the gasoline engine (and, if applicable, the electronic control system) is altered for direct application (E100), and a bigger fuel tank is used. However, since bioethanol (E100) vaporizes at a greater heat than regular gasoline, using it often results in problems starting the engine in cold weather or at low temperatures. Essential. It may not be necessary to change the engine in order to combine bioethanol with gasoline; instead, it will improve engine performance and ignition. The mixes that are most often utilized are E85 and E10. However, numerical studies on the performance of spark-ignition (SI) engines using gasoline and bioethanol blended fuels indicated an increase in NOx and CO2 emissions, while CO and HC concentrations decreased. To overcome these Nox emissions and to increase the performance of engine many researchers conducted experiment by adding nano particles to the bioethanol gasoline blend fuel and outcomes of their results showed the decline in the NO_x emission and increase in the performance of engine with increase in octane number and modifying fuel properties. To improve the engine performance and reduce the pollutant emission of bioethanol and base fuel blends, the use of additives is important. Nanoparticles, when used as fuel additives, significantly enhance engine performance and reduce harmful exhaust emissions. This is due to the oxidation and catalytic properties of the nanoparticles, which improve thermal efficiency during combustion by increasing the surface area-to-volume ratio. Fuels enhanced with nanoparticles exhibit superior thermophysical properties, especially higher thermal conductivity. However, one of the challenges in using nanoparticles as fuel additives is ensuring their uniform dispersion in the base fuel while maintaining stability. This issue can be addressed by using appropriate surfactants to improve the stability of the nanoparticles [35]. Nanoparticle additions are garnering interest from the scientific community for fuel enhancement, with several studies focused on optimizing combustion parameters, hence enhancing engine thermal efficiency and diminishing exhaust polluting gases. Numerous studies have been conducted on the use of metallic nanoparticles, such as cerium, iron, manganese, zinc, and copper, as fuel additives in various biofuels. These nanoparticles have shown potential to enhance the combustion process, improve fuel efficiency, and reduce harmful emissions in biofuels, making them an area of significant interest for improving engine performance and environmental sustainability [3]. The benefits of adding nano additives to the bioethanol blend fuel are: Improve octane number, Reduce exhaust emissions, Improve fluid stability, Reduce ignition delay time, Increase viscosity index, Improve chemical to chemical contact, Increase break thermal efficiency and Improve brake power and torque of engine.

8.1 Experimental setup for performance of engine

First prepare emulsions by mixing ethanol and base fuel in varying proportions. Then, introduce different amounts of nanoparticles into these emulsions. Additionally, add a surfactant, such as Cetyl Trimethyl Ammonium Bromide (CTAB), to ensure the uniform distribution and suspension of the nanoparticles within the fuel. To evaluate the performance and emission characteristics of the resulting fuel samples, set up a test rig comprising an engine, an eddy current dynamometer, a loading unit, a control interface, and a data management system. Employ a load cell to measure fuel consumption accurately during testing.

Table 3: Different nano additives blended with ethanol based gasoline or diesel fuels

Fuel blend name	Notation	Base fuel	Nano-additives	Reference
Gasoline	-	Gasoline	-	[12]
Gasoline + 10% Ethanol	E10	Gasoline	-	
Gasoline with 10% ethanol +10 ppm Mn_2O_3	E10Mn10	Gasoline	Metal oxide (Manganese and cobalt nano oxide)	
Gasoline with 10% ethanol + 20ppm Mn_2O_3	E10Mn20	Gasoline	Metal oxide (Manganese and cobalt nano oxide)	
Gasoline with 10% ethanol + 10 ppm Co_3O_4	E10C10	Gasoline	Metal oxide (Manganese and cobalt nano oxide)	
Gasoline with 10% ethanol + 20 ppm Co_3O_4	E10C20	Gasoline	Metal oxide (Manganese and cobalt nano oxide)	
Gasoline + 30 % Ethanol + 100 mg Ceo_2	E30C$_0$100	Gasoline	Cerium oxide	[7]
Gasoline + 40 % Ethanol + 150 mg Ceo_2	E40C$_0$150	Gasoline	Cerium oxide	
Gasoline + 40 % Ethanol + 200 mg Ceo_2	E50C$_0$200	Gasoline	Cerium oxide	
Gasoline + 20% Ethanol	E20	Gasoline	-	[3]
Gasoline with 20% ethanol + 10 ppm Alumina	E20N10	Gasoline	Alumina nano particle	
Gasoline with 20% ethanol + 20 ppm Alumina	E20N20	Gasoline	Alumina nano particle	
100 % Diesel	D100	Diesel	-	[36]
10% ethanol + 90% Diesel	E10D90	Diesel	-	
10%Ethanol + 10gm Cerium Oxide + 90% Diesel	E10C10D90	Diesel	Metal oxide (Cerium oxide)	
10%Ethanol + 15gm Cerium Oxide + 90% Diesel	E10C15D90	Diesel	Metal oxide (Cerium oxide)	
10%Ethanol + 20gm Cerium Oxide + 90% Diesel	E10C20D90	Diesel	Metal oxide (Cerium oxide)	
95% Diesel + 5% ethanol	D95E5	Diesel	-	[35]
90% Diesel + 10% Ethanol	D90E10	Diesel	-	
85% Diesel + 15 % Ethanol	D85E15	Diesel	-	
90% Diesel +10%Ethanol + 50ppm $NiZnFe_2O_4$	D90E10N50	Diesel	Nickel, Zinc Iron Oxide Nanoparticles	
90% Diesel +10%Ethanol + 100ppm $NiZnFe_2O_4$	D90E10N100	Diesel	Nickel, Zinc Iron Oxide Nanoparticles	

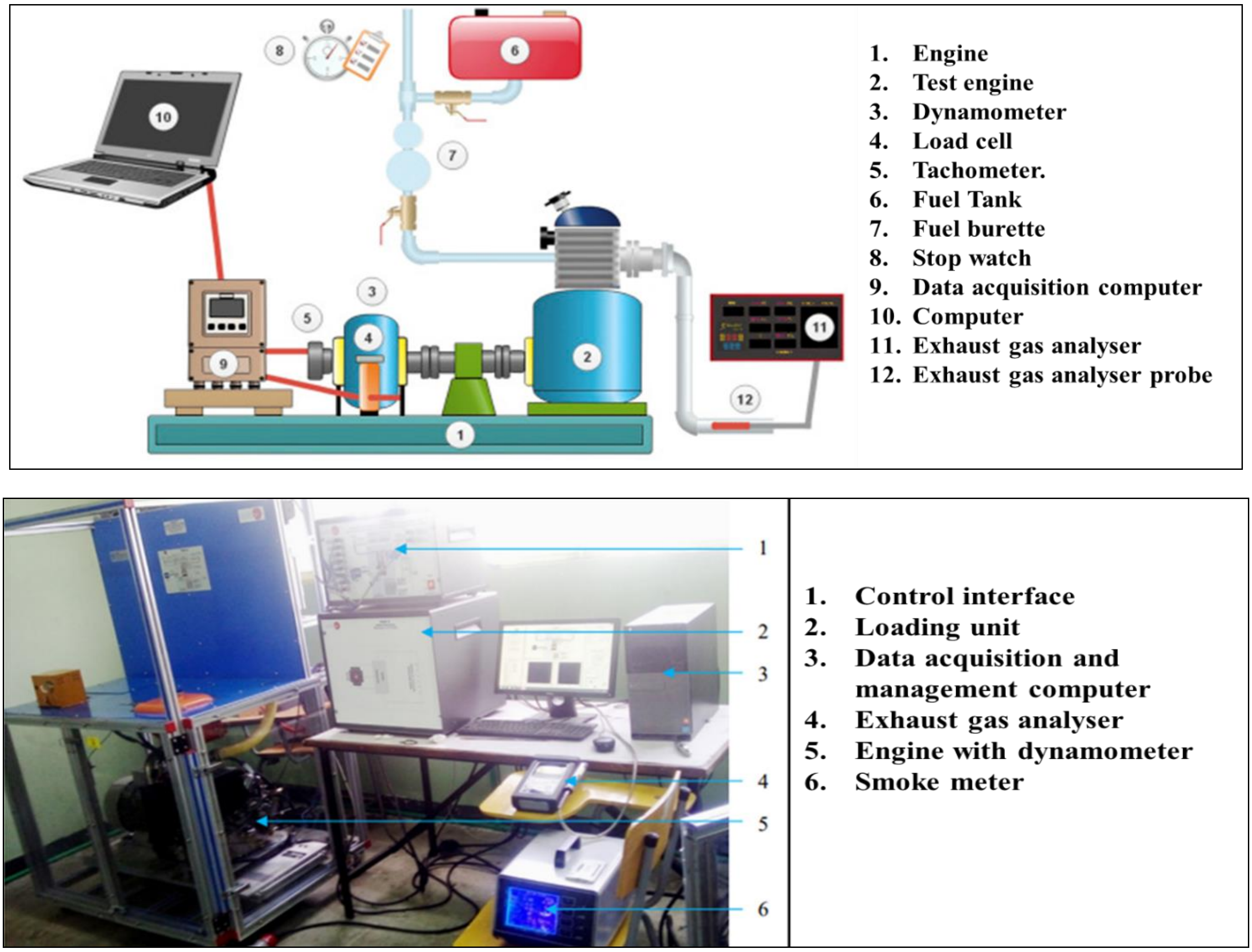


Fig 6: Experimental setup for engine performance (Source: [35])

To quantify the pollutants, connect the exhaust system to a gas analyzer. This will allow for the measurement of carbon dioxide, carbon monoxide, and hydrocarbons using the nondispersive infrared (NDIR) detection method. Nitrogen oxides can be measured through an electrochemical detection method [37].

Pour the gasoline mixture into the fuel tank, and connect it to the dynamometer before starting the engine. Once the engine and motor oil reach optimal operating temperature, adjust the engine speed and gradually increase the throttle to 50%. When the experimental conditions stabilize, record the engine power, torque, and pollutant emissions. Set the engine to full throttle and repeat the measurements. Conduct additional tests at varying RPMs under both half and full throttle conditions. After completing tests with the first fuel blend, add the second fuel mixture and repeat the experiment.

Table 4: Effect of nano particle additive in fuel properties

Fuel Properties	Gasoline	$E30C_0100$	$E40C_0150$	$E50C_0200$
Calorific value in MJ/kg	45.551	37.923	37.031	35.214
Specific gravity	0.728	0.750	0.751	0.757
Density@15°C in kg/m³	728	750	751	757
Kinematic viscosity @ 40°C in m²/sec.	0.88E-4	0.86E-4	0.84E-4	0.82 E-4

Table 5: Effect of nano particle additive in fuel properties

Fuel Properties	Diesel	Ethanol	E10Ce10D90	E10Ce15D90	E10Ce20D90
Density@15°C in kg/m³	843	831	833	836	838
viscosity @ 40°C in cP	2.48	1.86	1.88	1.92	1.92
Calorific value kJ/Kg	42	40.6	40.670	40.670	40.670
Flash point (°C).	50	13.8	14	14.2	14.3

9. Effect of nano additives in engine performance of bioethanol blended fuel

Incorporating nanoparticles into ethanol-gasoline or bioethanol-diesel blends significantly improves engine performance parameters such as fuel consumption, thermal efficiency, torque, power, exhaust gas temperature, and cylinder pressure. Nanoparticles like Mn_2O_3, Co_3O_4, and $NiZnFe_2O_4$ enhance catalytic activity and combustion efficiency, resulting in notable reductions in brake specific fuel consumption (BSFC). Amirabedia *et al*. (2019) [12] observed BSFC reductions of up to 36.72% with Mn_2O_3 and Co_3O_4 additives, while Firew *et al*. (2022) [35] reported 13.06% to 27.86% lower BSFC in $NiZnFe_2O_4$-doped fuels.

Brake thermal efficiency (BTE) increases with nanoparticle addition due to enhanced fuel-air mixing, prolonged combustion duration, and better oxidation of carbon residues. Srinivasan *et al*. (2017) [7] found a peak BTE of 30.98% for an E50 blend with 200 ppm cerium oxide. Improved atomization and higher surface-to-volume ratios also contribute to more efficient energy release.

Torque output shows a moderate increase with nanoparticles, especially under low-load conditions, due to faster ignition and reduced ignition delay. Firew *et al*. (2022) [35] reported torque increases of up to 3.53% for E10 blends with 100 ppm $NiZnFe_2O_4$. Likewise, engine power is enhanced by the oxygen-rich structure of ethanol and catalytic effects of nanoparticles, as seen in Amirabedia *et al*. (2019) [12], who reported power increases of up to 19.56% with Mn_2O_3 and Co_3O_4 additives. Exhaust gas temperature (EGT) rises with nanoparticle use due to improved combustion quality and reduced ignition delay. Manikandan and Sethuraman (2014) [36] linked higher EGTs to faster burning and higher enthalpy at engine exit.

Additionally, cylinder pressure increases with nanoparticle-enhanced blends owing to quicker combustion and greater fuel oxidation. Srinivasan *et al*. (2019)[7] observed up to 11% higher peak cylinder pressure with 200 ppm nano-additives in bioethanol blends. These enhancements demonstrate the comprehensive benefits of nanoparticles in optimizing engine performance.

9.1 Effect of nano additives in engine emission

Nanoparticles significantly reduce carbon monoxide (CO) emissions by enhancing combustion efficiency through improved atomization, oxygen availability, and better fuel-air mixing. Studies show that blending Mn_2O_3 nanoparticles with E10 fuel reduced CO emissions by up to 24.09% compared to ethanol-only blends [12].

The inclusion of nanoparticles also helps lower nitrogen oxide (NOx) emissions by shortening combustion duration and limiting the peak flame temperature. Their catalytic action accelerates fuel oxidation, reducing NOx formation. Cerium oxide addition demonstrated notable NOx reduction, with up to 250 ppm less NOx than base gasoline fuel [7].

Carbon Dioxide (CO_2) emissions increase with nanoparticle use due to more complete combustion. Bioethanol and nano-oxide additives raise oxygen availability, enhancing CO to CO_2 conversion. Blends with Mn_2O_3 and Co_3O_4 showed a rise in CO_2 emissions by approximately 13.27% and 13.34%, respectively [12].

Hydrocarbon (HC) emissions drop with nano-additives due to improved vaporization, fuel-air homogeneity, and secondary atomization. Their catalytic effect ensures fuller combustion, delaying flame quenching and minimizing unburned fuel. Cerium oxide in bioethanol blends reduced unburned HC emissions to as low as 10 ppm at moderate engine loads [7].

10. Conclusion

Nanomaterials exhibit significant potential in bioethanol-based energy systems owing to their high surface area, nanoscale dimensions, and catalytic effectiveness. Incorporating metal oxide and magnetic nanoparticles enhances enzyme immobilization, promotes efficient hydrolysis, and can improve ethanol yield by up to 93%. When blended with gasoline, metallic nano-oxides contribute to reduced fuel consumption and prolonged combustion, resulting in improved brake thermal efficiency at higher nanoparticle concentrations. These nanoparticles act as combustion catalysts, boosting engine output and thermal efficiency. Under full load conditions, ethanol-nanoparticle blends elevate exhaust gas temperatures. From an emissions perspective, such blends help lower carbon monoxide, unburned hydrocarbons, and nitrogen oxides, while slightly increasing carbon dioxide levels due to more complete combustion. Overall, nanoparticle additives offer notable benefits in optimizing fuel characteristics, enhancing engine performance, and minimizing pollutant emissions.

11. References

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